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Preface

Welcome to the 32nd Conference of the European Colloid and Interface Society (ECIS2018) in Ljubljana. This conference is putting Slovenia on the list of countries which have hosted this event since the first in 1987 in Como, Italy. With participating scientists from 47 countries, ECIS2018 has become a global event.

The conference was organized jointly by the University of Ljubljana (Faculty of Chemistry and Chemical Technology, Faculty of Pharmacy, Biotechnical Faculty, Faculty of Mathematics and Physics), National Institute of Chemistry, Jožef Stefan Institute and the Slovene Chemical Society. We hope that this conference will meet your expectations and serve, as previous ones have, to exchange ideas and findings, to promote contacts and networks and to strengthen old and establish new collaborations in the rapid growing field of colloid and interface research.

The topics cover fundamental and applied advances in interfaces, dispersed systems, wetting, complex fluids, micro- and nano-materials, nanoparticles, specific-ion effects, self-assembly of surfactants, polymers and proteins and advances in theory and instrumentation. Besides the 12 topics of the ECIS2018 conference, which will be organized in a traditional way, there will also be an additional Satellite Session entitled *Modern Engineering of Colloids and Interfaces*, hosting a selected group of invited speakers. Last year, the international colloid and interface community lost six prominent representatives of extreme professional authority: Hans Lyklema, Dotchi Exerowa, Dimo Platikanov, Kåre Larsson, Helmuth Möhwald and Ivan B. Ivanov. At ECIS2018 the European Colloid and Interface Society will honour them at the Memorial Session.

The scientific programme of the conference consists of 6 plenary lectures. Amongst these, one will be given by the Solvay prize winner and one by Overbeek medal winner. Furthermore, we have 37 keynote lectures, 13 invited and 24 selected by the International Scientific Committee, who has also selected 177 oral presentations from more than 400 submitted abstracts for oral presentations. Across three poster sessions, 375 posters will be presented. The participants have the possibility to submit manuscripts and reports about their oral and poster presentations for peer-review and rapid publication in special issues of Colloid and Surfaces A (Elsevier) and Polymers (MDPI).

We thank all the sponsors of the conference for their support.

Finally, we thank you for participating in the conference and for contributing to its scientific content.

The 32nd ECIS Conference Organizing Committee

Bridging the Gap between Molecules and Nanoparticles

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The concept of “colloidal molecules” builds on the analogy between colloidal particles and molecules. For about a hundred years, colloidal particles have been utilized to model the behavior of atoms or molecules. Recently, this approach has been reversed: reactions between molecules are now being used to model nanoparticle self-organization. In particular, polymer science offers unique strategies to address the challenges in nanoparticle assembly.

By using lessons of polymer physics and chemistry, we develop new paradigms for nanoparticle patterning and self-organization. A surface-pinned micelle approach has been utilized to create "colloidal molecules" [1,2]. A striking resemblance between block copolymers and amphiphilic nanoparticles enabled nanoparticle assembly in nanostructures with varying morphologies, all mapped by state diagrams. A marked similarity between step-growth polymerization and nanoparticle self-assembly enabled growth of nanopolymers, with a quantitative prediction of the architecture of linear, branched, and cyclic nanostructures, their aggregation number and size distribution, as well as the formation of isomers [3]. Building on this similarity, we proposed the concept of colloidal chain stoppers [4], as well as random and block copolymers [5].

This work has far-reaching implications for the molecular world (by offering simple, easy to visualize nanoscale models for polymerization reactions), and for the nano-world (by providing a polymer approach to nanostructures with structure-dependent electronic, optical, and magnetic properties).

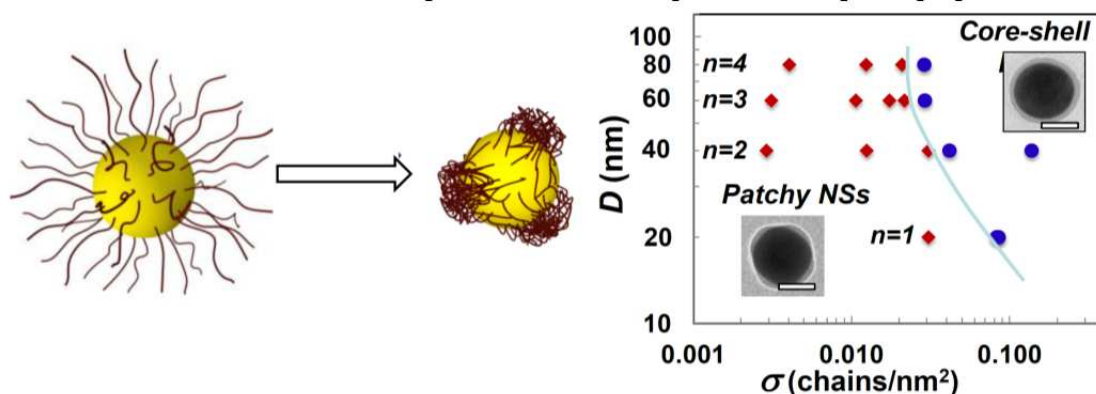


Figure 1. *Left:* Schematic of the nanopatterning strategy. *Right:* state diagram of nanoparticle states, plotted in the coordinates of nanoparticle diameter-polymer grafting density [1]

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Quantum dots and other nanocrystals: from basic science to applications in materials and life sciences

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Although nanocrystals are used already in many applications, the knowledge on their formation is still in its infancy. We will present results on the nucleation and growth of nanocrystals obtained from uv-vis spectroscopy and x-ray scattering data obtained in a rapid continuous flow apparatus and we will address examples of ion exchange processes.

Nanocrystals are currently used in many areas of materials science. We will present examples of nanocomposites with outstanding mechanical and thermal properties. Quantum dots are used for display and lighting applications. The talk describes the current status of their large-scale production and their fluorescence properties.

The key idea for using nanocrystals for biomedical diagnostics is to benefit from their outstanding physical properties in the visualization of biological events or malignant cells or tissues. This requires a special design of the ligand shell, which preserves the fluorescent, magnetic and plasmonic properties of the particles in the biological environment on one side and allows a specific targeting on the other. The lecture reports on different chemical approaches and describes factors determining the biological response on fully synthetic nanocrystals. We will highlight concepts based on PEGylation and show how small deviations in the ligand shell alters the behavior in biological environment substantially. Moreover, we will present combinatorial approaches for the functionalization of the nanocrystals with biological affinity molecules to improve targeting specificity and concepts to optimize the physical properties of the inorganic core to increase the sensitivity for the respective imaging techniques.

Nanoparticle delivery systems for antimicrobial peptides

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Due to rapidly increasing resistance development against conventional antibiotics, finding novel approaches for the treatment of infections has emerged as a major health issue. Antimicrobial peptides (AMPs) have attracted interest in this context, and there is by now a considerable literature on the identification such peptides, as well as on their optimization to reach potent antimicrobial and anti-inflammatory effects at simultaneously low toxicity against human cells. In comparison, delivery systems for antimicrobial peptides have attracted considerably less interest. However, such delivery systems are likely to play a key role in the development of potent and safe AMP-based therapeutics, e.g., through reducing chemical or biological degradation of AMPs either in the formulation or after administration, by reducing adverse side-effects, by controlling AMP release rate, by promoting biofilm penetration, or through achieving co-localization with intracellular pathogens.

Here, an overview is provided of some of our recent work on delivery systems for antimicrobial peptides, including polymer nanogels [1,2], mesoporous silica [3], nanoclays/nanosheets [4], and quantum dots, with special focus on AMP-carrier interactions, as well as consequences of these for membrane interactions, as well as for antimicrobial and related biological effects of AMP-containing formulations.

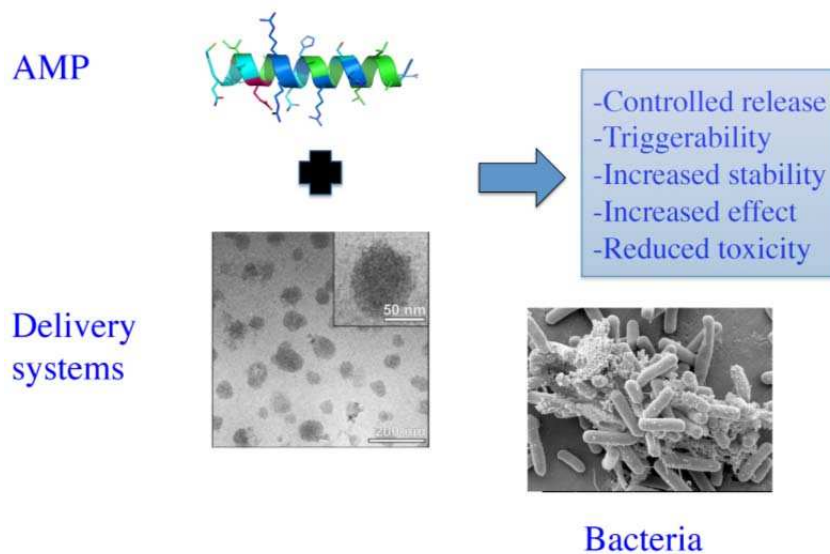


Figure 1. Nanoparticulate drug delivery systems provide various advantages for antimicrobial peptides.

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The Littlest Amphiphiles: Nanostructured Solvents and Self-Assembly

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Ionic liquids (ILs) have become objects of great interest over the past decade or so, but it is over 30 years since Evans' pioneering work that showed that surfactant self-assembly into micelles and lyotropic phases could occur in the IL ethylammonium nitrate [1-2]. Since then, the number and variety of ILs has increased exponentially, and they have insinuated themselves into almost every corner of chemistry. Recently, a number of studies have revealed new insights into the structure of ILs and their mixtures [3], including the novel class known as deep eutectic solvents (DESs).

This talk will review the use of neutron beam, X-ray and other complementary techniques that have revealed the inherent amphiphilic character of the bulk structure of ILs [4], how their surfactant character is affected by cation and anion structure [5], and how such inherently nanostructured solvents differ from familiar molecular solvents. I will then examine how ILs behave as solvents for simple polar and non-polar solutes [6], in mixtures with molecular species including as DESs, and for genuine amphiphiles including small molecule surfactants [7], cosurfactants [8], and block copolymers [9]. Finally I will examine the similarities and differences between solvophobic self-assembly into micelles, microemulsions, and lyotropic liquid crystals in water and ILs.

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Liquid Crystal Colloids

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Nematic colloids are dispersions of microparticles in nematic liquid crystals [1]. These are fascinating materials, showing several novel classes of colloidal forces, which do not exist in ordinary colloids with isotropic solvents. The interaction of liquid crystal molecules with the surfaces of particles induces topological defects in a form of points and closed loops, which are the generators of forces between colloidal inclusions. Because of the inevitable presence of topological defects, nematic colloids are also called topological colloids, where the topology is responsible for topological-defect-mediated colloidal interactions. This provides colloidal assembly in 2D and 3D nematic colloidal crystals [2] and colloidal interactions mediated by colloidal entanglement [3], where knotted and linked topological defect loops form knots and links of arbitrary complexity [4]. In all cases, the colloidal binding energy is of the order of several $1000 k_B T$. This is several orders of magnitude higher than for water-based colloids and could provide new strategies for topological soft materials and applications in photonics. An overview of this rapidly developing field is presented, together with some interesting applications to soft matter photonics and recent studies of topological charge production and control [5].

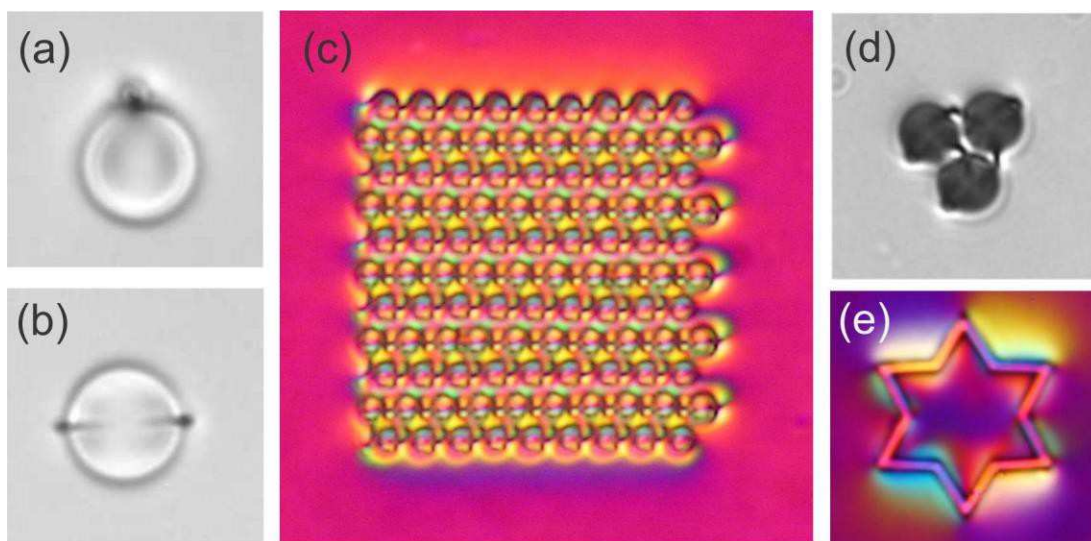


Figure 1. Selected examples of liquid crystal colloids. (a) Glass microsphere is accompanied by a point topological defect. (b) A glass microsphere could be encircled by a closed defect ring. (c) Colloidal crystals can be assembled from microspheres. (d) Particles in the liquid crystals can be entangled, knotted and linked. (e) Koch star colloidal particles in nematics show huge number of topological defects.

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Self-organised structures in suspensions of mineral colloidal plates: From colloidal liquid crystals to self-assembled nanocomposites

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One of the most remarkable phenomena exhibited by concentrated suspensions of colloidal particles is the spontaneous transition from fluid-like structures to those exhibiting long-range spatial and/or orientational order (colloidal crystals and colloidal liquid crystals). The fact that such ordering can occur in suspensions in which interparticle forces are purely repulsive provides a dramatic realization of the predictions made by Lars Onsager in the 1940's and later substantiated by computer simulations. From these studies it is clear, that the ordering is driven by entropy.

Liquid crystalline phases in suspensions of rod like mineral colloidal particles have been known for a long time. As early as 1925 Zocher reported on the observation of a nematic phase in suspensions of V_2O_5 . A decade later Langmuir reported on sols of platelike clay particles that after standing for several 100 hours separated into an isotropic and nematic phase. However the experiment of Langmuir could not be repeated, instead a birefringent gel was observed. The first unambiguous experimental observation of a nematic phase and columnar phase in a suspension of plate like colloids dates from, predicted by Frenkel and coworkers by computer simulations [1] dates from 2000 [2]. In the last decade interesting liquid crystal phase transitions have been observed in suspensions of both natural (clay) plate like particles as well as synthetic nanosheets. After a brief review of some of these results I will focus on the competition between liquid crystal formation and gelation in suspensions of plate like colloids Results of liquid crystal phases of colloidal platelets as templates for the generation of ordered silicastructures and polymer nanocomposites will be presented.

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Illuminating interfaces in soft matter by single-molecule localization microscopy

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Self-organization provides a fast, efficient, and low-cost pathway to functional and responsive hierarchically structured materials that are difficult if not impossible to prepare by other means [1-4]. One of the key challenges in the field is the direct visualization in these soft multicomponent materials of the structural hierarchy at sub- μm length scales with minimal perturbation and chemical specificity.

Aiming to enable in-situ, three-dimensional, sub-diffraction imaging of complex soft materials with minimal perturbation, we recently developed a straight forward strategy for single-molecule localization microscopy that we coined interface Point Accumulation for Imaging in nanoscale Topography, in short ‘iPAINT’ [5]. I will showcase examples of iPAINT imaging of solid/liquid, liquid/liquid and liquid/air interfaces [5], supramolecular fibers in organic solvents [6, 7], complex coacervate core micelles (C3Ms) [8], and particle- laden interfaces, demonstrating the general applicability of the method which opens up a new vista on nanostructured soft matter [9].

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Smart Air-Water Interfaces with Arylazopyrazole Surfactants and their Role in Photoresponsive Aqueous Foam

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Foams are ubiquitous in our daily lives and in industrial applications. The vast number of possibilities to use foam in industrial processes and products originate from their unique physico-chemical properties. Classically, surfactants, polyelectrolytes and proteins are used as molecular building blocks to stabilize aqueous foam. In order to formulate foam with specific properties, its structure must be controlled at the molecular level of the air-water interface and structure-property relations can be applied through the hierarchy of foam [1-3]. Molecular-level characterization of the interface with methods like tensiometry, vibrational sum-frequency generation (SFG) are in this case essential.

In this contribution, we introduce a new class of photo-switchable surfactants and their 2D assemblies at the air-water interface, which make the interface as well as macroscopic foam responsive to light irradiation. This opens exciting new possibilities for foams such as self-healing capabilities or the possibility to adapt foam properties by photo-switching of the surfactants. Specifically, we have used arylazopyrazole tetraethylene glycol carboxylic acid (AAP-E₄) surfactants to functionalize aqueous foam and the ubiquitous air-water interface. The AAP-E₄ surfactants were studied in the bulk solution with UV/Vis spectroscopy and at the interface with vibrational SFG spectroscopy as well as with tensiometry. Additional foaming experiments were performed with a dynamic foam analyzer in order to study the role of AAP-E₄ surfactants at the ubiquitous air/water interface as well as within macroscopic foam. In the bulk, it is possible to switch the AAP-E₄ surfactant reversibly from trans to cis configurations and vice versa using 380 nm UV and 520 nm green light, respectively.

At the interface, we demonstrate excellent switching ability of AAP-E₄ surfactants and a substantial modification of the surface tension. In addition, we show that the response of the interface is strongly influenced by lateral electrostatic interactions, which can be tuned by the charging state of AAP-E₄. Consequently, the electrostatic disjoining pressure and thus the foam stability are highly dependent on the bulk pH and the charging state of the interface. For that reason, we have studied both the surface net charge (SFG) and the surface excess (tensiometry) as important parameters that determine foam stability in this system and show that neutral pH conditions lead to the optimal compromise between switching ability, surface excess and surface charging. Measurements on the foam stability demonstrated that foams under irradiation with green light are more stable than foams irradiated with UV light.

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Rough particles at fluid interfaces

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Surface heterogeneities, including surface roughness, significantly affect the adsorption, motion and interactions of particles at fluid interfaces. These aspects have been the focus of many studies, but there is still a lack of systematic experimental work where roughness is tailored over a broad range of length scales and where its effect on particle wettability is investigated at the single-particle level. Here, we synthesize a library of all-silica microparticles with uniform surface chemistry, but tuneable surface roughness [1] and study both their spontaneous adsorption [2] and forced desorption [3] at/from oil-water interfaces. Akin to contact-line pinning for macroscopic droplets on structured surfaces, we demonstrate that surface roughness strongly pins the contact lines of particles. As a consequence, their spontaneous adsorption is arrested in long-lived metastable positions and the interface around each particle is deformed as predicted by capillary theory. Moreover, pinning imparts tremendous contact angle hysteresis for rough particles adsorbing either from the polar, or the non-polar phase. For large enough roughness, this can practically invert the particle wettability, irrespective of their chemical nature, e.g. rough hydrophilic particles can behave as hydrophobic ones if adsorbing from the oil. As a unique consequence, the same rough particles can be used as universal stabilizers for both water-in-oil and oil-in-water emulsions by just changing the phase in which they are initially dispersed. Similarly, desorption may also be affected by pinning of the contact line at surface features. Depending on roughness, both pinning- and sliding-dominated desorption events are observed. Moreover, the link between the input load exerted on the colloid during adsorption and the resulting maximal adhesion force upon desorption can be described as function of the surface roughness and surface chemistry, as measured by AFM. These results both shed light on fundamental phenomena concerning particle adsorption/desorption and indicate surface roughness as an engineering parameter to tune the wetting properties of colloidal particles.

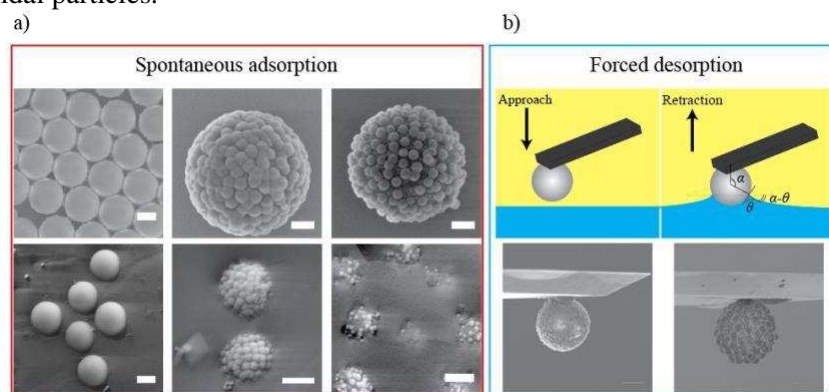


Figure 1. a) All-silica raspberry-like colloids with different surface roughness (upper row) and the same colloids spontaneously adsorbed at a water-oil interface (lower row). b) Schematics of forced desorption measurements by means of an AFM (upper row) and an example of two rough colloidal probes (lower row).

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Slow lipid flip-flop revealed by neutron scattering experiments

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The phospholipid bilayer is the basic structural motif of most biological membranes. As such, many biological processes occur within or in the proximity of the cell membrane, and therefore, interest in the properties and behavior of lipids in membranes is considerable. For example, it is found that in nature the lipid distribution across the inner and outer leaflet of cell membranes is asymmetric and this asymmetry plays a prominent role in processes like cell fusion, activation of the coagulation processes and the recognition and removal of apoptotic cells by macrophages [1]. Therefore, there is great interest in studying the factors determining lipid movement across membranes as well as the resulting lipid mapping in the membrane, both of which are far from being understood and characterized.

In the literature, big discrepancies in the timescale of the occurrence of lipid flip-flop in model bilayer systems are found, partly due to the fact that these measurements were based on the indirect observation of the process [2,3]. Combining time resolved small angle neutron scattering and neutron reflectometry, we have shown that it is possible to capture inter and intra vesicular exchange as well as lipid composition differences in the leaflets of a model bilayer with the sub-nanometer spatial resolution and for times scales as short as a few minutes [4–6].

In this presentation I will provide new insight on the characteristics of inter- and intra-bilayer rearrangement processes. In particular, I will report on the **rates** and **energetics** of pure lipids as well as cholesterol transfer in different lipids environments. These results will be discussed with respect to MD predictions and to the presence of defects that can render the lipid intra-bilayer movement (flip-flop) the time limiting process or not.

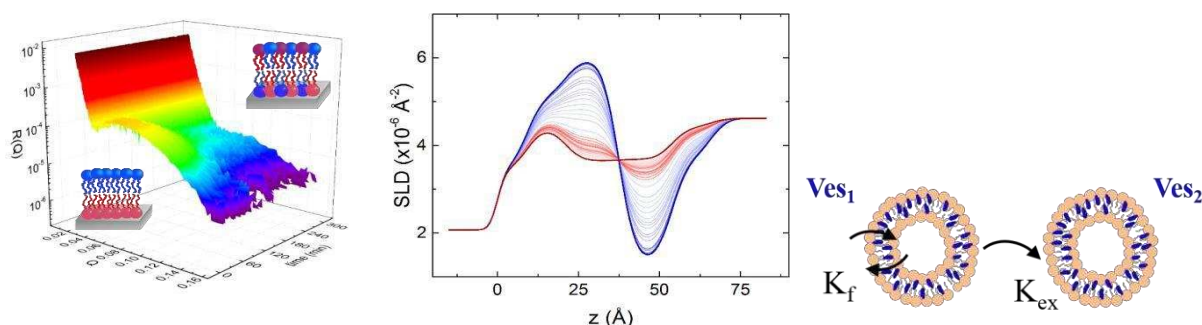


Figure 1.

Left. Time- and temperature resolved NR experimental data following the equilibration of an asymmetric bilayer as caused by the lipid flip-flop. The sketches of the initial and final bilayers are shown. **Center.** Evolution of the scattering length density profile extracted from the data shown on the left panel. The blue curve represent the initial asymmetric structure while the red one the final symmetric bilayer. **Right.** Sketch of the flip-flop and exchange processes that can be characterized simultaneously by SANS.

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Gas permeation through Pickering membranes

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As described by S. U. Pickering in 1907 [1], particles spontaneously adsorb to the surface of droplets and emulsify them for a long period of time (so-called Pickering emulsions). This effect can be enhanced by giving the particle a hydrophilic and a hydrophobic region (Janus particles) [2]. These particles arrange themselves preferably at interfaces between two non-miscible fluids [3].

Our idea is: We increase the number of regions on the surface of the particles by one. Liquid films should be able to be stabilized by these particles instead of spherical droplets. We regard these films as membranes and call them Pickering membranes, and we call the particles we use for this approach Saturn particles (others call them triblock Janus or patchy particles).

The used Saturn particles are produced by masking the caps of hydrophobically coated silica particles and etching the equatorial region in between them via hydrofluoric acid in one step [4].

According to our experience, it is far easier to create such water films stabilized by Saturn particles in air as a foam than in a hydrophobic fluid. We do this by suspending Saturn particles in ultrapure water and carefully pumping air bubbles into the water from below. A Pickering membrane is formed. The Saturn particles self-assemble in the water film and protrude it on both sides (see Figure 1). Instead of rupturing the film via the bridging-dewetting mechanism, the Saturn particles stabilize the water film for several days.

When replacing the air above the Pickering membrane with one of two gases (CO_2 or SF_6), the gas or air permeates through the stabilized water film and the Pickering membrane moves. When replacing the gas with air, the Pickering membrane moves back again (see Figure 2). We capture the movement of the Pickering membrane on video to determine the movement speed and therefrom calculate the experimental permeance in quite good agreement with theoretical predictions.

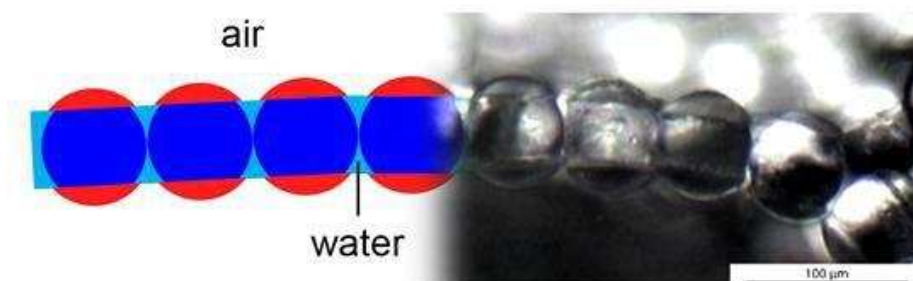


Figure 1: Schematic drawing and light microscope picture of a Saturn particle stabilized water film (Pickering membrane).

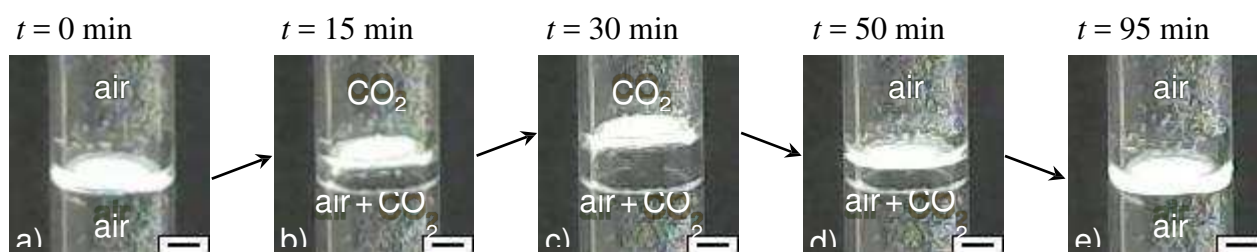


Figure 2: The permeation of CO_2 through a Pickering membrane. The CO_2 above the membrane permeates through it (a–c). The CO_2 is replaced by air after 30 min. The CO_2 below the membrane permeates back through the membrane until there is only air left (c–e). Scale bar is 2 mm.

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Continuous bottom-up production of nanoemulsions under conditions simulating deep-sea hydrothermal vents

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Deep-sea hydrothermal vents are hot springs occurring on the bottom of the ocean (Figure 1), from which hot and compressed water, sometimes in the supercritical state ($T_c = 374\text{ }^{\circ}\text{C}$, $P_c = 22.1\text{ MPa}$) [1] gushes out [2]. Molecules in the surrounding cold deep-sea water is instantaneously heated to ultra-high temperatures when they are engulfed in the vent-water stream, and immediately quenched to near-freezing temperature when they get out of it. Supercritical water (SCW) exhibit properties that are remarkably different from those of ambient water. For example, the dielectric constant of water decreases from 79 at $25\text{ }^{\circ}\text{C}$ to 2.5 at $400\text{ }^{\circ}\text{C}$ under a constant pressure of 25 MPa. Accordingly, various oils freely mix with SCW [3].

The unique physicochemical environments of the deep-sea hydrothermal vent inspired us to develop a novel bottom-up process for making nanoemulsions called MAGIQ (Monodisperse nAnodroplet Generation In Quenched hydrothermal solution) [4]. In MAGIQ, emulsification was performed by chilling homogeneous solutions of oils in SCW, and oil droplets were formed in a bottom-up manner by self-assembly of oil molecules. The process is completely different from conventional top-down processes for making emulsions, where large droplets are repeatedly disrupted to finer ones.

A flow-type instrument was developed to perform MAGIQ. The instrument allows us to apply fast and deep temperature-quenching, $\sim 200\text{ }^{\circ}\text{C}/\text{sec}$, to homogeneous solutions of oils in SCW so that the oil phase-separated rapidly to generate nano-sized droplets. In tests using dodecane and a nonionic surfactant, Brij 97, emulsions containing dodecane droplets with an average diameter of 61 nm were obtained in less than 10 seconds.

Recent developments of MAGIQ will be presented in this talk. These include fabrication of wax nanoparticles [5] and development of a high-temperature and high-pressure microfluidic device for continuous production of nanoemulsions (Figure 2).

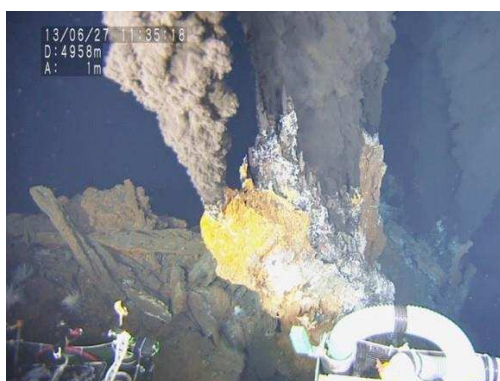


Figure 1. Deep-sea hydrothermal vent.



Figure 2. A microfluidic device for continuous production of nanoemulsions by MAGIQ.

Acknowledgements: This work was supported by Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) by Japan Science and Technology Agency (JST).

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Self-assembly of mixed nanoparticle/surfactant thin films in colloidosome shells

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Utilizing colloidal particles for the assembly of the shell of nano- and microcapsules holds great promise for the tailor-made design of new functional materials. As recently reviewed by us, increasing research efforts are devoted to the synthesis of such colloidal capsules, by which the integration of modular building-blocks with distinct physical, chemical, or morphological characteristics in a capsule's shell can result in novel properties, not present in previous encapsulation structures [1].

Since there is basically no limitation in the type of nanoparticle used for the formation of these vesicles, it is possible to introduce distinct functionality (i.e. superparamagnetism, fluorescence, plasmonic coupling, drug-loaded particles) into the shell of colloidosomes and similar capsules. Colloidal capsules therefore have great potential for biomedical applications, as is demonstrated in a diverse range of reports from this field which aim at pharmaceutical agent encapsulation, targeted drug delivery and theranostics.

However, many fundamental questions about the assembly of such capsules remain, especially regarding the complex interplay of surfactants and particles at liquid interfaces (Figure 1). In our work [2], we use a combination of oil-soluble surfactants (lipids) and hydrophilic nanoparticles to produce submicron colloidosomes from Pickering emulsions. In this system, the lipids partially dissociate at the emulsion droplet interface and introduce a charge, which mitigates the electrostatic repulsion between the nanoparticles at the interface and between interface and adsorbing nanoparticles, resulting in the formation of rigid nanoparticle films at the emulsion droplet interface. We are studying film formation by both interfacial shear rheology and pendant drop dilational rheology in combination with analyzing the dynamic surface tension of the system. This allows us to separate the contributions of surfactants and particles to the interfacial energy and the rheological properties of the interface and with that increase our understanding of the formation of colloidosome shells.

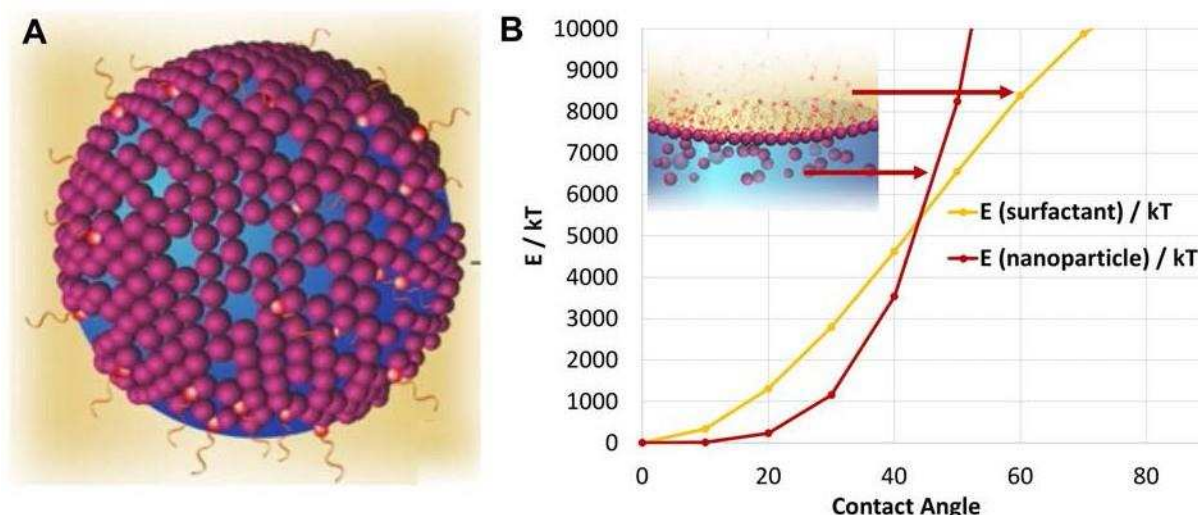


Figure 1. (A) Formation of a submicron colloidosome via a Pickering emulsion in the presence of surfactants, (B) Competitive adsorption energies at the decane/water interface between nanoparticles and surfactants occupying the same area as the nanoparticles.

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Role of glycolipids in higher plants: A surface force study combining neutron diffraction on multilayer lipid membranes and MD simulations

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Membrane systems that naturally occur as densely packed membrane stacks (thylakoids in plants or myelin in the nervous system of higher vertebrates) contain high amounts of glycolipids. The common feature of these glycolipids is their sugar headgroups that display multiple small electric dipoles in the form of hydroxyl groups. The repulsion between these glycolipid rich membranes is of much shorter range than that between zwitterionic phospholipids, whose headgroups are dominated by a single large dipole. In thylakoids from higher plants their composition is dominated by a high fraction of 2 uncharged glycolipids, the mono- and di-galactoglycerolipids MGDG and DGDG, and the anionic sulfolipid SQDG that have been conserved by evolution, together with the anionic phospholipid phosphatidylglycerol (PG). Using neutron diffraction under controlled humidity, we observed that the thylakoid lipid mixture self-organizes as a regular stack of bilayers. This natural lipid mixture was shown to switch from hexagonal II toward lamellar phase on hydration. This transition and the observed phase coexistence are modulated by the fine-tuning of the lipid profile, in particular the MGDG/DGDG ratio, and by the hydration. Our analysis highlights the critical role of DGDG as a contributing component to the membrane stacking. DGDG interactions balance the short range hydration repulsion as well as the longer range electrostatic contribution of the charged lipids PG and SQDG and allow the persistence of regularly stacked membranes at high hydration. Using MD simulations, we were able to reproduce the repulsion forces between DGDG membranes, as measured by neutron diffraction (ND) under controlled humidity. The simulations reveal that the repulsion between glycolipid membranes is solely governed by the hydrogen-bond balance between water and the sugars featuring water-like dipoles. Additional repulsion mechanisms, which require correlated large dipoles and are responsible for the stronger swelling of phospholipid membranes, are inoperative for the glycolipids. These results explain the tight cohesion between glycolipid bilayers from thylakoid membranes, which is essential for the biogenesis of photosynthetic membranes.

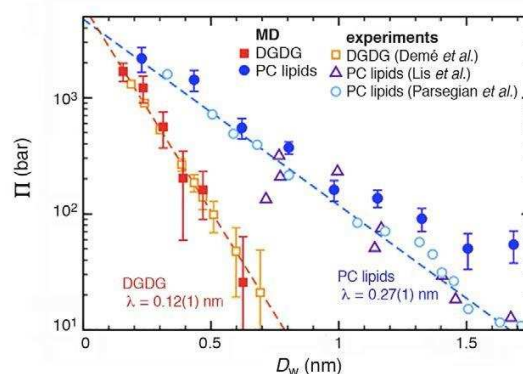


Figure 1. Comparison of pressure-distance curves obtained experimentally and by MD simulations for DGDG and PC lipids.

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Experimental approach of the self-propelled motion of a sodium oleate tablet and boat at an oil-water interface

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In non-equilibrium open systems involving interfaces, macroscopic molecular transport is observed in isothermal processes with the spontaneous motion of objects carried in the fluid. Given the existence of a large variety of systems with their own inherent chemical properties, the kinematics of the self-propelled motion and the dynamics of the forces driving these systems often remain largely unknown. Quasi-elastic laser scattering (QELS) method involves light scattering by capillary waves, and is one of the most useful tools non-invasively for measuring interfacial tension in such non-equilibrium systems [1]. We focus on the characteristics of the self-propelled motion of a sodium oleate tablet and a plastic sheet bearing sodium oleate tablets, i.e. a sodium oleate boat. In this presentation we aim to clarify their propulsion mechanism experimentally using the QELS method

We investigated the spontaneous motion of sodium oleate tablets at air-water and water-nitrobenzene interfaces. Although no motion was observed on the water surface, the sodium oleate tablets were self-propelled at the water-nitrobenzene interface. We quantitatively elucidated the dynamics of this motion through measurements of the interfacial tension distribution around the sodium oleate tablets at both interfaces. A uniform surface tension distribution at the water surface induced by the homogeneous adsorption of oleate/oleic acid molecules explained the absence of motion. On the other hand, the uneven interfacial tension distribution generated by the inhomogeneous adsorption of oleate/oleic acid was observed at the water-nitrobenzene interface. Although oleic acid molecules cannot be desorbed from sodium oleate in water, they can be desorbed in an oil phase and get unevenly adsorbed to the interface. The induced interfacial tension gradient at the water-oil interface becomes the driving force of the tablet.

In the self-propelled motion of a sodium oleate boat at an aqueous solution-nitrobenzene interface, we successfully measured the interfacial tension difference at the front and rear of the boat for different boat speeds. We quantitatively proved that the driving force of the motion of the boat is the interfacial tension difference at the front and rear of the boat, as shown in Fig.1. In addition, the greater the interfacial tension difference driving the boat, the faster was the boat. However, the increasing rate of the boat speed was gradually reduced as the interfacial tension gradient became higher. This was thought to be due to the decelerating effect of the Marangoni flow generated by the interfacial tension behind the boat, whose flow became progressively faster as the boat speed increased.

In conclusion, we quantitatively showed through QELS measurements that the interfacial tension gradient was the key factor behind the continued self-propelled motion of the objects.

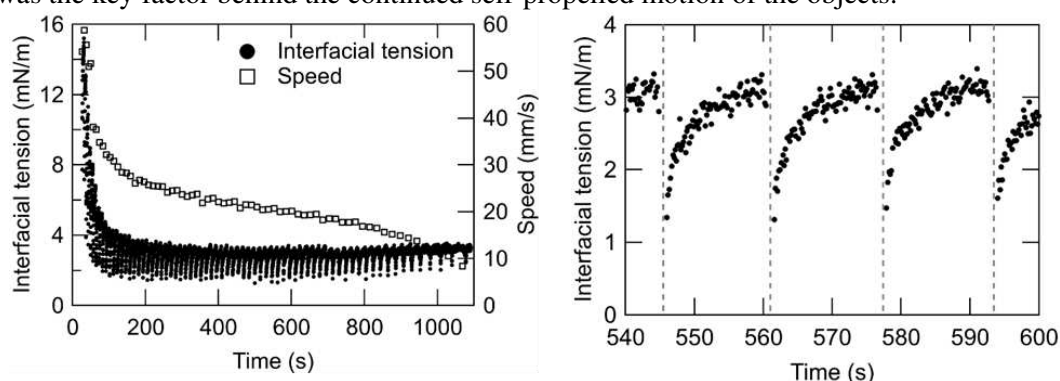


Figure 1. (a) Time change in the interfacial tension of the aqueous solution-nitrobenzene interface. The average speed of the sodium oleate boat during each lap is also shown. (b) Extended view of a selected time range of (a). The dashed lines represent the times when the boat passed through the measurement point.

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Structural resolution of responsive polymer brushes with neutron reflectometry: findings, limitations and a model-free Monte Carlo analysis method

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Surfaces decorated with densely-tethered polymer chains – referred to as polymer brushes – have been shown to possess desirable anti-biofouling and lubricating properties that are directly dependent on their structure [1]. These surfaces can be engineered to exhibit a structural response to stimuli such as pH, temperature, and the presence of specific ions and molecules, resulting in surfaces with controllable properties. Understanding and observing the structure of these systems is of great importance if the mechanisms behind their behaviour and function are to be understood. Neutron Reflectometry is the technique best suited for examining the physical structure of solvated polymer brushes in-situ [2] however the analysis of collected data is plagued with systemic issues, which are especially pronounced for diffuse, low-contrast interfaces such as polymer brushes and the molecules adsorbed within (fig.1).

Here we present a cross-section of our work on stimuli responsive polymer brushes and report on the development of a new method for the analysis of neutron reflectometry data from these diffuse interfaces. This method utilises a freeform spline (fig.1) in conjunction with a parallel-tempered Markov-Chain Monte Carlo approach for model fitting and uncertainty analysis, overcoming contemporary problems such as model-dependence, solution multiplicity and local-minima acceptance. We present a case study of this method, focusing on the interaction between the anionic surfactant sodium dodecyl sulfate (SDS) and a thermoresponsive Poly(N-isopropylacrylamide) (NIPAM) brush, in which we use our method to find all viable fits to data (fig.1, ■) and rigorously approximate profile uncertainty (fig.1). Using this method, we can extract useful information from extremely diffuse ‘low-information’ interfaces (fig.1, ■) and follow the structural response of NIPAM to SDS across a wide temperature and concentration range.

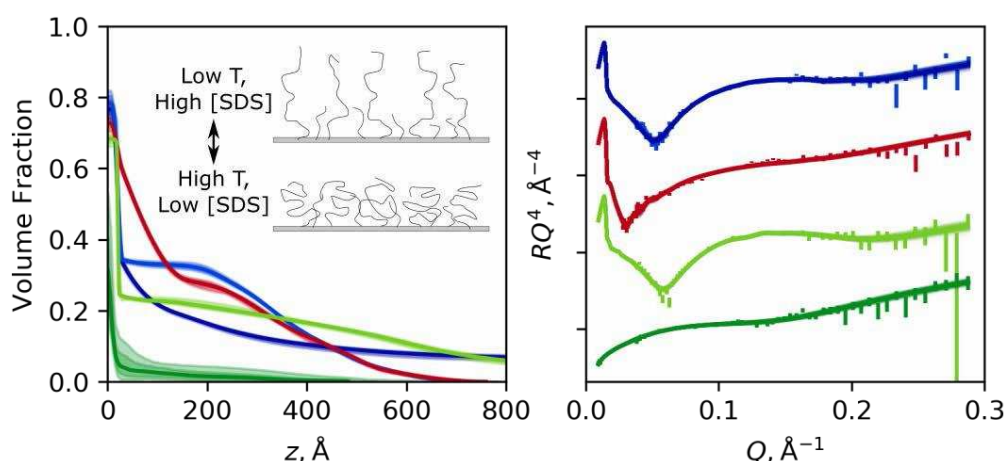


Figure 1. Selected fits from a NIPAM brush system for which temperature and SDS concentration was varied. ■ Brush extended at 27.5°C, exhibiting profile multimodality (■ accepted fit). ■ Brush collapsing at 32.5°C. ■ Brush extended at 27.5°C, further swollen by exposure to a 3.5mM SDS solution. ■ SDS within the brush at 27.5°C. One and two sigma profile regions are shaded.

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A new ultrasensitive acousto-optic method to study liquid-liquid interface

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We present here a significant extension of the confocal optical microscope designed by Mario Corti for gas bubbles (presented ECIS Bordeaux 2015) and that is used since several years to investigate nanometre surface waves on oil droplets suspended in an aqueous solutions (presented by Paola Brocca in Madrid 2017).

The surface waves in the initial arrangement were produced by typically 30V/cm alternating electrical field that is inducing surface vibration modes that are detected optically. The problem with this arrangement is that electrochemical effects at the liquid-liquid interface are intimately mixed with the surface elasticity that has to be investigated.

In the new arrangement presented, the surface waves are generated mechanically. Hence they can be detected optically and also by induction electrodes located near the bubble. Instead of electro-acoustic coupling, we use acousto-electrical coupling in the same time than acoustic detection. The Onsager principle is used in order to identify acousto-electric and electro-acoustic coupling, while electrical response unambiguously detects surface diffuse layer effects.

We will show the first results obtained by this modified device, that represents a new ultra-sensitive experimental method to study nanometre amplitude waves produced on mm-size droplets.

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Inner Structure Information and Mechanical Properties of Responsive Microgels Adsorbed at Solid Interfaces by SFM

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Microgels are highly interfacial active, although not being amphiphilic. They readily adsorb to liquid/liquid, liquid/air or solid interfaces and deform [1]. Their interfacial behavior makes microgels useful for many applications in the field of advanced polymeric coatings [2]. Not only the temperature-induced changes in topography but also of the mechanical properties of the microgels play an important role, e.g. for cell adhesion on a microgel coated surface [3].

We studied microgels with unique internal structures, (i) one with a rigid silica core and a PNIPAM shell, (ii) hollow microgels obtained by dissolving the silica core, and (iii) ultra-low cross-linked microgels. The morphology and nanomechanical properties of these microgels at surfaces were investigated with an scanning force microscope (SFM). An important parameter is the size of the probe compared to the dimensions of the microgel [4]. We will demonstrate that indentation experiments using a sharp tip lead to penetration of the porous swollen microgel networks. Therefore, force-distance curve measurements enable to probe the segment density distribution orthogonal to the substrate of adsorbed single microgels. Measurements using blunt tips are causing a compression of the microgel and provide information on their global mechanical properties.

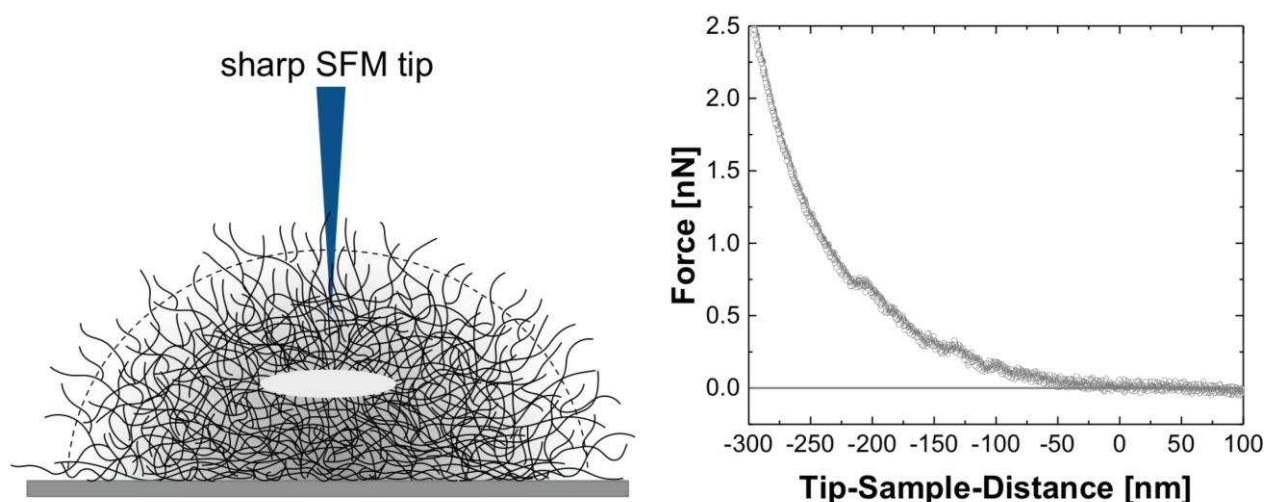


Figure 1. Schematic illustration of a sharp SFM tip approaching the water/microgel interface. The density variation close to the tip is probed for a swollen hollow microgel by force-distance curve measurements.

Acknowledgements: The Deutsche Forschungsgemeinschaft (DFG) is acknowledged for financial support within the Sonderforschungsbereich SFB 985 “Functional Microgels and Microgel Systems”.

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Interfacial structuring of ionic liquids in the presence of water: From neat liquids to aqueous solutions

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Bio and aqueous applications of ionic liquids (IL) such as catalysis in micelles formed in aqueous IL solutions or extraction of chemicals from biologic materials rely on surface-active and self-assembly properties of ILs. Here, we discuss qualitative relations of the interfacial and bulk structuring of a water-soluble surface-active IL ([C₈MIm][Cl]) on chemically controlled surfaces over a wide range of water concentrations using both force probe and X-ray scattering experiments.

As shown in **Figure 1**, our data indicate that IL structuring evolves from surfactant-like surface adsorption at low IL concentrations, to micellar bulk structure adsorption above the critical micelle concentration, to planar bilayer formation in ILs with <1 wt % of water and at high charging of the surface. Interfacial structuring is controlled by mesoscopic bulk structuring at high water concentrations. Surface chemistry and surface charges decisively steer interfacial ordering of ions if the water concentration is low and/or the surface charge is high. We also demonstrate that controlling the interfacial forces by using self-assembled monolayer chemistry allows tuning of interfacial structures. Both the ratio of the head group size to the hydrophobic tail volume as well as the surface charging trigger the bulk structure and offer a tool for predicting interfacial structures. Based on the applied techniques and analyses, a qualitative prediction of molecular layering of ILs in aqueous systems is possible.

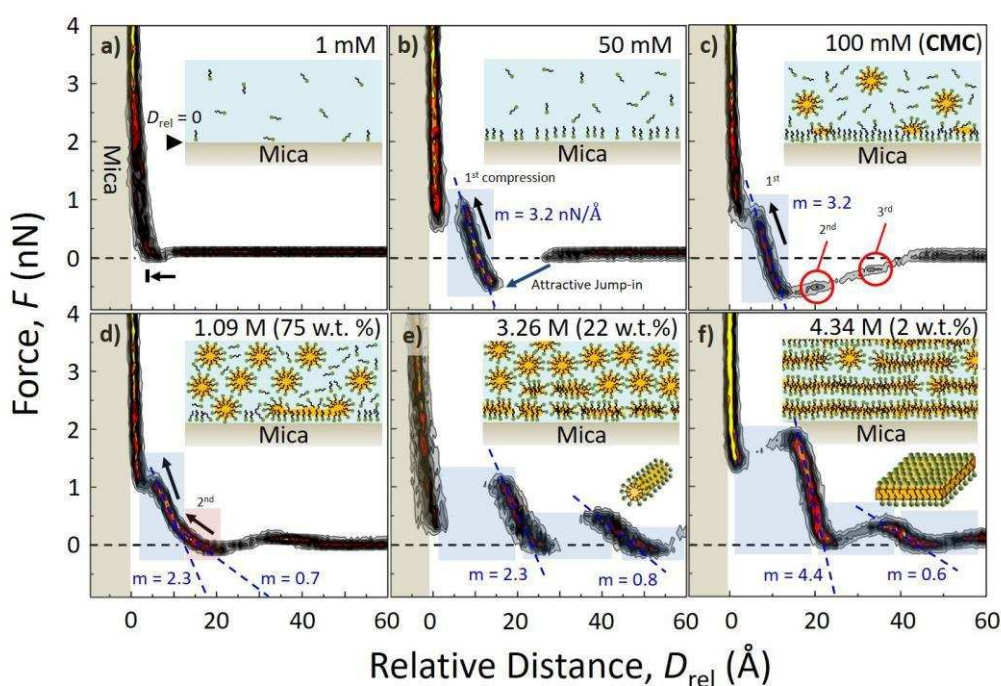


Figure 1. 2D-FD AFM measurements of water-concentration dependent interfacial structuring of [C₈MIm][Cl]/water mixtures on freshly cleaved mica surfaces with schematic structural interpretations as inset.

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Interactions of anionic surfactants with cationic vesicles under confinement

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Cationic vesicles, such as those of quaternary ammonium surfactant DEEDMAC, are mimics to liposomes and promising delivery vectors. It is of fundamental, as well as practical, importance to study the interactions between such vesicles and oppositely charged (anionic) surfactants, as these interactions can account for improved performance in their applications, but also contribute to the vesicular rupture and destabilisation of such dispersions. SFA studies of DEEDMAC bilayers prepared using the Langmuir-Blodgett deposition method have been reported previously [1, 2], investigating DEEDMAC interactions with cationic polymers. However, there is a lack of understanding of the interfacial behaviour of DEEDMAC/SDS complexes.

In this study, we have employed synchrotron X-ray reflectivity (XRR) [3] and surface force apparatus (SFA) [4] to study the structure and interactions of DEEDMAC bilayers at the solid-liquid interface, to correlate with their solution behaviour revealed using small angle neutron scattering (SANS) and dynamic light scattering (DLS). Here, DLS and zeta potential measurements of DEEDMAC and SDS showed a charge inversion at high enough SDS concentrations, suggesting that their complexation has taken place [5].

For the XRR characterisation at the solid-liquid interface, a dispersion of 5 mg/mL DEEDMAC vesicles of ~100 nm in diameter prepared by the extrusion method was ruptured to form a bilayer on the negatively charged mica surface. The thickness of the bilayer was ~3 nm, which agrees with that of a DEEDMAC bilayer in a vesicle (~3.5 nm) as previously reported [6].

Our SFA results confirm formation of a DEEDMAC bilayer (3 to 4 nm thick; Fig.1), in agreement with the XRR data. The interactions between such cationic bilayers immersed in increasing concentrations of SDS were studied. Upon addition of SDS above its cmc, the presence of a ~40 nm thick surface layer was observed, indicating adsorption of SDS aggregates on the cationic bilayer. The behaviour of such surface complex layers under confinement and shear was also investigated, revealing a relatively low friction coefficient, with a distinct stick-slip behaviour. These SFA results on DEEDMAC bilayers from vesicle rupturing in the presence of oppositely charged surfactant aggregates are unprecedented. We will compare these results with previous SFA measurements on the interactions between Langmuir-Blodgett deposited DEEDMAC layers and cationic polymers [1, 2].

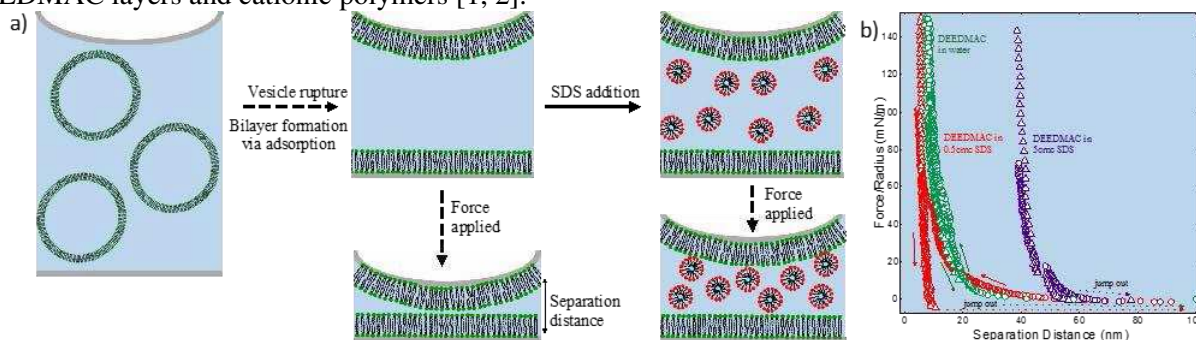


Figure 1. a) A schematic representation of DEEDMAC-bilayer formation via vesicle rupture, and their interactions with SDS aggregates at the solid-liquid interface; and b) the force vs separation distance data in different SDS concentrations, collected when the surfaces were approaching and separating.

Acknowledgements: Funding from BBRSC CBMNet is gratefully acknowledged.

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Emulsion stability at minimal surfactant concentrations: a multiscale study

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We investigate the stability of a classical oil-in-water emulsion in the limit of very low surfactant concentration, by employing a combination of different techniques covering a wide range of scales. Structural information from macro-imaging and microscopy is combined with dynamics investigated by Differential Dynamic Microscopy (DDM) and Diffusing Wave Spectroscopy (DWS), to access the mean square displacement of droplets and rheological properties of the system. DDM analyses time sequences of microimages, accessing dynamics on the mm- μ m length range at times >0.01 s [1]. DWS is a spectroscopic technique sensitive to tiniest motions and to fast time scales by analysing the time evolution of coherent light that has been multiply scattered within a turbid sample [2].

Focusing on DWS, we discuss different experimental approaches to experiments and analysis applied to emulsions; we investigate the obtainable accuracy of the correlation functions, of the mean square displacements and of the complex shear modulus that from them can be deduced [3]. This point -critical to avoid artifacts- is often overlooked in the literature.

We report on the application of these techniques to the study of long-time ageing and stability of prototypical SDS dodecane-in-water emulsions at low SDS concentration [3,4]. The combination of macro-imaging, micro-imaging, DDM and DWS, in conjunction with interface properties analysis, offers a consistent picture of the mechanisms stabilizing this emulsion, well below the CMC. Stability with minimal concentration of surfactant is a relevant applicative topic e.g. for environment reasons.

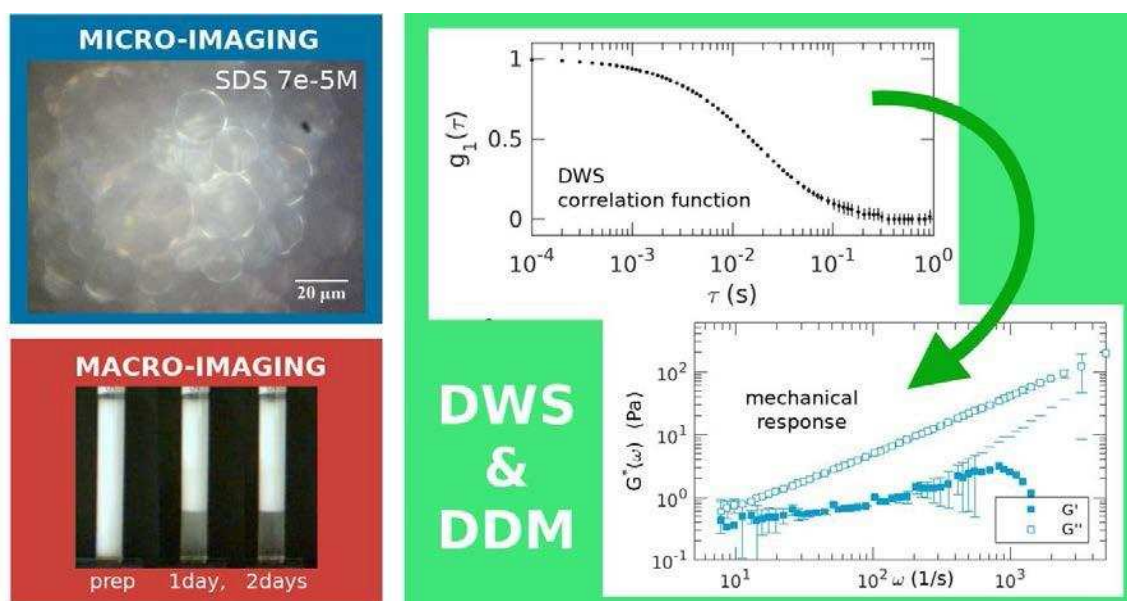


Figure 1. The combination of macro-imaging, micro-imaging, DDM and DWS enables the characterization of emulsion stability at very low surfactant concentrations, well the below CMC.

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Controlling the formation of surface active material reservoirs in spread polyelectrolyte/surfactant films at the air/water interface

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In this work, we demonstrate the possibility of controlling and tuning the formation of extended structures, acting as surface active material reservoirs, in surface loaded, out-of-equilibrium films of poly(sodium styrene sulfonate)/dodecyltrimethylammonium bromide (NaPSS/DTAB). The films are formed by exploiting the Marangoni spreading from dispersions of highly surface active NaPSS/DTAB aggregates in combination with their fast dissociation upon contact with the air/water interface [1]. This investigation has been carried out by the means of ellipsometry, Brewster angle microscopy (BAM), surface pressure vs. area isotherms (Wilhelmy method) and neutron reflectometry (NR) [2].

The formation of surface active material reservoirs in contact with the film is triggered by the presence of compact NaPSS/DTAB aggregates embedded in the film, and the process is favoured only when the charge of the aggregates matches that of the surfactant. Moreover, it is possible to control the reservoirs formation both in terms of morphology and surface excess of the two components, either by consecutively dispensing small aliquot of NaPSS/DTAB dispersions onto the water surface or by compressing a surface loaded film. Upon expansion, the fast re-supply of surface active material from the extended structures delays the relaxation of the surface pressure. Although there are of course important differences in the composition of the system with that of lung surfactant, in which protein activates the formation of reservoirs upon compression that resupply the interface upon expansion [3], excitingly there is analogy in the behavior that has not been observed before, which we are actively exploiting as we continue this work.

This study could open up new possibilities to control such film dynamics in related systems through the rational design of particles in the future. In addition it can have some immediate practical application for the efficient and eco-sustainable production of organic thin films prior to transfer application.

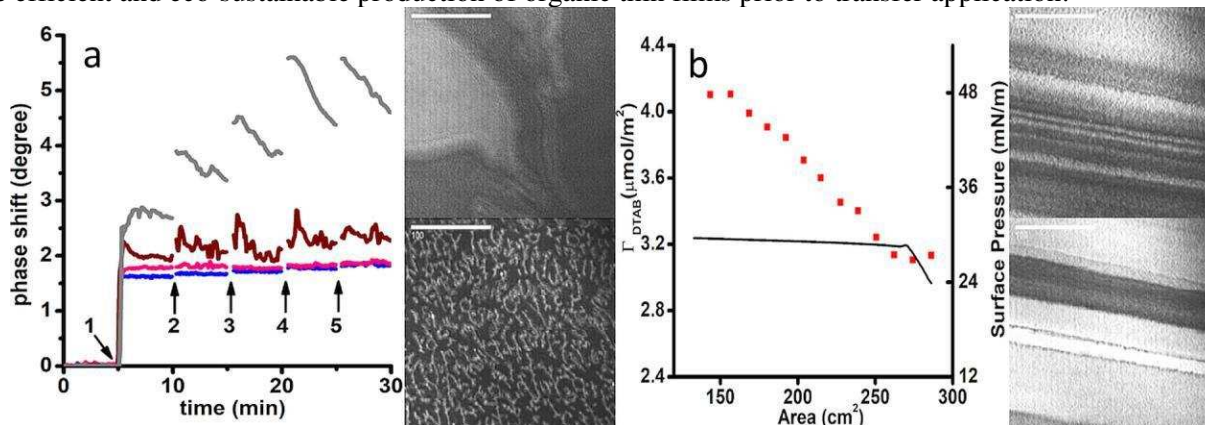


Figure 1. a) Dynamic phase shift of the air/water interface during five consecutive additions of NaPSS/DTAB dispersion with different charge/structure. b) Surfactant surface excess derived from *in-situ* NR measurements during the compression of the interface. The respective BAM images are on the right side of each panel for 2 different surface ages.

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Adsorbed macromolecules as steric stabilisers at the oil/water interface: specific ion effects and complexation with surfactants

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Industrial formulations commonly use amphiphilic macromolecules as steric stabilisers and the chosen polymers may be required to remain adsorbed across a wide range of dilutions, ionic strengths and in the presence of additional surface active species. A typical hair conditioner formulation, for example, contains low molecular weight poly(dimethyl siloxane), PDMS oil, emulsified by Pluronic polymers (including F127) in a buffer solution; at point of use, it can be subjected to significant dilution and be brought into contact with anionic and non-ionic surfactants. The complex interactions between the polymers, surfactants and the electrolytes at the interface will affect the performance of the final product.

We have developed a covalently anchored PDMS film as an immobilised oil layer to study the structures of Pluronic F127 adsorbed at the oil/water interface. We will describe the changes in the adsorbed structure in a salty environment as well as the interfacial structures of mixed stabiliser systems F127/SDS and F127/C16TAB, looking also at the impact that these environments have on the steric barrier provided by the polymer.

Results from neutron reflection and QCM highlight that the structures at the oil/water and air/water interfaces differ. It was found that F127 forms a loosely packed thin layer at the PDMS/water interface, while addition of SDS and CTAB causes desorption of F127 from the interface. Mixed stabilisers exhibit competitive adsorption behaviour where low concentrations of surfactants cause swelling of the PEO segments of F127 and high concentrations of surfactants completely solubilise the F127 (Figure 1).

The effect of salt on the adsorption behaviour was also investigated. Both UV-Vis absorbance and QCM studies showed addition of different sodium halide salts leads to dehydration and collapse of the adsorbed F127 layer and that the effect is larger for more kosmotropic anions.

These results help elucidate the mechanism of adsorption of amphiphilic polymers, their function as colloidal stabilisers at the oil/water interface and guide the selection of polymeric stabilisers for industrial formulation.

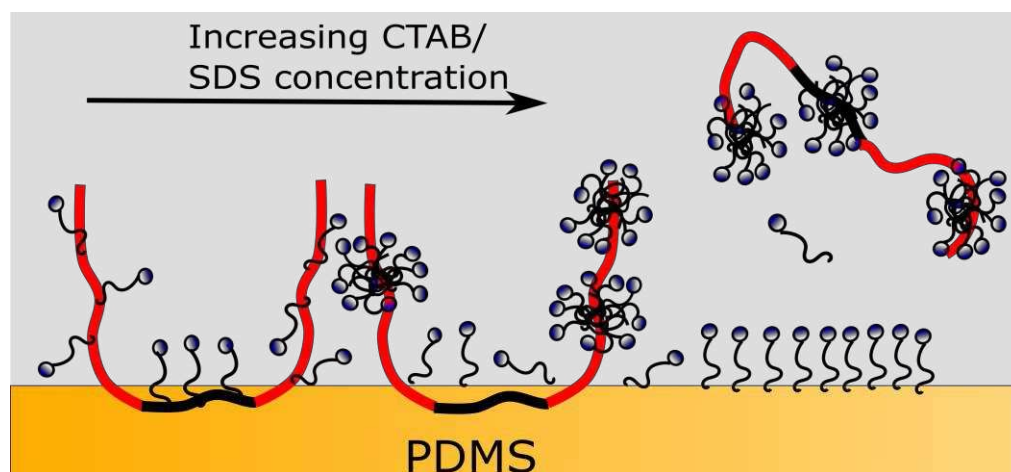


Figure 1. Changes to the conformation of the Pluronic polymer on the surface, and eventual displacement from the surface, as a result of added surfactants.

Cohesive and non-cohesive adsorption of surfactants at liquid interfaces

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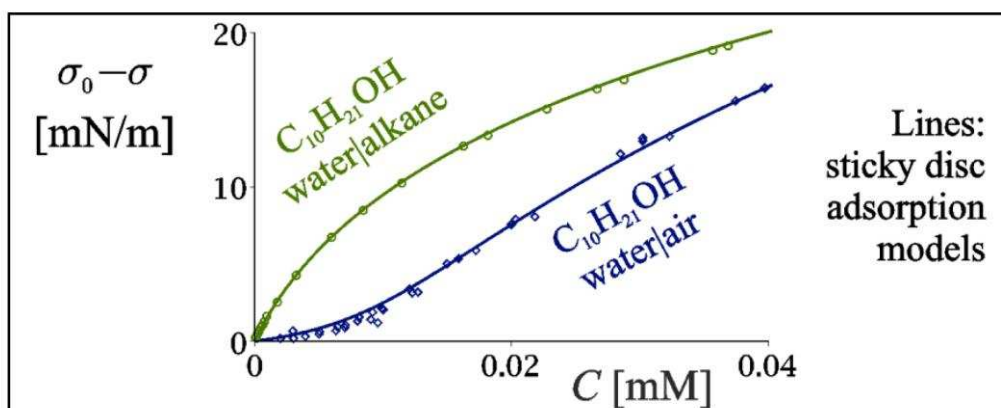
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The basic statistical mechanical models of delocalized (liquid interface) adsorption of surfactants involve three well-defined parameters: the adsorption energy, the hard-disc area of the molecule, and the lateral attraction parameter. However, many studies of the adsorption at water|oil interfaces report unexpected negative values of the attraction parameter, and hard-disc areas that are significantly larger than the crystallographic cross-section area of the surfactant. We show that the new sticky disc adsorption model [1] has serious advantages over other, more popular adsorption theories:

- it is the only model that is compatible with the experimental crystallographic area per molecule, both at water|air and water|oil interfaces;
- it predicts correctly the transition from non-cohesive to cohesive behaviour of the monolayer with the increase of the chain length or the decrease of temperature.

A model of the lateral attraction (the 2nd virial coefficient of the adsorption layer) is presented, from which it follows that β has strongly non-linear dependence on the hydrocarbon chain length, the area of the head group and the temperature. Using the model of β , experimental data, and the law of corresponding states, the critical point of the adsorbed layer could be determined, allowing one to predict the transition from sub-critical to super-critical behaviour with respect to the gaseous-liquid expanded phase transition.

We also discuss the explicit effect of the solvent molecules in the adsorption layer on its properties. It is shown that the osmotic effect from the solvent can be rigorously represented as an effective lateral attraction.



Acknowledgements: support from BP through the BP International Centre for Advanced Materials (BP-ICAM) is gratefully acknowledged.

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Preparation of Novel Film-Forming Armoured Latexes Using Silica Nanoparticles as a Pickering Emulsion Stabiliser

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Polymer latex particles of diameter <300 nm have been prepared in the absence of surfactants through a Pickering-type emulsion polymerisation process stabilised in part by silica nanoparticles [1]. Control of the silica wettability through modulation of reaction pH or by reaction of the nanoparticles with a hydrophobic silane resulted in silica-covered latex particles. Conditions were investigated to maximise adsorption of nanoparticles onto the surface of the latex such that the resultant latex was both film-forming and completely armoured in nano-silica. The oil-in-water emulsion polymerisation process used methyl methacrylate (MMA) and n-butyl acrylate (BA) as co-monomers, along with a water-soluble initiator, in the presence of a commercially available colloidal nano-silica (Ludox®- TM40). It was found that precise pH control before polymerisation using methacrylic acid (MAA) facilitated the formation of armoured latexes, and mechanistic features of this process are discussed. An alternate method of the preparation of these latexes were identified whereby the addition of vinyltriethoxysilane (VTES) to control wettability readily resulted in latexes completely armoured in colloidal nano-silica (Figure 1). The latexes were characterised using SEM, cryo-TEM and AFM imaging techniques and the mechanism behind the adsorption was investigated through surface pressure and contact angle measurements in order to understand the factors that influence this irreversible adsorption. Results indicate that nanoparticle attachment (but intriguingly not latex size) is dependent on particle wettability, providing new insight into the formation of nanoparticle-armoured latexes, along with opportunities for further development of diversely functionalized inorganic/organic polymer composite particles.

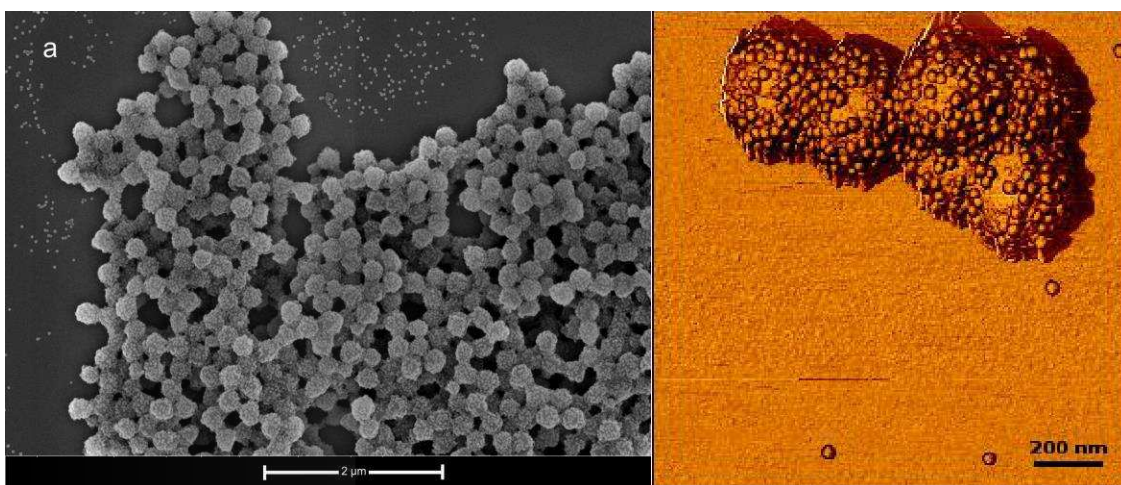


Figure 1. a) SEM image and b) AFM image of latexes prepared using MMA+VTES at pH 4.5 showing attachment of nanosilica onto the particle surface

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Linking molecular architecture and interfacial structure to the lubrication mediated by oil-soluble copolymer additives

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Chemical additives are added to automotive lubricating oils for two main purposes: to minimise degradative processes within the engine (such as oxidation, wear and corrosion) and to confer other beneficial properties to the oil and engine (such as increased viscosity index, improved fuel economy and reduced particulate/gaseous emissions). Low friction between components is highly important, as it results in both improved fuel economy and a reduction in wear. However, in the mixed and boundary lubrication regimes between metal surfaces in contact as shown in the Stribeck curve [1], the low viscosity of the lubricating oil limits its load bearing capacity, leading to high wear. This problem can be circumvented by the addition of chemical species termed 'friction modifier additives' to engine oil formulations, which maintain a separating film between surfaces even in the boundary regime [2]. It has been demonstrated that certain amphiphilic copolymers can adsorb onto polar surfaces from a selective, non-polar solvent and reduce friction in these regimes while maintaining wear performance [3,4]. However, the polymer structures at the solid-liquid interface under such tribological conditions are not currently well understood, which is critical to rational design of polymer molecular architecture for its optimal friction and wear performance as lubricant additives.

Our system of interest is a class of functionalised amphiphilic copolymers, bearing up to 10% by weight of polar graft groups. A Langmuir-Blodgett trough has been used to control the lateral packing density of monolayers of these polymers and observe their surface activity at the air-water interface *via* a Π -A isotherm study and Brewster angle microscopy (BAM). Subsequent probing of their interfacial structure *in situ* and when transferred to the mica-air interface *via* Langmuir-Blodgett (LB) deposition has been performed using synchrotron X-ray reflectivity (XRR) [5]. The XRR data demonstrate the formation of surprisingly thick layers (20-70 nm, increasing with packing density) at the air-water interface, which are retained when transferred to a mica substrate and suggests that either multilayer or brush structures are formed by the polymers as opposed to a simple adsorbed monolayer. Adsorption isotherms for these polymers onto iron (III) oxide powder (a model engine surface) from *n*-dodecane have also demonstrated evidence for aggregate adsorption from solution at higher bulk polymer concentrations.

Finally, the surface forces apparatus (SFA) has been used to measure the interactions between two symmetrical LB-deposited layers of polymer in *n*-dodecane between two mica surfaces. The normal force profiles can be fitted to the Alexander-de Gennes model describing the interactions between symmetrical polymer brush layers under confinement, shedding light on the possible interfacial structure adopted by these polymers in a tribocontact. Future shear measurements in the SFA will help to correlate the confined interfacial structure to the lubrication mediated by these polymers. This will help to link the polymer molecular architecture to their interfacial structure and the lubrication they mediate, the understanding of which is crucial to the future rational design of new polymeric friction modifiers.

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In silico modelling of microgels in bulk and at interfaces

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In contrast to solid colloidal particles, microgels respond to external stimuli such as the temperature and the pH of the solution. This peculiarity has been widely applied in bulk experiments, where the subsequent size changes can be used to tune the particle volume fraction with no change in its number density [1]. Recently, stimuli-sensitive microgels have also demonstrated to provide a unique approach to stabilize emulsions: their porosity and softness allow them to deform and flatten in presence of liquid-liquid interfaces [2]. Despite the plain experimental interest, theory stands behind, as models lack a comprehensive description in terms of the internal polymeric nature of the microgels, which is fundamental to describe their elasticity and deformability, especially in high density states.

We aim to fill this gap by modelling *in silico* realistic PNIPAM microgels whose form factors and swelling behavior reproduce experimental outcomes [3]. Moreover, by extending this protocol to treat explicitly the solvent [4], we are able to perform Molecular Dynamics simulations of liquid-liquid interfaces. Indeed, varying the parameters of the monomer-solvent potential, we can selectively tune the surface tension enabling the asymmetric squeeze of the network, as expected for solvents of different qualities. Moreover, we note a dependence on the number of crosslinks of the microgel: the higher their amount, the stiffer the polymer network. The newly designed protocol will allow us to provide a three-dimensional characterization of the microgels positioning and microstructure both at interfaces and in bulk, paving the way to the calculation of multiple particles' effective interactions.

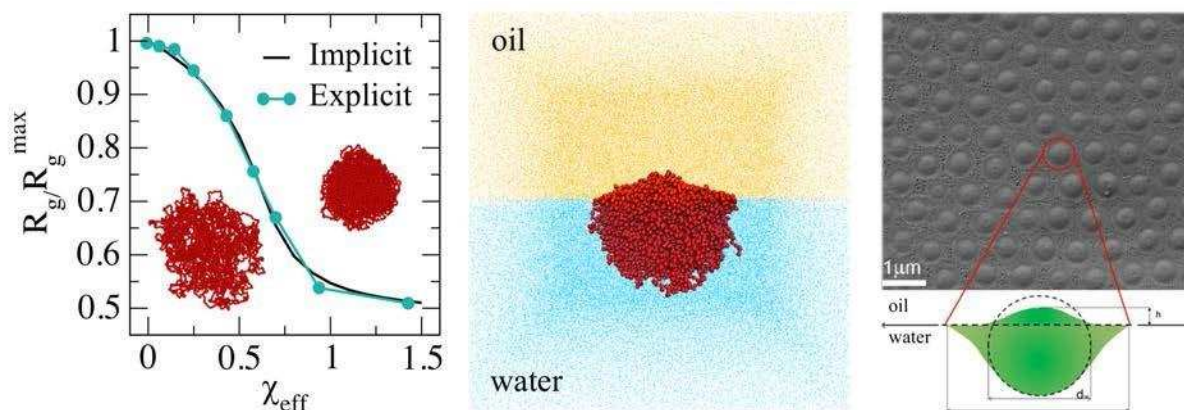


Figure 1. The left panel reports a comparison between swelling curves of the microgel in bulk obtained with implicit and explicit solvent models; both are reported in terms of the rescaled gyration radius as function of an effective swelling parameter. The central and right panels, instead, show the computational and the experimental realizations of a microgel at the water-oil interface (experiments taken from Ref. [2]).

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Control of the sign and magnitude of Casimir-Lifshitz torque by material manipulation and intervening liquid medium

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The introduction of a pair of material slabs in vacuum breaks its translational symmetry giving rise to the Casimir-Lifshitz force between the slabs. If, in addition, the material slabs are birefringent or anisotropic, the rotational symmetry of vacuum is broken in which case a torque appears between the slabs tending to rotate and align their principal optical axes [1]. While the existence of the Casimir-Lifshitz torque is of great fundamental interest, its experimental realization will pave way for device applications such as nano-switches and actuators.

We present a perturbative theory of the Casimir-Lifshitz torque between planar biaxial materials and demonstrate that the torque in the retarded limit between a pair of biaxially polarizable anisotropic slabs can exhibit a change of sign over separation distance [2]. The sign-reversal is a consequence of the intersection of the in-planar dielectric components of one of the material slabs or of both the slabs but at significantly different frequencies. In the present work, this feature is exploited to change and enhance the magnitude and the sign of torque from material manipulation such as injection of carriers. In particular, with the aid of our perturbative theory, we will demonstrate the effect on torque due to the presence of an intervening liquid medium between the pair of interacting planar slabs. The feasibility of experimental detection of torque employing the sign-reversal effect is discussed.

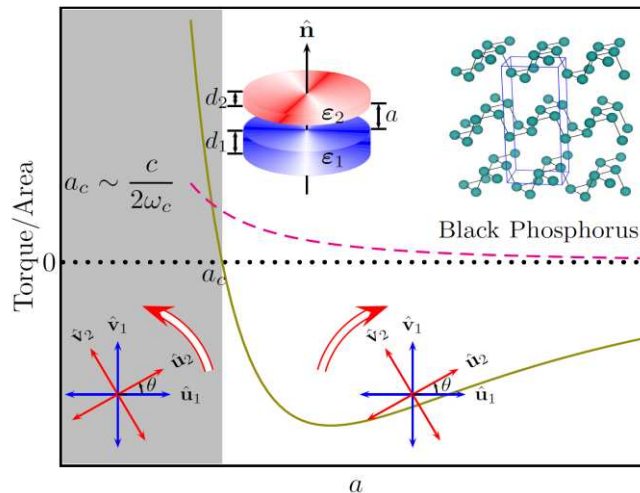


Figure 1. Schematic figure displaying the reversal of sign of torque with distance. (Figure courtesy [2])

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Monolayers of poly(amido amine) dendrimers and poly(diallyldimethylammonium chloride) studied by *in situ* streaming potential measurements and AFM

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The adsorption of globular poly(amido amine) dendrimers of generation 8 (PAMAMG8) and elongated poly(diallyldimethylammonium chloride) (PDADMAC) on mica at various ionic strengths and pHs was studied by *in situ* streaming potential measurements and AFM.

The macrocations were characterized in the bulk using the dynamic light scattering (DLS) and electrophoretic mobility measurements (LDV). The hydrodynamic diameters of PAMAMG8 and PDADMAC derived from the DLS measurements were independent of ionic strength and buffer type. At pH range 4-10 they were equal to 10.4 nm and 38.5 nm, respectively [1,2]. The electrophoretic mobility, the zeta potential and the electrokinetic charge of these macroions were also determined. It was found that both they were positively charged at pH up to 10 for the ionic strength range 10^{-2} -0.15 M [1, 2].

The adsorption of these macrocations on negatively charged mica substrate was studied by *in situ* streaming potential measurements interpreted in terms of the electrokinetic model [1, 2]. Additionally, the PAMAMG8 kinetics was determined using a direct AFM imaging at various pHs [1]. The acid-base properties of the dendrimer layers adsorbed on mica were also determined (Fig. 1). The desorption kinetics of macroions from monolayers of various coverage under forced convection conditions was also studied. It was found that the dendrimer and PDADMAC adsorption was partially reversible for pH above 5.8 [1]. The obtained results were quantitatively interpreted in terms of the random sequential adsorption (RSA) model. This allowed us to evaluate the equilibrium adsorption constant and the binding energy for the macroions at various ionic strengths, and pHs. The binding energy of dendrimers at pH 5.8 for the ionic strength of 10^{-2} M was equal to -19 kT, which was close to the value of -20 kT theoretically predicted applying the mean-field DLVO theory [1]. The binding energy of PDADMAC molecules was equal to -20 kT [2]. The PAMAMG8 and PDADMAC monolayers can be exploited as an effective platform to investigate the binding kinetics of various ligands such as anticancer and antiviral drugs, antibodies and bacteria.

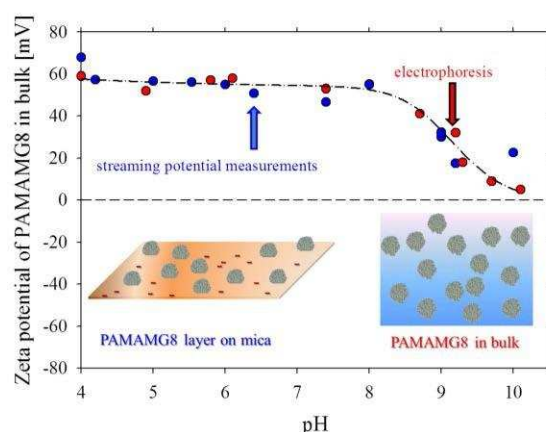


Figure 1. Zeta potential of PAMAMG8 dendrimers determined by electrokinetic methods.

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Strategies for functionalizing nanofibrillated cellulose and producing antimicrobial foam-like materials

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The increasing requirements for sustainability and multifunctionality in nowadays' society encourage research and development on materials derived from renewable, naturally occurring resources featuring active properties, particularly antibacterial activity. This is of noteworthy importance for the food industry, which requires that products reach remote regions as a result of recent food-consuming trends driven by globalization and industrialization. During storage and transportation, though, food items are susceptible to microbial spoilage [1]. Another important aspect from a food supply chain standpoint is weight, provided that it is directly related to distribution costs.

In this sense, cellulose stands out as a promising material because it combines the aforementioned renewability with wide availability and extremely high capacity of undergoing surface modification as a result of its chemical structure [2], which is also herein exploited. In this contribution, highly porous, light-weight foam-like materials based on nanofibrillated cellulose (NFC) are addressed, as well as physical and chemical functionalization routes aimed at providing them with antimicrobial activity against relevant pathogenic bacteria.

More specifically, different surface chemical modification routes have been used to induce cationic groups onto NFC surfaces in order to boost their electrostatic interaction with microbial cells, leading to the leakage of their essential contents (*i.e.*, lysis). Examples include reactions of NFC with Girard's reagent T and glycidyltrimethylammonium chloride (EPTMAC) to end up with positively charged quaternary ammonium groups. Another chemical means of providing NFC-based foam-like materials with antimicrobial activity is chemically grafting antimicrobially active peptides onto NFC surface. Both of these strategies are carried out in aqueous NFC dispersions, which are subsequently dried by freeze-, supercritical CO₂- or oven-drying to form cryogels, aerogels, or xerogels, respectively [3]. Adsorption of antimicrobial polyelectrolytes (*e.g.*, chitosan and sodium alginate) through layer-by-layer approach onto NFC-based aerogels is also discussed.

In summary, the production of *quasi*-cylindrical *ca.* 15-mm-long, 12.5-mm-diameter NFC-based aerogels will be addressed, as well as physical and chemical strategies to provide these with antibacterial activity. Morphological, mechanical, and water-holding properties will be presented in details.

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Soft foams as acoustic gradient index metasurfaces

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Metasurfaces are 2D objects of thickness t that strongly interact with waves of characteristic wavelength $\lambda \gg t$. Such objects may be used as focusing devices, beam deflector, filters, mirrors etc.... The general action of such devices is to shape a given phase front in order to achieve various properties [1]. To perform such devices, researchers may use resonators, which consist of small entities strongly interacting with the incoming wave [2]. Another method is the use of Gradient Index Materials (GRIN), which are most of the time obtained by shaping the structure of the material [3]. In such cases, the device remains most of the time larger than the wavelength. Here we present a novel class of GRIN metasurfaces made of porous soft silicone rubbers for focusing, deflecting, rotating and absorbing acoustic wave in water, with thicknesses around $\lambda/5$.

We use the dependence of the refractive index n of soft porous polymer materials with their porosity ϕ ($n = \frac{c_0}{c_L}$ where c_0 and c_L are the longitudinal sound speed in a reference medium and in a given material respectively) that we showed in previous works [4]. Here, we achieve a spatial gradient of porosity in the materials using soft-matter technology to fulfil required refractive index profile (Figure 1). These subwavelength GRIN metasurfaces were achieved by a control over the spatial distribution of porosities in soft silicone rubbers using an emulsion templating method (referred to as “polyHipe” for polymerized High Internal Phase Emulsion). The obtained GRIN samples were fabricated by UV polymerizing successive layer of emulsion exhibiting different and fully controlled volume fractions. The final wet samples were dried using supercritical CO₂, without collapse and deformation of the pore structures. Once dried, the samples were positioned in front of an ultrasound transducer and its effect on the acoustic field is measured.

The ultrasonic experiment characterizations have an excellent quantitative agreement with finite element simulations. Our GRIN metasurfaces permit portable, low-cost and efficient applications such as biomedical imaging/detection and micro particle control [5].

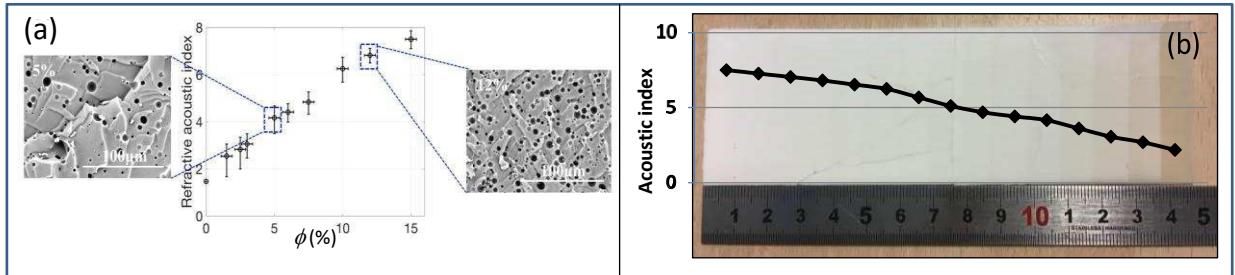


Figure 1. (a) Evolution of n as a function of porosity; Insert : SEM images of porous PDMS materials (with $\phi = 5\%$ and 12%); (b) Porous sample with gradient of porosity resulting in a gradient of acoustic index. Each stripe of the sample is 9 mm wide with a porosity that decreases from left (15 %) to right (1%).

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Emulsion destabilization by confinement

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Emulsions play an important role in everyday life and can be found in for example food, cosmetics and paints. The destabilization of emulsions is a key step in for example oil recovery, to extract water from crude oil. Present techniques to destabilize these crude oil emulsions are often energy-intensive and/or use chemical additives that end up in the water [1]. Recently, it was shown that mechanical destabilization during spreading can be used to destabilize emulsions also [2]; however its mechanism remained unclear.

We study the destabilization of surfactant-stabilized oil-in water emulsions placed between two glass plates that are pressed together. Using confocal microscopy, we observe the deformation of the oil droplets from perfectly spherical to ellipsoidal. Applying more pressure the sample thickness becomes comparable to the drop size and the emulsion film between the droplets becomes clearly visible. This film thins and eventually breaks, leading to the massive coalescence of droplets occurred and hence the destabilization of the emulsion. This new technique then allows for separation of the oil and water phases from an initial emulsion in a simple manner.

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Understanding blood cell stabilization – Effect of plasticizer on lipid monolayers

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Plastic bags are used to collect and store blood for transfusion purposes. The most common material used for these bags is polyvinylchloride (PVC) which is plasticized with di(2-ethylhexyl) phthalate (DEHP). DEHP is inherently toxic [1] and leeches out of the polymer matrix. However, DEHP has been shown to stabilize red blood cells and thereby increase the shelf life of stored blood [2,3]. We have studied how DEHP interacts with a lipid monolayer by utilizing a simple binary model system, consisting of the lipid 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and the plasticizer DEHP. This investigation has been performed primarily by surface pressure measurements, using a Langmuir trough, and by neutron reflectometry. Deuterated DEHP was synthesized and used in the reflectivity measurements to identify that component directly.

Monolayers of DMPC behave significantly differently when DEHP is introduced. First, a monolayer with high surface pressure is formed at larger areas when DEHP is present. Further, a plateau in the surface pressure becomes apparent as the DEHP content is increased in the monolayer. Following the isotherm studies, neutron reflectivity was measured at surface pressures above and below the plateau-region for four different compositions (0, 20, 40 and 60 mol% DEHP respectively) and in two different contrasts (deuterated DMPC + hydrogenous DEHP and hydrogenous DMPC + deuterated DEHP). Data could be well-fitted as uniform monolayers which suggests that there is intermixing at a molecular level. At 60 mol% initial DEHP content, DEHP content is reduced in the monolayer as the surface pressure increases. This is not the case for the other monolayer compositions which indicates that DEHP is squeezed out of the monolayer at high surface pressures when the content is too high. At least 25 mol% of DEHP remains at surface pressures of 30 mN/m. Data representing this are shown in Figure 1.

Given that the DEHP mixes with the DMPC in the monolayer, we conclude from the pressure-area isotherms that DEHP helps the formation of a more compact monolayer even at large surface areas.

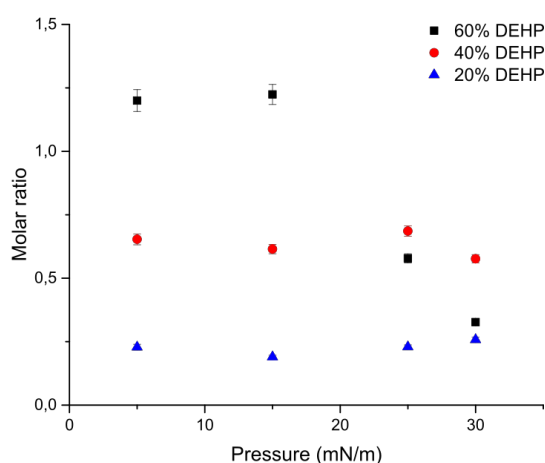


Figure 1. Molar ratio between DEHP and DMPC for different surface pressures as obtained from fitting reflectivity data.

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The effect of ions on lipid membrane elasticity - from vesicle fusion to cell penetrating peptides

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Ions and charged peptides can have dramatic effects on the properties of membranes. A case in point is Calcium and its crucial role in vesicle fusion [1]. We simulated Calcium-mediated vesicle fusion using All-atom molecular dynamics [2] and described the effect of Calcium on membrane curvature [3]. With the help of a new approach to determining membrane elastic properties [4] we gained new insights into the mechanism of membrane fusion and curvature generation by ions. Specifically, we explore the effect of calcium on the curvature and elastic properties of membranes of different composition. Another example of prominent membrane deformations caused by ions is the internalization of arginine rich cell penetrating peptides. We present an investigation of the role of ion pairing [5] and a new mechanism for entry driven by curvature elasticity [1]. Furthermore, we apply our methodology to a host of other ions and membrane compositions in order to explore the molecular origins of curvature generation and membrane stiffening by charged adsorbates.

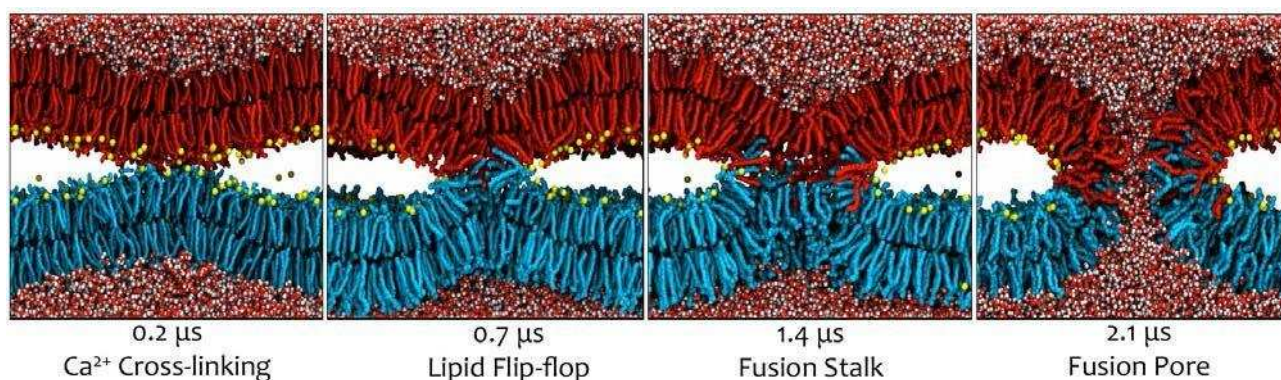


Figure 1. All atom simulation of Ca²⁺-mediated vesicle fusion

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Geometric pinning and antimixing of scaffolded lipid membranes

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Cellular membranes can feature lipid domains relevant for signalling, intracellular transport and cell division [1-3]. Their shape is set by the cytoskeleton and varies from elongated neurons to disk-like red blood cells. Previous studies were not able to model the scaffolding properties of the cytoskeleton and test how its shape influences the localization of lipid domains [4-7].

Here, we present a new class of multicomponent vesicles supported by colloidal scaffolds of designed shape (Figure 1). We find that the domain composition adapts to the geometry, giving rise to a novel "antimixed" state. Theoretical modelling allows us to link geometric pinning of domains to the material parameters of the membrane.

Our results provide key insights into phase separation in cellular membranes and on curved surfaces in general.

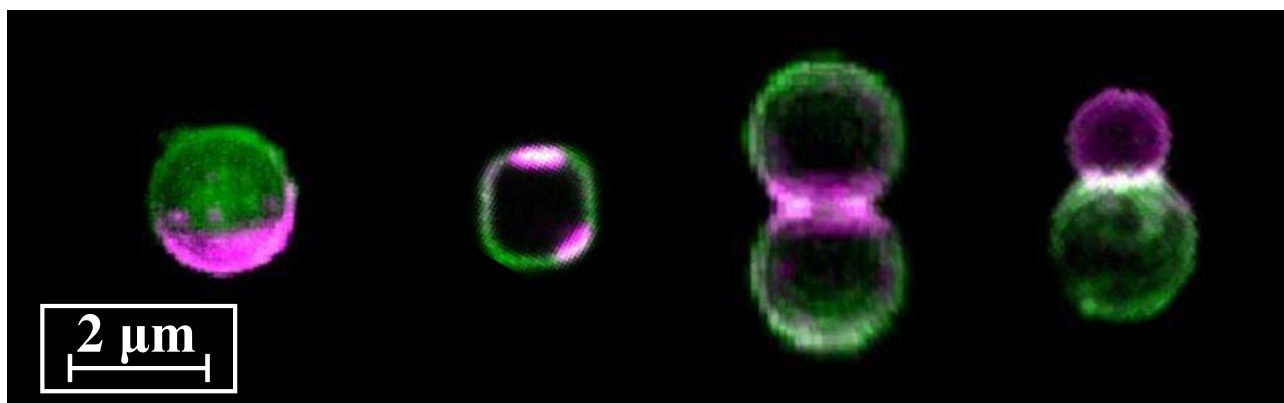


Figure 1. Four multicomponent lipid vesicles supported by colloidal scaffolds of designed shape used in the present study. Green and magenta colours label, respectively, the saturated and unsaturated lipids and show a striking interplay between the geometry of the substrate and the chemical composition of the lipids.

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Targeting the cell pole: Membrane composition or curvature?

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Several key cellular events require accurate placement and timing in the assembly of complex protein machineries. Unlike eukaryotes, prokaryotes lack the dedicated cell machinery that help in transporting protein to a targeted region. As a result all such transport is diffusion limited [1]. It is therefore intriguing how proteins find and associate with particular regions of the plasma membrane in prokaryotes. Among the potential candidates that seem to promote protein association - membrane curvature and (or) composition have emerged as the frontrunners. Local curvature of membrane, as defined by the shape of the cell or certain organelles, may be specifically recognized by certain shape-sensing proteins while local membrane composition might strongly influence the membrane association of certain proteins that interact preferentially with specific phospholipids.

Using fluorescence microscopy, we have tried to comprehend the role played by membrane curvature and composition in protein localization and assembly on cell membranes. We have investigated the interaction of the bacterial protein DivIVA with model lipid membranes that closely mimic the composition of the inner leaflet of the plasma membrane in the gram positive bacteria, *Streptomyces coelicolor* [2]. DivIVA is a determinant of cell polarity that is ubiquitous in gram-positive bacteria [3-5]. In *Streptomyces* and other Actinobacteria, it is essential for viability and for orchestrating cell polarity, polar growth and cell shape determination [6,7].

We find that the association of DivIVA with GUVs is strongly influenced by the composition of the membrane [Fig.1c]. Our results indicate that cardiolipin plays a key role in facilitating the association of DivIVA irrespective of the size of the GUVs hinting that membrane curvature might not be an essential parameter for the case of DivIVA. As an ongoing part of our research we are trying to elucidate the contribution of local membrane curvature towards this interaction.

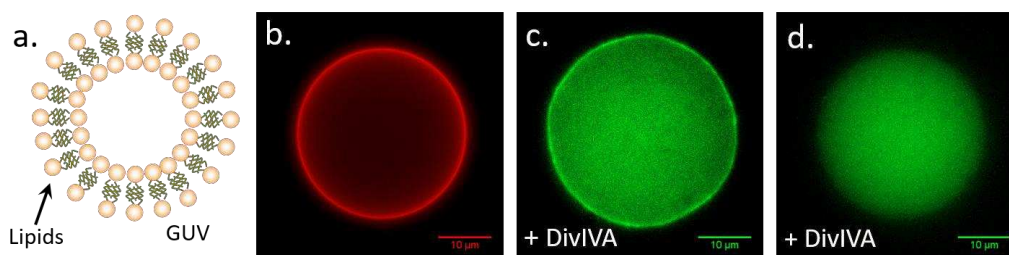


Figure 1. Biomimetic model membrane system. **a.** Schematic of a giant unilamellar vesicle – GUV. **b.** GUVs prepared in physiological buffer and labelled with ATTO647N dye. **c.** DivIVA-mNeongreen binds to GUVs that have cardiolipin. **d.** Binding of DivIVA-mNeongreen not observed in the absence of cardiolipin.

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Effects of oxidative stress on physicochemical properties and disruption of polyunsaturated phospholipid membranes

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Oxidation of lipid membranes is widely known to play a crucial role in many cellular processes and pathological conditions such as apoptosis, inflammation, infection, or sepsis, through direct damage of the cell membrane. Both enzymatic and non-enzymatic oxidation, the latter occurring via direct exposure to reactive oxygen species (ROS), lead to lipid peroxidation in living cells and tissues. ROS attack lipids containing C-C double bonds, especially those containing polyunsaturated fatty acids (PUFA). This leads to lipid degradation into oxidation products such as truncated phospholipids or carbonyl compounds, which appear to function as signalling molecules and danger markers for damaged tissue, and have dramatic effects on membrane structure, stability, and subsequent protein interactions. PUFAs are highly abundant in biological tissues, representing between 30-60% of the total fatty acid composition depending on the tissue and animal, so their inclusion in model systems designed to study oxidation of biologically relevant membranes is crucial.

In this study, we have used a combination of different biophysical and surface-chemical techniques in order to characterize the effect of oxidation on the structure, stability, and disruption of PUFA-containing membranes. Particularly, we have studied model lipid bilayers containing arachidonic acid, the most abundant amongst the different PUFA species found in mammalian tissues. We have used fluorescence-based assays to study lipid peroxidation, MDA production, stability, and content leakage of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine/1-palmitoyl-2-arachidonoyl-sn-glycero-3-phosphocholine (POPC/PAPC) large unilamellar vesicles (LUV) under various oxidative conditions, finding that short- λ UV was the most effective oxidation treatment, especially in the presence of H₂O₂. Employing a quartz crystal microbalance with dissipation monitoring (QCM-D) and vibrational spectroscopy (FTIR-ATR), we have found evidences for partial material loss from deposited POPC/PAPC bilayers, possibly by acyl chain fragmentation. We have also detected surface charge rearrangements by z-potential measurements before and after UV exposure and H₂O₂ addition. Furthermore, small angle X-ray scattering (SAXS) has been employed to investigate bilayer structure and thickness of these systems, finding that both PAPC contents and UV exposure appeared to induce bilayer thinning. Finally, preliminary neutron reflectometry studies have been performed in supported bilayers formed at solid-liquid interfaces, providing further information on oxidation-induced desorption and structural rearrangements thereof. Together, these experiments will establish the conditions to induce and quantify membrane oxidation in cell-like model membranes as a precursor to future experiments addressing nanoparticle-induced oxidative stress and disruption pathways.

Membrane Dynamics in Polyelectrolyte Mediated Multilamellar Vesicles and their Influence on the Vesicle's Structure

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Vesicles are closed surfactant bilayers. They can be found in many formulations we use on a daily basis but they also serve as simple model systems for cells. Depending on the exact composition and preparation of the formulation, either uni- or multilamellar vesicles can be formed, where unilamellar vesicles (ULVs) consist of only a single closed surfactant bilayer and multilamellar vesicles (MLVs) have an onion-like shape with several consecutive bilayers.

One of the key parameters determining the stability of vesicles is the bending elasticity of the membrane. Neutron Spin-Echo Spectroscopy (NSE) is the neutron scattering method which allows to monitor the smallest energy changes and is therefore well suited to observe relatively slow motions such as the undulation movements of vesicle membranes which are studied here [1].

Adding oppositely charged polyelectrolyte (PE) to ULVs can lead to the formation of MLVs consisting of consecutive layers of surfactant bilayers connected by mixed layers of water and polyelectrolyte [2].

The bending rigidity of a membrane strongly depends on its thickness, as is shown for ULVs and therefore, strong changes are to be expected when changing from ULVs to MLVs, the membrane thickness of the latter being much larger than the former. However, whether changes are observed depends on the chemical nature of the PE, as shown here, where 2 different systems, one of them containing flexible polyacrylic acid, the other one containing rigid chitosan, are compared and it is seen that vesicles with many surfactant bilayers are only formed when the flexibility of the membrane is retained even in MLVs.

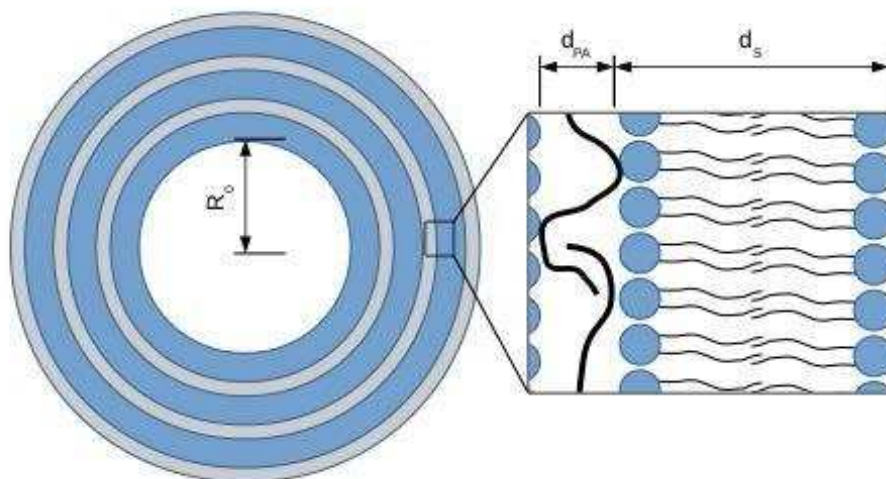


Figure 1. Sketch of a MLV with consecutive surfactant bilayers, separated by PE layers.

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Pickering emulsions stabilized by microgels: link between microgel adsorption at model interfaces and emulsion properties

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Microgels are deformable polymeric particles used to stabilize so-called Pickering emulsions [1] due to their ability to adsorb at interfaces. These microgels are known to flatten at drop surfaces [2]. In order to improve the understanding of the emulsion stabilization mechanism and of emulsion properties, the role of microgels adsorption at model liquid interfaces [3] has been studied. In this work, we examined, using the pendent drop method, the spontaneous adsorption of thermo-sensitive microgels, composed totally or in part by p(N-isopropylacrylamide) (pNIPAM). We screened various parameters either during the synthesis like the cross-linking density *i.e.* the microgel deformability and the presence of charges through the use of pH sensitive groups or *in-situ* (pH, electrolyte concentrations). We show how all these parameters, as well as the microgel bulk concentration impact their kinetics of adsorption. Moreover, we measured the interface dilatational visco-elasticity using the oscillatory drop method. We show that the maximal dilatational interfacial elastic modulus increases as the cross-linking density decreases. We then attempt to correlate these interfacial properties with the emulsions properties (stability, aggregation...). We also make the link between the kinetics of adsorption and the required conditions to prepare emulsions using microfluidics.

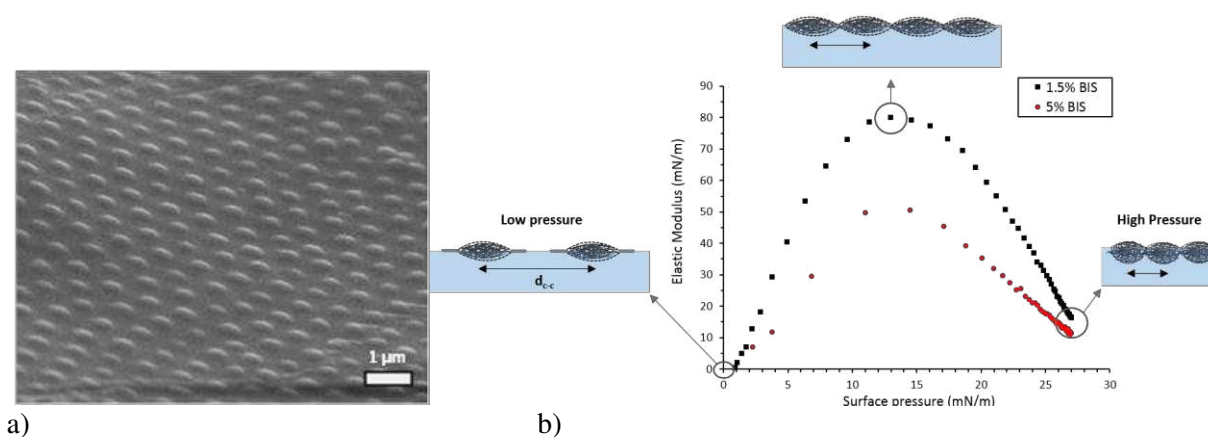


Figure 1. Microgels at interfaces: a) CryoSEM picture of microgels adsorbed at the surface of a drop and b) Elastic modulus as a function of surface pressure for microgels with two different cross-linking densities more deformable microgels (black square) and less deformable ones (red circle) and scheme of their profile view in different conformations at different surface pressures.

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Aerated emulsions stabilized by Pickering effect

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Aerated emulsions solely stabilized with the help of adsorbed particles have been prepared. Pickering emulsions where oil droplets are stabilized by solid particles in place of surfactant are well-known. Pickering foams have received more recent attention. Aerated emulsions combine the two.

The stabilization of aerated emulsion by solid particles with no help of additional surfactant has been studied. Large uptake of air was achieved by whipping an oil-in-water Pickering emulsion using squalane as oil and hydrophobic colloidal silica for stabilization.

Non-aggregated silica colloidal nanoparticles of 20 nm diameter (Ludox) were hydrophobized by adsorption of a short-chain amphiphilic molecule (*n*-butyl amine) in order to stabilize an o/w emulsion by Pickering effect. It has been shown by Gonzenbach, Studart, Tervoort and Glaucker [1,2] that such silica nanoparticles made hydrophobic by adsorption of short amphiphilic molecules were able to stabilize Pickering foams for long durations. Arriaga and Langevin [3] argued that origin of such high stability was gelation of particles in the aqueous layers. The same system has been used for the preparation of aerated emulsions. Stable Pickering emulsions of squalane could be prepared over wide concentration ranges of oil and silica. Aerated emulsions were prepared by whipping the o/w emulsions, reaching expansion coefficients of 4. This system stabilizes aerated Pickering emulsions only with nanoparticles modified with short-chained amphiphilic molecules that could not stabilize the foam alone.

Adsorption of *n*-butyl amine on silica and emulsion droplet size and stability were investigated. The amounts of oil, silica and butyl amine were varied so as to optimize expansion and foam stability. 20% oil led to highest expansion but quite poor stability. The stability is critical since destabilization could start before the natural gelation of the system. High stability was reached for concentrated emulsions (60%oil); but improved stability was at the expense of expansion. The mechanism of foam stabilization was adsorption of oil droplets at the surface of air bubbles (Fig 1).

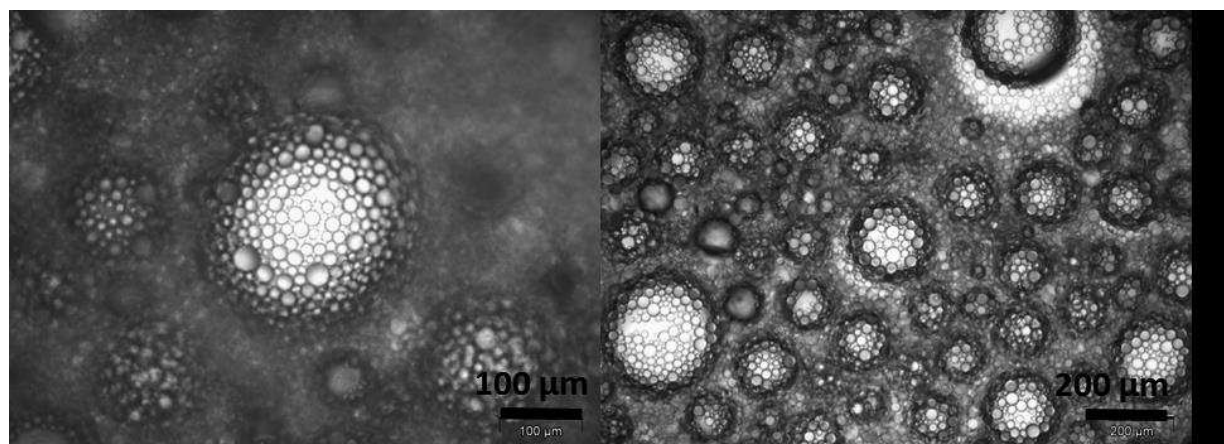


Figure 1. Air bubbles stabilized by oil droplets of Pickering emulsion. Composition of the samples: Left: 5 wt% *n*-butylamine, 22 wt% silica, 60 wt% squalane. Right: 3 wt% *n*-butylamine, 11.5 wt% silica, 20 wt% squalane.

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Inverse pickering emulsion stabilized by exfoliated hexagonal boron nitride (h-BN)

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Pickering emulsions or solid-stabilized emulsions were defined at the beginning of the 20th century in pioneering works of Ramsden [1] and Pickering [2]. In the last years, many researchers have paid attention to the ability of two-dimensional (2D) materials to promote the formation of special classes of Pickering emulsions [3]. We focus our attention in exfoliated boron nitride due to its high surface area and its planar structures [4]. BN monolayer has demonstrated outstanding properties such as biocompatibility, high temperature stability and corrosion resistance, enhanced oxidation resistance and large thermal conductivity.

In this study, we reported for the first time a simple method to prepare inverse Pickering emulsions using non-modified exfoliated hexagonal boron nitride (h-BN) as stabilizer agent. Ethyl benzoate was ascribed as the oil phase, because this aromatic organic solvent is almost completely insoluble in water and has been already successfully used for preparing Pickering emulsion with graphene oxide [5]. The stability and type of h-BN Pickering emulsions formulated with different BN concentrations and by varying oil/water (o/w) ratios are studied and discussed. Besides, the BN nanosheets are characterized by AFM, water contact angle (WCA) and SAXS and the characteristics of emulsions are discussed using a multiscale approach. First the emulsion structure is analyzed microscopically through optical and epifluorescence microscopy, and macroscopically by the study of the rheological behaviors. The average droplet size decreases with h-BN concentration whereas the emulsions achieve good stability at high BN concentrations and high o/w ratios. In all formulations, the emulsions are water-in-oil (W/O) type due mainly to the hydrophobicity of h-BN. The Pickering emulsion formulated with 2 wt% of BN is the most interesting due to its high long-term stability and its high viscosity [6]. This research paves the way for the fabrication of boron nitride-based functional materials with novel nanostructures and microstructures using Pickering emulsions as soft template.

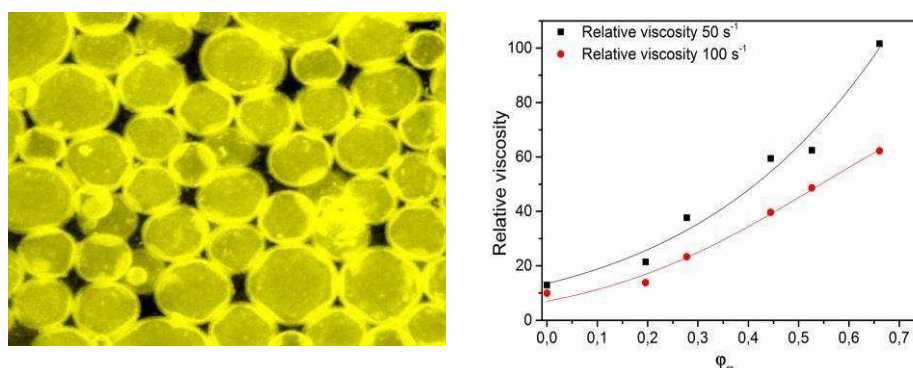


Figure 1. Microscopy image of 2 wt% BN emulsion and viscosity curves at different shear rates.

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Laser assisted device for micro/nano-emulsion production

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Low bioavailability of drugs due to their insolubility in biological fluids, polymorphism and stability phenomena is one of the problems in pharmaceuticals. This is correlated with the need to develop new dosage and delivery systems, for the selected drugs, to specific targets. In sclerotherapy, the use of foams containing active medicines reduces the quantities of drugs needed for the treatment while it enhances medicines effects due to the fact that the contact surface area with veins walls is increased (by filling it entirely for veins smaller than 12 mm) and prevent intravascular haemorrhage. These sclerosing agents are injected into the blood vessel as foams [1,2]. Encapsulating a drug in emulsions could improve its bioavailability, given its solubility in that system, and could allow its delivery to a specific target.

This work describes: a) a new laser-assisted device developed to generate emulsions with nano/micro structure containing drugs that may be used as transport vectors to specific targets; b) spectroscopic, microfluidic and optical microscopy studies of such emulsions formed by a sclerosing medicine/ surfactant and oily Vitamin A.

The effect of laser radiation on emulsions and their components constitutes an important part of this work. Therefore, the UV-Vis absorption, FTIR and Raman spectra of the solutions and of the generated emulsions were recorded before and after exposure to laser beams. Optical microscopy was employed to characterize the dimensions of the component droplets before and after the emulsions were irradiated.

Figure 1 presents the set-up used to generate the nano/micro-emulsions. The double syringe system mixes the two liquids while the focused beam breaks the obtained droplets within the emulsion into nm sized droplets.

This type of laser-assisted device that generates emulsions with micro- and nano- structures is a novel emulsifying system, for the best of our knowledge, and has the advantage to allow the use of small quantities of solutions, as low as few hundreds of μl .

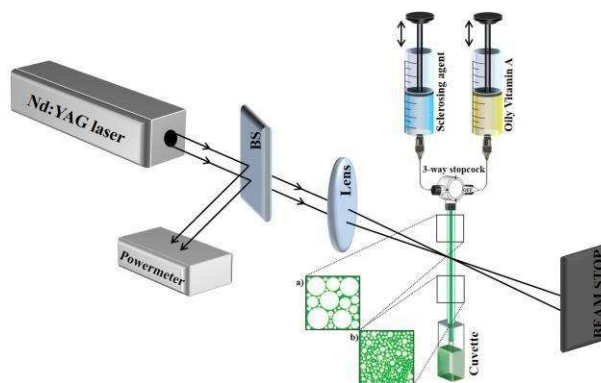


Figure 1. Schematic representation of the laser-assisted device developed to generate emulsions.

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Formulating pharmaceutically acceptable non-aqueous microemulsions

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Microemulsions are clear, homogeneous and easy to prepare dispersions of water and oil stabilised by one or more amphiphiles - typically a surfactant and a cosurfactant. Due to their numerous beneficial properties, including long-term stability, clarity and low viscosity, and their ability to solubilize large quantities of hydrophilic and/or lipophilic materials, microemulsions have been widely studied for their potential as formulation media and encapsulation vehicles in a variety of areas. Nonetheless, few commercial food- and drug-grade microemulsions have been developed over the years, mainly due to the need to use high surfactant concentrations and/or cosurfactants to promote microemulsification, which results in poor toxicology profiles of the systems.

To address this issue, the aim of this project is to increase the understanding of the guiding principles for the formation of pharmaceutically acceptable cosurfactant-free non-aqueous microemulsions, in which the naturally occurring lipid soybean phosphatidylcholine (SPC) is employed as the surfactant and various generally regarded as safe (GRAS) solvents are used. To this end, a large range of polar solvents (PSs, used in place of water) and non-polar solvents (NPSs, oils) were employed for the systematic study of the effect of solvent structure and physico-chemical properties on the phase behaviour, air-solvent interface lipid packing and bulk microstructure of non-aqueous SPC systems. The results of these studies suggest a relationship between the changes in lipid surface packing upon introduction of different solvents, the extent of the clear (microemulsion) area in the corresponding phase diagrams and the microstructure characteristics of the bulk PS/SPC and PS/SPC/NPS mixtures. In particular, it appears that there are two key structural solvent characteristics that affect the behaviour of the systems: the amphiphilicity of the polar solvent and the molecular volume of the non-polar solvent, which when increased and decreased, respectively, promote increased lipid/solvent interfacial mixing and flexibility, an increase in the microemulsion (clear) area of existence in the phase diagrams and a transition of the microstructures observed from lamellar to large ellipsoidal to smaller more spherical structures (Figure 1).

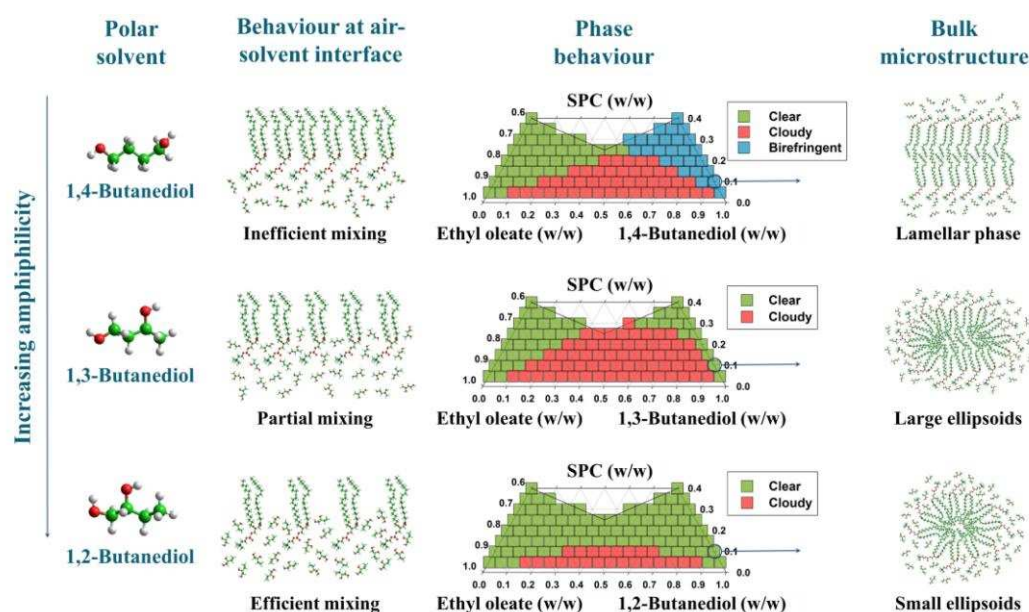


Figure 1. Effect of polar solvent amphiphilicity on lipid air-solvent interface packing, phase behaviour and microstructure in PS/SPC and PS/SPC/NPS systems.

Designing Graphene Oxide LC Films Structures through Drying Instabilities

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The assembly of graphene oxide (GO) flakes into macroscopic films has risen the problem of wrinkling. The behaviour is a direct consequence of 2D buckling instabilities generated by a compressive stress. During film compression, hydrogen-bonding interactions impede GO flakes slippage, forcing the film in bending in the third dimension. Some research efforts have been devoted [1,2] in defining and controlling this peculiar behaviour in GO liquid crystals dispersions. However, only simple wrinkles alignment has been produced through the applications of shear flows. Here, we show how basic physical-chemical parameters (concentration, temperature, rheology) control the onset of wrinkling in GO macroscopic films [3]. In addition, we define and discuss easy scalable processes to design different wrinkling patterns. The successful procedures derived from evaporation control, contact angle and surface tension effects during film drying.

The relation between GO film roughness and its antimicrobial activity has already been demonstrated. We expect that tuning wrinkles spacing and structure may add selectivity. Patterned films can be also used as templates for controlled nanoparticles deposition for SERS.

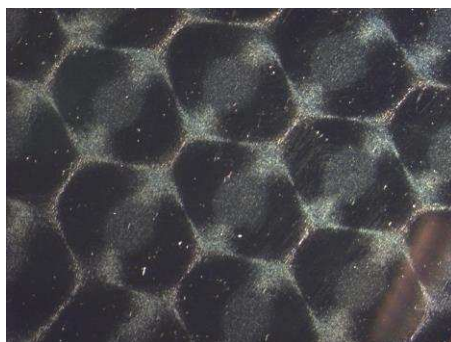


Figure 1. Cross-polarizing micrograph of a GO film with controlled design.

Acknowledgements The financial support of ANR project GAELIC and ANR LABEX Amadeus

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Surface activity of esterquat and amidoquat surfactants

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Esterquats are surface active quaternary ammonium compounds having long alkyl chains, in which the hydrophobic part of the moieties are linked to the charged head group via ester bonds R–CO–O– or ROC(O)– [1]. As a consequence of that specific structure, esterquats upon hydrolysis decompose into fragments characterized by various surface activity. Therefore, they may be referred to as „cleavable surfactants”, which usually biodegrade more rapidly than the related alkylquats as they are stable in aqueous solutions only in a narrow pH window for a certain period of time. We investigated four esterquat surfactants: regular esterquats, N,N,N-trimethyl-2– (dodecanoyloxy)ethane-ammonium bromide (DMM-11) and N,N,N-trimethyl-2–(dodecanoyloxy) –1–methylethaneammonium bromide (DMP2M-11)) having –O–CO– bond between quaternary amine and hydrophobic tail and betaine esters with –CO–O– bond: dodecyloxycarbonyl-methyl-N,N,N-trimethyl ammonium bromide (DMGM-12)), and dodecyloxycarbonyl-1–ethyl-N,N,N– trimethylammonium bromide (DMALM-12)). We demonstrated that depending on the surfactant structure, partial hydrolysis of ester bond can lead to increase of the relative surface activity, more pronounced in the basic conditions (pH 10), that can be explained by formation of surface active hydrolysis products dodecanoate anion or dodecanol that exhibit synergistic effect with the surfactants in decreasing surface tension. The differences of the hydrolysis rate were explained by the results of DFT calculation of the reaction energetics that allowed to substantiate some of the “surface quasi two-dimensional electrolyte” (STDE) model parameters used for the description of surface tensions isotherms [2].

Additionally we examined adsorption properties of four amidoquats, i.e., surface active quaternary ammonium compounds, in which the hydrophobic part of the moieties (C10 and C12 alkyl chains) are linked to the charged head group via amide bonds R–CO–NH– or R–NH–CO–. As the DFT calculation suggested that the effect of hydrolysis is less pronounced than for esterquats, the alternative explanation for differences of surface activity was proposed based on formation of a hydrogen bounded dimers.

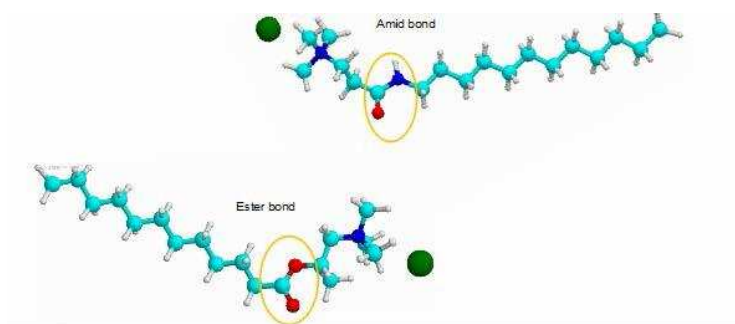


Figure 1. Examples of the molecular structure of investigated surfactants.

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First Macro-Mesoporous Silica Monoliths: Conditions for Obtaining Self-Standing Materials

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Materials exhibiting dual or hierarchical porosities have today attracted widespread interest for industrial applications and generated fascination in materials science¹. Here, we present a new method to create monolithic materials with both highly ordered mesoporosity and macroporosity. These materials have been synthesized by combining the sol-gel process, emulsion templating² and the ternary phase behavior of Pluronic (P123)/dodecane/water in the presence of salt.

We showed the importance of the salt's chemical nature and we introduce the kosmotrope/chaotrope balance effect on sol-gel polycondensation process. Results show that the salt plays a dual role. First, at the macroscopic level it decreases the stability of the oil-in-water emulsion, which involves an increase of the cell diameter with the salt concentration. Second, at the mesoscale level sulfate anions strengthen the hydrophobic interactions leading to mesopore ordering. Nevertheless, at very high concentration, the kosmotrope effect of sulfate anions disturbs the cooperative templating mechanism and the mesoporous network of the final material becomes less ordered. The effect of synthesis temperature was also studied.

The materials obtained called SBA-15_xSi(HIPE) self-standing monoliths exhibit thereby highly ordered mesopores, high specific surface areas, tunable open macroporosity while offering mechanical strengths (Young's modulus) of 0.15-1 MPa without collapsing at high strains³. These new kinds of materials offer new perspectives for the synthesis of highly organize porous materials at every scale (from tunable macropores to order mesopores).

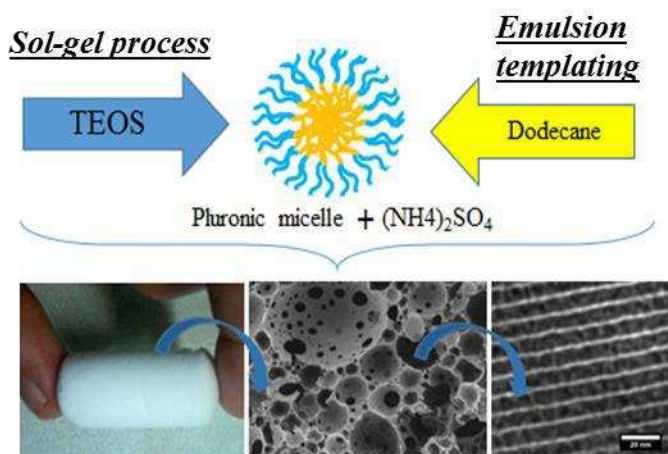


Figure 1. Scheme of the synthesis of the self standing porous silica monoliths, exhibiting both macroporosity and ordered mesoporosity.

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Nano-scale roughness and hydrophobicity: the case of cellulose nano- crystals.

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Surface roughness plays a key role in modulating the hydrophobicity of a surface. Nevertheless as we go to smaller length scales the spatial distribution of the chemical interactions plays a key role in the hydrophobic character of a surface.

In this work we focused our efforts in trying to understand the complex interplay between nano-scale roughness and chemistry in a widely used material: Cellulose Nano Crystals (CNC). Cellulose Nano Crystals (CNC) have a wide range of applications due to its biocompatibility, nanostructure and surface chemistry [1]. But one of the most complex characteristics of cellulose is its amphiphilic character, which is a topic of on going debate [2].

In this study we presented a series of molecular dynamic simulations of a CNC cellulose interface [3]. We simulated two characteristic cellulose crystallographic planes with different hydrophobicity and nano-scale structure. These exposed crystal planes were studied interacting with different molecules to better understand the surface hydrophobic character and the role of the nano-scale roughness. In particular we studied the following systems: water nano-droplet interacting with CNC to analyze the interface water/cellulose, water/tetraphenylborate/CNC to analyze the interaction with a super-hydrophobic ion and water/methane/CNC to analyze the interaction with a small hydrophobic molecule.

The results of this work provide a framework to better understanding of the driving forces at the surface of CNC and other cellulose materials, and would help towards the rational design of future applications.

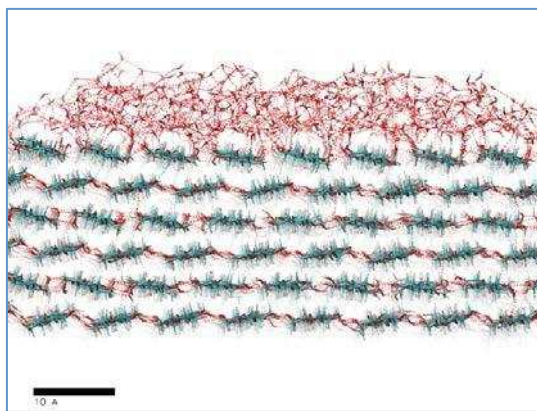


Figure 1. Snapshot of the simulation of a water nano-droplet over CNC.

Acknowledgements: This work has been supported by the Spanish Government Grant MAT2015-64442-R. D.C.M is supported by the EU Horizon 2020 program under Marie Skłodowska-Curie grant agreement No 6655919. We thank the CESGA Supercomputer Center for access to computational resources and technical support.

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Adsorption-desorption kinetics of surfactants at the water surface: dependence of the barrier rate constant on surface density and temperature

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The isobaric desorption from air-water interface of decanol and dodecanol monolayers is shown to proceed under mixed energy barrier-diffusion control (" k_d & D " in fig. 1); the role of the convective diffusion is also discussed. The decrease of the area A of the monolayer at fixed surface pressure was followed in order to determine the rate constant of barrier desorption, k_d , as a function of the surface pressure, the surfactant structure, and the salt concentration. All other characteristics of the studied systems (surface activity, diffusion coefficient, solubility) have been determined independently, using auxiliary measurements of the spreading pressure around surfactant crystals. Pure diffusion-controlled desorption (" D " in fig. 1) greatly overestimates the desorption rate; the first 30-60 s of the desorption process are actually under barrier control.

We further show that the barrier desorption rate increases as the monolayer approaches the collapse area per molecule (in contrast to some of the existing literature models) and is also phase-dependant. For both the liquid expanded and the liquid condensed states of the monolayer, the dependence of the average desorption time $1/k_d$ of a surfactant molecule is a linear function of the area per molecule (fig. 2). It is also demonstrated that the desorption rate changes with the salt concentration and the structure of the amphiphile.

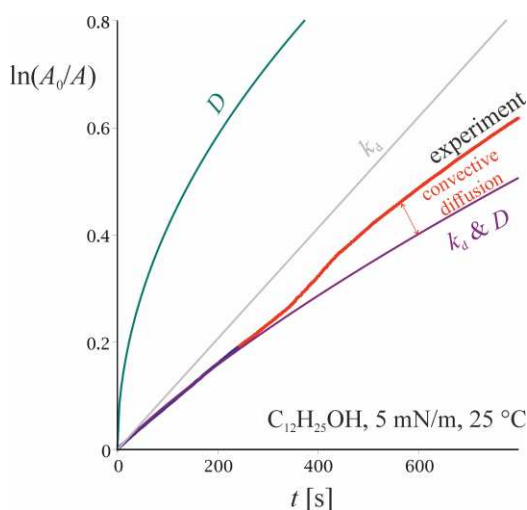


Figure 1. Isobaric desorption of dodecanol: Decrease of the area A of the monolayer with time.

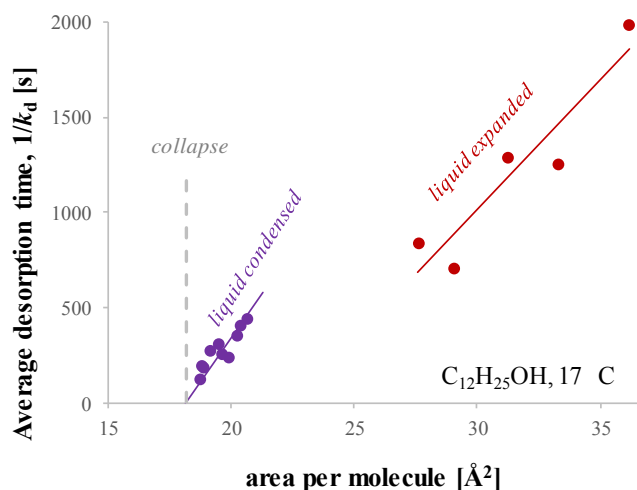


Figure 2. Average desorption time ($1/k_d$) vs. area per molecule of the monolayer.

Acknowledgements: The work is funded by National Science Fund through Contract № 80-10-131 from 25.04.2018 with Sofia University.

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Measuring tactile friction of Pickering formulations on excised skin

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Consumer perception of topical formulations plays a central role in the cosmetic industry and there is a constant demand on formulators to develop new formulations that appeal to costumers in terms of functionality as well as sensory feel. Even in the pharmaceutical industry, there is a requirement for cosmetic appeal of the formulations for better patient-compliance. Film formation upon application and subsequent reformulation due to evaporation of volatile excipients will have a major impact on tactile (i.e. sensory, cosmetic) perception of the skin.

Finger friction measurements on artificial skin (Vitro-Skin®) have shown great potential in the evaluation of tactile perception of formulations using a ForceBoard™ [1-2]. Measurements were performed by moving the index finger across the skin substrate and the friction coefficient (μ) was calculated as the ratio between normalized applied load (L) and the friction force (F).

In the current study, we introduce excised skin as an alternative to Vitro-Skin®. Measurements were performed to evaluate the perception of touch and possible effect of film formation under controlled ambient conditions. Novel particle stabilized (Pickering) formulations [3-4] were compared to commercial creams. The present investigation presents a method to perform friction measurements on excised skin and evaluate formulation properties responsible for a pleasant sensory perception.

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Quantifying Surface Potentials at Liquid-Gas Interfaces from Vibrational Sum-Frequency Spectroscopy

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Knowing the double layer potential (DLP) of the liquid-gas interface is essential to analyse the mechanisms of foam stabilization. However, no straightforward method is available to measure DLP. Sum-frequency generation (SFG) spectroscopy is tested to measure *in situ* the DLP at the liquid-gas interface of mixed solutions of non-ionic and cationic surfactants: tetraethyleneglycol-monodecylether ($C_{10}E_4$) and hexadecyltrimethylammonium bromide ($C_{16}TAB$), respectively. Different surfactant molar ratios were used to tune the DLP. The intrinsic negative charging of the surface of pure water is significantly modified by adsorbing $C_{16}TAB$ while $C_{10}E_4$ changes only slightly the DLP-magnitude [1-3]. On charged interfaces, the SFG intensity depends not only on the second-order of susceptibility ($\chi^{(2)}$) but also on the third-order of susceptibility ($\chi^{(3)}$) due to the contribution of the local electric field generated by the water molecules in a few molecular layers below the interface [4-6]. The proposed SFG approach for quantifying the DLP requires first its calibration to untangle the $\chi^{(2)}$ and $\chi^{(3)}$ from the spectra. DLP is estimated from theoretical (DLVO) analysis of experimental disjoining pressure isotherm for foam films; as measured with the thin-film pressure balance (TFPB) technique [7] and used to validate the SFG data. This approach will allow to measure the DLP at the liquid-air interface combining a single calibration of foam film measurement and multiple set of SFG spectra.

Our preliminary results shows a good agreement between both techniques, however SFG shows lower DLP values. This approach has its limitations due to the assumptions taken to detangle the SFG spectra. This is the first study to our knowledge that combines TFPB and SFG experiments for studying soft interfaces.

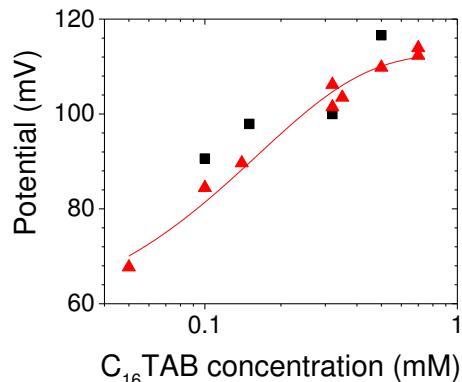


Figure 1. Double layer potential versus $C_{16}TAB$ concentration measured by the TFPB (black square) and SFG spectroscopy (red triangle).

Acknowledgements: This project receives funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 638278).

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Antifoam Agents in Cell Culture Media: Mechanism of Operation and Efficiency Enhancement

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Foam is a serious problem during bioprocesses [1]. Uncontrolled foam formation can bring either to a decrease of mass/heat transfer, or it can damage the cells by the bubble bursting, or, in very severe cases, it can cause the leakage of culture fluids from the exit lines, the loss of sterility and contamination problems [2].

The main reasons of foam formation can be relative either to the procedure parameters, like the stirring or the introduction of gases inside the bioreactor or to the formulation of the cell culture media or to the production of proteins and by-products by the cells during the bioprocesses [3].

Foam can be minimized by lowering the rates of aeration and agitation or it can be removed by mechanical foam breakers (e.g., pressure changes, acoustic waves, electric discharge, and change of temperature) but not always those parameters can be changed or the methods can be applied, because the cells are quite sensitive to such factors [4].

Another way to prevent or decrease the foam is to add a chemical antifoam agent, which is generally a surface-active substance, hydrophobic and with low solubility [4]. Many antifoam agents are already commercially available but, most of the time, they are employed without a specific evaluation of their characteristics, their performances and their potential effects upon the process [3].

The main task of the project is to understand the chemical and physical causes behind the formation and the stabilization of foams in bioprocesses and to identify the crucial aspects that can be addressed. Surface properties, such as surface tension, interfacial tension and spreading parameters are evaluated to shed light on what is responsible for the foam during the cell culture. The other principal goal is the investigation of the working principles of the chemical antifoam agents, to select their characteristics, tailor their surface and chemical properties to each bioprocess and improve their efficiency.

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The effect of Minerval on model B16 melanoma cell membranes

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As plenty of cancer types are characterised by a high resistance to chemotherapy, conventional antitumor agents frequently act unspecifically and cause serious side effects, the development of alternative therapeutic strategies employing substances with high pharmacological activity and low toxicity seems to be crucial. Minerval (2-hydroxyoleic acid, HOA) is Membrane Lipid Therapy drug with confirmed anticancer activity. Its effectiveness in the treatment of such disorders as leukemia, melanoma, glioma and lung cancer has been described [1-3]. Therapeutic effect of this substance is associated with its incorporation into cell membrane and modification of the membrane-lipid composition. This alternations influence the localization and activity of pivotal membrane proteins with subsequent modulation of important cellular functions and cell signaling pathways. Despite its effectiveness in cancer treatment and lack of side effects, its molecular mechanism of action is not fully elucidated. A deeper knowledge about HOA antitumoral mechanism may facilitate application of this compound in treatment of other cancer types and improve the efficacy by structural modifications of oleic acid or Minerval molecule.

The aim of this study was to investigate the influence of HOA on stability, fluidity, permeability and molecular organization of artificial lipid membranes in the context of its membrane-related anticancer properties. The experiments were performed for main components of B16 melanoma cell membranes [4]. As the model of biomembranes Langmuir films and liposomes were applied.

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Control of initial adsorption coverage over detaching bubble surface - implications for kinetics of dynamic adsorption layer formation

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Dynamics of bubble motion is important for mass transfer applications and is of great interest whenever it comes to technological processes involving multiphase flow. A bubble's velocity in fluids depends mainly on bubble's size, density difference between liquid and gas phases, liquid viscosity and properties of the liquid/gas interface. In pure liquids, a bubble surface is fully mobile and, as a consequence, the viscous drag is significantly reduced. Adsorption of surface-active substances (SAS) at the bubble surface affects the fluidity of the liquid/gas interface, which leads to lowering of the bubble velocity. In solution of SAS, as a result of the viscous drag, a non-uniform distribution of the adsorbed SAS molecules, i.e. dynamic adsorption layer (DAL), is formed over the surface of the rising bubble [1]. Kinetic of the DAL formation is very important parameter, determining not only bubble rising dynamics but also stability of liquid films formed by the colliding bubble at various interfaces [2].

We report results of systematic experiments, during which monitoring of course of the rising bubble (radius 0.74 mm) velocity variations, correlated with deformation changes, was used as a marker of different stages of the DAL structure formation and full establishment. The bubble formation and the degree of adsorption coverage at its surface at the moment of detachment were controlled using an elaborated automatic bubble generator coupled with a programmable bubble trap, allowing precise control of (i) bubble detaching interval and (ii) time available for adsorption of SAS molecules at the motionless (captured) bubble interface. It was found that increase in the adsorption times (in the range of 1.6 – 300 s), i.e. increase in precisely controlled degree of the initial bubble adsorption coverage (calculated theoretically from chosen adsorption model), has a profound influence on the kinetics of dynamic adsorption layer (DAL) development. When the adsorption time was longer (initial adsorption coverage was higher) the maxima at the velocity profiles were smaller, narrower and the bubble terminal velocity (full DAL structure) was established faster (after shorter distance covered by the bubble). Accordingly, similar trend was observed in the case of bubble shape pulsations. Example of this effect is presented in Fig. 1, where velocity and shape pulsation profiles are presented for bubble detaching with different initial adsorption coverage in Tween80 solution of constant concentration (1×10^{-6} M).

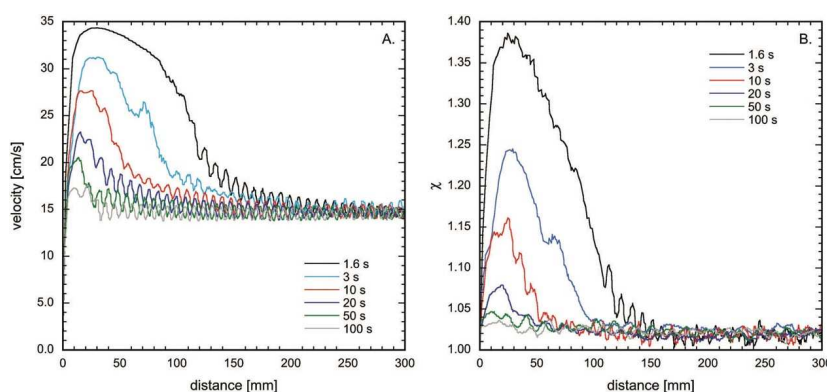


Figure 1. Variations in (A) bubble local velocities and (B) its deformation ratio, as a function of distance in Tween80 solution of constant concentration (1×10^{-6} M) and different controlled adsorption times.

Acknowledgements: Partial financial support from the Polish National Science Centre (NCN) grant No. 2017/25/B/ST8/01247 is acknowledged with gratitude.

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Role of the interfacial elasticity for the bulk properties of emulsions, stabilized with saponins

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Saponins are natural surfactants which are widely used in food and pharmaceutical industries. In our previous study [1] we characterized the surface rheological properties of saponins on air-water interface, subjected to shear and dilatational deformations. We established that triterpenoid saponins (such as Escin, Tea saponin, Berry saponin concentrate and Quillaja Dry) formed adsorption layers with very high surface elasticities and viscosities. In the current study we measured the rheological response of the adsorption layers formed on hexadecane-water and sunflower oil-water interfaces under dilatational deformation by using Capillary Pressure Tensiometry (CPT). We found that the adsorption layers formed from Quillaja Dry and Berry saponin concentrate solutions behave as a solid shell (see Figure 1). The other studied saponins have high dilatational elasticity on oil-water interface which allow us to determine the effect of dilatational surface elasticity on the rheological response of formed emulsions from these solutions. We prepared emulsions with oil fractions between 65 wt% and 75 wt% and measured their elastic modulus. The obtained experimental results showed that the dimensionless elasticity of emulsions depends significantly on the dilatational elasticity of adsorption layers formed on the drop surface. When dilatational surface elasticity is below 40 mN/m the dimensionless elasticity is very close to one predicted by theoretical expressions derived by Mason and Princen [2-3], whereas when the dilatational surface elasticity is above 40 mN/m the dimensionless elasticity of emulsions becomes higher than theoretically calculated ones, in some cases more than 3-times.

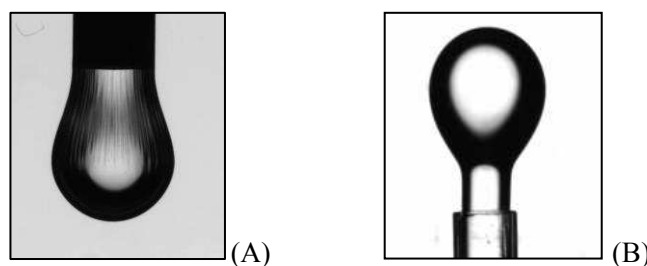


Figure 1. Drop of (A) BSC solution in sunflower oil (B) sunflower oil in QD solution. Oil or solution is pushed into the drop, the whole surface starts moving as a solid body.

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Role of lysolipids on the surface properties of enzymatically modified egg yolk

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This study aimed to establish the similarities and differences in the behavior of adsorption layers of native egg yolk (EY) and enzymatically modified egg yolk (MEY) at the oil-water interface. The properties of adsorption layers were characterized by measuring interfacial tension and surface dilatational modulus. The interactions between adsorption layers formed on two oil-water interfaces were evaluated by optical observations of emulsion films formed in the capillary cell. The chemical composition, electrokinetic properties and rheological properties of the studied egg yolk solutions were also determined. It was found that the rate of adsorption is faster and dilatational surface moduli are lower, whereas the equilibrium surface tension is higher for adsorption layers formed from a solution of MEY. Faster film thinning and thinner films are formed from modified egg yolk solutions. To explain these differences between EY and MEY, it was assumed that the interfacial properties of MEY are mainly determined by the lysophospholipids, which are products of the enzymatic modification of the egg yolk. The addition of lysolipid even at a relatively low concentration (corresponding to 60 % degree of conversion) into the solution of EY leads to properties of adsorption layers and emulsion films which are typical for enzymatically modified egg yolk.

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Emulsification by rotor-stator homogenizer: Comparison of experimental and predicted drop sizes

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The size distribution of droplets is an important characteristic of every emulsion as it affects its stability, optical and rheological properties. We studied the main factors affecting the drop size and polydispersity in oil-in-water emulsions with low weight fraction of the oil phase ($\Phi_{\text{OIL}} = 0.05$), prepared by using rotor-stator homogenizer. The obtained results demonstrate that increasing the viscosity of the aqueous phase, η_c , above a certain critical value, leads to a transition from inertial to viscous turbulent regime of emulsification. The analysis of the results showed that the maximum diameter, d_{v95} , of the drops, obtained in the inertial regime, is well described by the classic Davies model [1], whereas the model of Kolmogorov [2] and Hinze [3] for emulsification in viscous turbulent regime is not appropriate for description of the maximum drop diameters obtained at high aqueous phase viscosity. The major aims of the current study was to carefully analyze the results obtained by the emulsification experiments in viscous turbulent regime with rotor-stator homogenizer and to find an appropriate equation that adequately accounts for the contributions of (1) continuous phase viscosity; (2) rotor speed; (3) interfacial tension on the droplet size. The proposed new equation describes very well the drop sizes of all emulsions obtained in viscous turbulent regime. To check the validity of the new equation, we carried out additional experiments at high oil concentrations. We found that the proposed equation describes very well also the experimental results about the drop size in emulsions with $\Phi_{\text{OIL}} \geq 0.6$.

Acknowledgements: Authors are grateful to Operational programme "Science and Education for Smart Growth", project BG05M2OP001-2.009-0028 for the financial support for participation in the international scientific forum ECIS 2018, Ljubljana, Slovenia.

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The phase transition behaviour of the adsorbed layer of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers at air-water interface

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The biocompatible triblock copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO- PEO), also known as Pluronics, can reduce interfacial tension and are commonly used as an emulsifier or a dispersion stabilizer in pharmaceutical industry. The effectiveness of this compound is closely related to its adsorption behavior at interface. In this study, the adsorption isotherms of surface pressures and film thickness were monitored in-situ for a series of Pluronics with different molecular weight or hydrophobicity to delineate the adsorption mechanism of Pluronics at air-water interface.

Phase transition behavior of Pluronics molecules was observed and a phase transition model was applied to quantitatively describe this behavior. For Pluronics with 80% of EO, one observed two phase transition regions from the adsorption isotherms of surface pressure before CMC. The two transition regions occur at bulk concentration of about 10^{-6} ~ 10^{-5} mM, and 10^{-3} ~ 10^{-2} mM and with corresponding surface pressures of ~10 and 25 dyne/cm, which are close to the pure-PEO and pure-PPO monolayer saturation surface pressure, respectively. Together with the surface concentration evaluated for each transition states, it is suggested that the phase transition behavior of Pluronics can be described by different corresponding adsorption conformations: for very low concentration ($<10^{-6}$ mM), both PEO and PPO segments of Pluronics adsorb on the interface in a fully extended form without obvious increasing surface pressure and thickness. Followed the increases in solution concentration, the adsorbed PEO chain becomes saturate at the 1st transition region, i.e. bulk concentration of around 10^{-6} ~ 10^{-5} mM. For $C >$ the 1st transition region, PEO chains becomes oversaturated and thus is expected to protrude into the aqueous solution. At concentration ranging from 10^{-4} to 10^{-3} mM, Pluronics turned into “brush” configuration and the PEO chains are completely expelled into the aqueous solution while the PPO region is remained on the interface. Further increasing solution concentration, for $PEO \ll PPO$, the adsorbed PPO chain will saturate and even become more coiled, while for $PEO \gg PPO$, the PEO coils in solution might be compressed and become more extended, which is accompanied with an increase in the adsorbed film thickness.

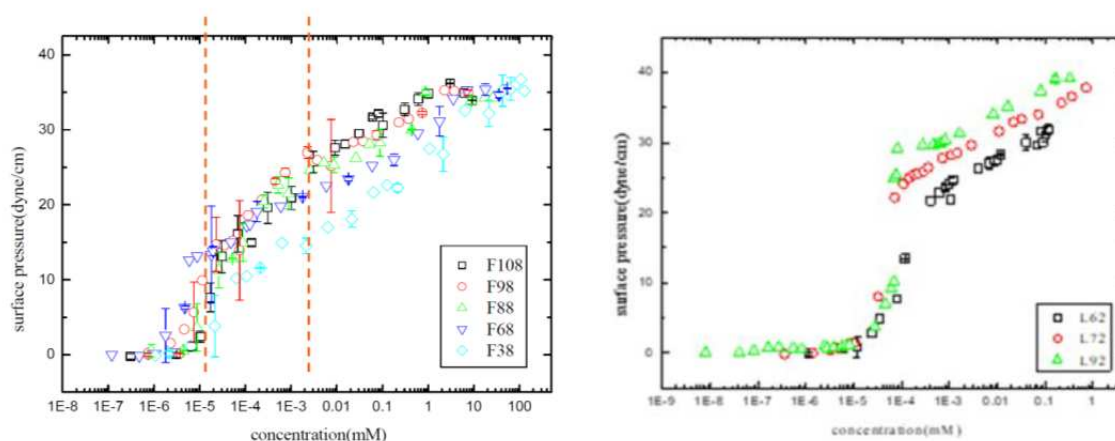


Figure 1. Adsorption isotherm of Pluronics with (a) EO=80%; (b) EO=20%

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The influence of structure of bioactive particles on molecular organization of model lipid rafts.

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In recent years, many studies have focused on the search the new carriers of drugs or genetic material. One of the interesting group of compounds using in drug delivery systems are cationic lipids. These synthetic bioactive molecules of amphiphilic structure exhibit similar properties to natural lipids. However, a lot of them demonstrate strong toxicity limiting their in vivo application [1-3]. The triesters of phosphatidylcholine are a particular group of cationic lipids which as derivatives of natural phosphocholines are characterized by relatively lower toxicity [4].

Progress in increasing effectiveness of lipofection or drug delivery by cationic lipids is impeded due to not completely known mechanism these processes. It is supposed that it proceeds through many stages. Nevertheless, the biological membrane is the first place an action of these bioactive molecules.

The goal of the surveys were to determine the impact of the structure of two bioactive molecules - 1-palmitoyl-2-oleoyl-sn-glycero-3-ethylphosphocholine (EOPC) and 1,2-dipalmitoyl-sn-glycero-3-ethylphosphocholine (EDPPC) on the properties of model mammalian membranes. The investigations included the analysis of the influence of selected cationic lipids on the molecular organization of mixed phosphatidylcholine/ sphingomyelin/cholesterol system in which the molar ratio of lipids reflected the proportion of these lipids in the lipid rafts. In studies were used Langmuir monolayer technique in combination with Brewster angle microscopy and liposomal systems with the application of dynamic light scattering (DLS), zeta potential measurements, the experiments concerning the release of calcein entrapped in the liposomes after titration with surfactant solution and steady-state fluorescence anisotropy of DPH.

The obtained results indicated that the structure of bioactive molecules exert huge effect on properties of model membrane. The incorporation of cationic lipids lead to the weakness of intermolecular interaction in model lipid raft wherein EDPPC exert more unfavourable impact (appear more repulsive interactions) on membrane components than EOPC. Furthermore, cationic lipid with saturated bindings in acyl chains is more destabilizing model membrane by decrease of condensation and ordering degree. Otherwise, the changes of structure in hydrophobic part also contribute to the emergence of differences in the fluidity and permeability of lipid raft.

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Vesicles with tubular protrusions: experimental study via thermally induced shape fluctuations and Monte Carlo computer modelling

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Morphological behavior study of giant quasispherical vesicles with long tubular protrusions (tethers) in various environment conditions was performed both experimentally and using Monte Carlo computer modeling. The effect of the local change of the membrane curvature on the shape of the studied objects was visualized and simulated over time. The experimental observation of the vesicles was carried out via inverted phase contrast microscopy. The bending elastic modulus of the lipid membrane of vesicle containing tethers is measured at various environmental condition using the method of thermally induced shape fluctuations [1].

The Monte Carlo method on randomly triangulated mesh [2] was used to simulate thermal fluctuations of the vesicle membrane. Meshed model includes membrane patches with intrinsic curvature with radius much smaller than the average radius of the whole vesicle. Due to random movement of the patches (diffusion) they cluster up to form areas where small local curvatures of the membrane are energetically favorable. This results in budding effect and long tubular protrusions formation which is the topic of the presenting poster.

The experimental results were compared with the Monte Carlo simulations. The model predictions are in good agreement with the experimental data, demonstrating the validity of the proposed model.

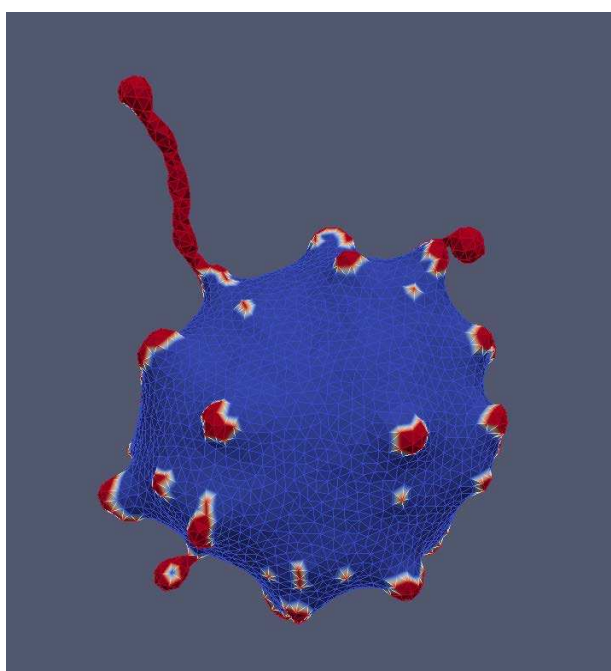


Figure 1. The result of simulated vesicle with protrusions. The vertices on the mesh shown in red represents points of attachment of proteins with intrinsic curvature.

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The influence of length of PEGylated chains on properties of cationic liposomes

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Recently, cationic liposomes have generated enormous interest in the field of nanotechnology as excellent candidates for application as carriers of genetic material or drugs. For this reason, it is important to know their properties and impact on the components of animal cell membranes. An example of compound that forms this type of nanostructure is DC – Cholesterol (3 β -[N-(N',N'-dimethylaminoethane)-carbamoyl]cholesterol), which has a tertiary amino group and carbamoyl bond which can be hydrolyzed by cellular esterases. This structure makes that DC – Cholesterol is biodegradable and less toxic [1].

One of the ways to prolong the circulation lifetime of cationic liposomes is the incorporation of poly(ethylene glycol) (PEG) in lipid – based carriers. PEG is a linear polyether diol which is characterized by biocompatibility, lack of toxicity, low immunogenicity and excellent excretion kinetics. The most common hypothesis which explains the ability of PEG to improve circulation time of liposomes in blood stream is based on “steric stabilization” that can reduce liposomal aggregation and plasma protein adsorption. At present, the most popular method of surface modification of liposomal formulations with PEG is anchoring the polymer in the liposomal membrane via a cross – linked lipid, such as DSPE-PEG, during liposomes preparation. The attached PEG can have increasing polymer length from PEG350 to PEG5000. PEGylated liposomes display prolonged blood circulation, whereby enhances the distribution in targeted tissues. What is more, the presence of PEG chains on the liposomal surface increases drug solubility and avoids the liposomal aggregation, improving stability of vesicles [2-3].

The aim of the research was to investigate the influence of poly(ethylene glycol) length (PEG350 and PEG2000) on the interactions between DC – Cholesterol and POPC – phospholipid naturally occurring in animal cells. The investigations included also the analysis of the influence of polymer length on the properties of cationic liposomes (DC – Chol/POPC). The study were conducted with the application of Langmuir Monolayer Technique which enables for registering the dependence of the surface pressure (π) from the surface per single molecule in the monolayer (A). The morphology of surface films was examined with usage of Brewster Angle Microscopy (BAM). The liposomal formulations were researched with using of Dynamic Light Scattering (DLS, zeta potential measurements and Spectrofluorimetry which allowed for following the release of calcein encapsulated in liposomes and changes of fluorescence anisotropy of DPH.

The obtained results of research proved that the length of PEG chains significantly changes the interactions between components in artificial model membranes. What is more, addition of DSPE – PEG which has different polymer length (PEG350 and PEG2000) in cationic liposomes changes their stability, permeability and anisotropy.

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Interfacial phenomena in silicone emulsions

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Silicone emulsions are advantageously used when one wants building materials to become water-repellent [1], textiles to become softer, leather to become more resistant to abrasion, paper to become anti-adherent, hair to become easier to comb, etc. They can also provide lubrication and demolding between various surfaces, and allow to prevent the formation of undesired foam in various media [2]. Such emulsions may be made from reactive or non-reactive silicones, from fluid or highly viscous oils, from linear or network structures, and are stabilized by surfactants, polymers or particles [3,4].

Behind this diversity lies a set of common interfacial phenomena that one needs to take into account when formulating a silicone emulsion (as represented in Figure 1). What makes it especially challenging is the fact that most of the phenomena at stake tend to be antagonistic: oil droplets must be efficiently stabilized while air bubbles should simultaneously be unfavored; coalescence must be promoted as soon as the droplets reach the targeted surface but avoided during the whole process leading to that step; providing hydrophobicity via silicone emulsions implies the need for emulsifiers that are inherently hydrophilic; reactivity should be preserved during storage but triggered in the final film.

Those interfacial phenomena are primarily governed by the emulsifying system, which should provide simultaneously low interfacial tension, steric and/or electrostatic repulsion, thermal resistance, ability to spread and coalesce on the surface, while complying with specific regulatory constraints (personal care, food-contact, ecolabels...). Challenges for future formulations include the search for emulsifying systems which minimize the rate of organic matter, which allow to stabilize concentrated emulsions while maintaining a reasonable viscosity, or which provide a better compromise between shear stability and coalescence upon application.

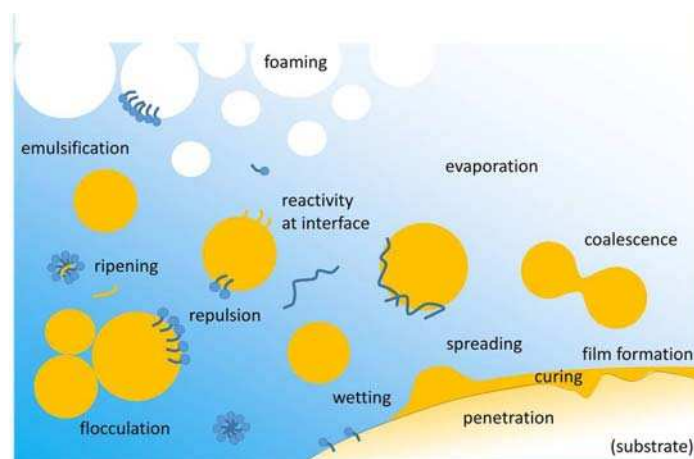


Figure 1. Interfacial phenomena related to silicone emulsions when applied on a surface.

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Interactions between charge macroions induced by nanoparticles

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Electrostatic interactions between charged macroions in electrolyte solutions are of fundamental importance in surface and colloid chemistry [1]. Mobile ions and nanoparticles of an electrolyte interact with a charged macroion and an electric double layer is formed. In this work, we consider large charged macroions in an aqueous solution composed of nanoparticles with given spatial charge distribution. We perform the minimization of an appropriate free energy functional. The result is the non-linear integral-differential equation for the electrostatic potential with appropriate boundary conditions. The equations were solved numerically. We discuss how various model parameters of the system influence structural properties of the electric double layer. We consider conditions for attractive interaction between charge macroions embedded in a water solution of continuously charged spherical nanoparticles [2,3].

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Effect of cholesterol concentration on membrane tension and fluidity of free-standing black lipid membranes

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The lipid bilayer that separates the interior of the cell from the outside environment is an important component of the cell membrane. The properties of the cell membranes can be affected by various parameters of the lipid bilayer membrane, such as shape, composition, embedded molecules and surrounding environment. The membrane tension is also an important parameter, which is sensitive to any applied forces, deformations and the functions of some membrane proteins. The lipid structures and compositions are also related to the deformation and fine structure of the membranes. However, the relations between membrane tension, composition and fluidity have not been investigated even for the model membranes because of limitations in the measurement methods.

We have constructed an optical system for laser-induced surface deformation spectroscopy (LISD) [1]. This enabled us to carry out non-invasive measurements of the interfacial tension of liquid/liquid interfaces even for values below several $\mu\text{N/m}$. The LISD method was applied to models of the cell membranes, such as free-standing black lipid membranes (BLMs). These membranes were formed using the folding method that enables small deformations and involves low amounts of residual organic solvents. By using BLMs, the effect of any co-existing components on the membrane properties can be individually and accurately evaluated. For the evaluation of the fluidity, the fluorescence recovery after photobleaching (FRAP) technique [2] was also applied to the BLMs formed in the same chamber and with the same geometry. By measuring both the membrane tension and diffusion coefficient with the LISD and FRAP methods for similarly prepared BLMs, a systematic study of the relation between membrane tension, molecular composition and diffusion coefficient was successfully completed.

For the evaluation of the effect of cholesterol on the membrane tension and fluidity, the cholesterol concentration in 1, 2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC)-based BLMs was varied and LISD and FRAP measurements were conducted. When the cholesterol concentration was raised, the membrane tension increased whereas the diffusion coefficient decreased. As the increase of cholesterol induced a stronger hydrophobic interaction between the membrane components, we can also expect that such strengthening of the molecular interaction, in turn, resulted in a larger membrane tension and a lower fluidity of the compositions. This is because the stronger interaction suppressed the motion of molecules.

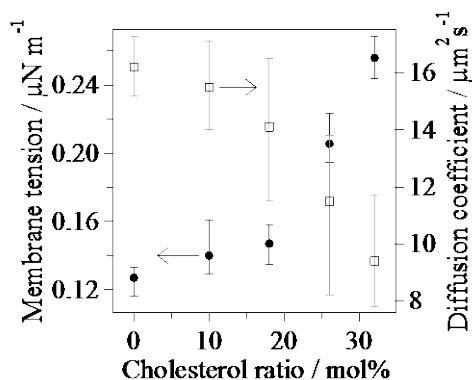


Figure 1. Membrane tension and diffusion coefficient of the DOPC-based BLMs for various cholesterol concentrations.

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Isomer effect of phenylenediamine on Gibbs monolayer of sodium dodecyl sulfate

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Mixtures of surfactants and organic additives are increasingly attracting attention because of their unique viscoelastic properties in aqueous solutions. Moreover, it is well known that organic additives cause an abrupt decline in the critical micelle concentration in surfactant solutions. It is inferred that organic additives affect, not only the bulk solution, but also Gibbs monolayers organized at the air-solution interface [1,2]. However, the effects of the isomer and concentration of organic additives on the Gibbs monolayer have not been investigated in detail. In this study, we have investigated the effects of the isomer and concentration by measuring infrared reflection spectra, ultraviolet-visible reflection spectra, and surface tensions of Gibbs monolayers of mixtures of sodium dodecyl sulfate (SDS) and *p*-phenylenediamine or *o*-phenylenediamine for a constant concentration of SDS (2 mM) and different concentrations of phenylenediamine.

We observed an initial abrupt decrease and a subsequent flattening out of the surface tension on increasing the phenylenediamine concentration (Figure 1). The surface-tension-lowering effect was more pronounced for *o*-phenylenediamine compared to that for *p*-phenylenediamine. The peak intensities of the methylene antisymmetric stretching band of SDS in the infrared reflection spectra were slightly enhanced on adding phenylenediamine. The peak intensities remained nearly constant on increasing the phenylenediamine concentration. The peak arising due to *o*-phenylenediamine was visible in the ultraviolet-visible reflection spectrum. However, the corresponding peak for *p*-phenylenediamine was not visible. These results indicate that these amines, which are not surface active, enhance the surface activity of the surfactant solution because of their adsorption on the water surface. Moreover, the extent of the effect depends on the molecular structure of the organic additive.

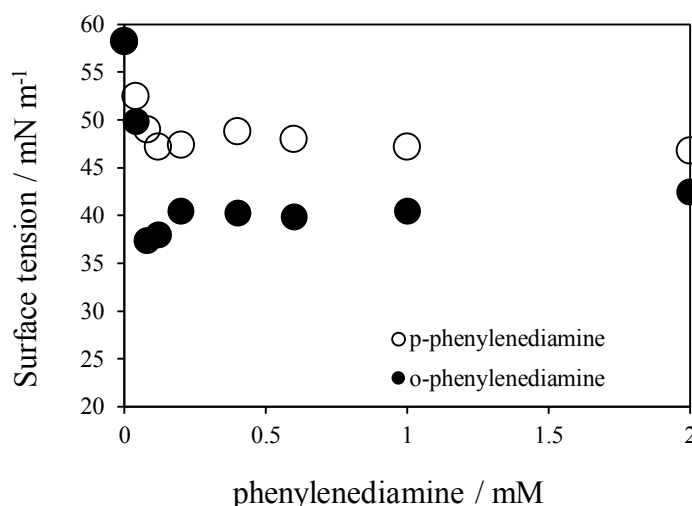


Figure 1. Surface tension of mixtures of SDS (2mM) and phenylenediamine aqueous solutions as a function of the phenylenediamine concentration.

Acknowledgements: This work was supported by JSPS KAKENHI Grant Number JP16K12705.

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Line Tension for Ternary DSPC/DOPC/Chol and bSM/DOPC/Chol Bilayers

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Study on line tension arising between liquid-order (Lo) and liquid-disorder (Ld) domains is essentially important to understand a raft structure formation of biological membrane because of its effect on domain size and shape. In this research, we challenged ourselves to measure and calculate line tension values at the bilayer compositions on various tie lines drawn in the phase diagram constructed by Feigenson group [1,2].

Two ternary systems were investigated: (1) distearoyl phosphatidylcholine (DSPC)/dioleoyl phosphatidylcholine (DOPC)/cholesterol (Chol), and (2) brain sphingomyelin (bSM)/DOPC/Chol. Giant unilamellar vesicle (GUV) was prepared by electroformation method [3]. The domain was visualized using a wide-field fluorescence microscope, and the line tension was measured at 21 °C by flicker spectroscopy [4]. To limit light-induced artifact effect on line tension, only 0.2 mol% of fluorescent dye; 1,1-didodecyl-3,3,3,3-tetramethylindocarbocyanine perchlorate (C12:0 DiI) was added.

Representatively, a result for DSPC/DOPC/Chol system was summarized in Figure 1. For both systems, the line tension values reduce as lipid compositions of Lo and Ld phases get closer to each other. The experimental values are inconsistent with theoretical ones calculated based on elastic theory [5]. Evaluation of line tension using modified elastic theory is on-going [6], and so far, the values are expected to be lower than former theory, suggesting that outer and inner leaflets of bilayer lipid domain are not completely in register. A result of evaluation and an interpretation of dependence of line tension on lipid compositions of both phases will be presented.

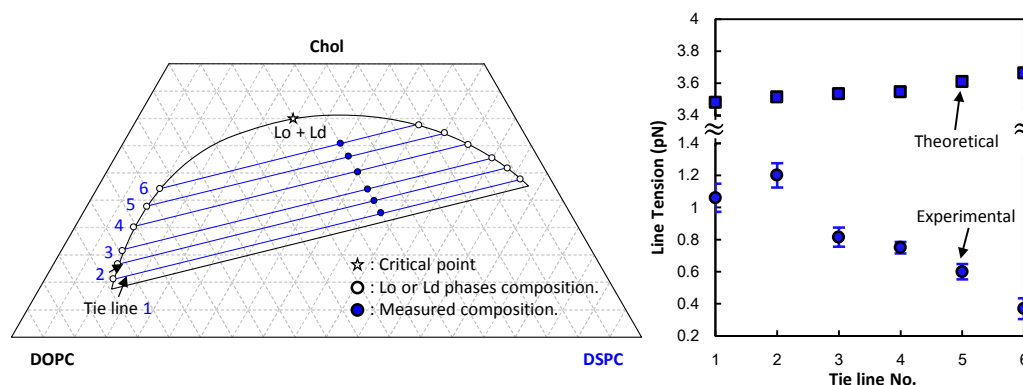


Figure 1. Phase diagram and line tension values for DSPC/DOPC/Chol.

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Microrheology of turbid systems by Diffusing-Wave Spectroscopy

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We analyse the possibilities offered by Diffusing-Wave Spectroscopy (DWS) to characterize rheological properties of turbid samples. In these samples, light has experienced an enormous number of scattering events over a total volume that spans several mm³; DWS, through time-correlation analysis of the light intensity, yields a measurement of the average nanoscopic motion of the scattering centres -i.e. of the mean square displacement (MSD)- over times spanning from the nanosecond up to hours. Microrheology results are obtained by the application of Generalized Stokes-Einstein Relations [1] which relate MSD to the frequency dependent complex shear modulus $G^*(\omega) = G'(\omega) + i G''(\omega)$, where G' and G'' are respectively the elastic and viscous moduli. In this respect, DWS is analogous to Multiple Particle Tracking; its advantages are a) the applicability to turbid samples, b) superior statistics, due to the larger number of scattering particles probed, and c) the sensitivity to tiny displacement.

We discuss advantages and critical points of different experimental approaches to DWS measurements. The accuracy of the DWS correlation functions is a key factor ruling the attainable sensitivity in $G^*(\omega)$ measurements [2]. We report on the influence of experimental setup and correlation algorithms on the Signal-To-Noise ratio of DWS microrheology, with particular focus on the advantages provided by fast multipixel detectors. We also review different numerical approaches to extract the frequency dependent complex shear modulus $G^*(\omega)$ from the MSD.

The proposed strategies have been applied to study the mechanical modulus of emulsions [3] and gel systems as a function of ageing time. This approach has also been used to investigate the change in the mechanical response of photosensitive wormlike micelles, that show a decrease of $G^*(\omega)$ of several order of magnitudes upon UV irradiation [4].

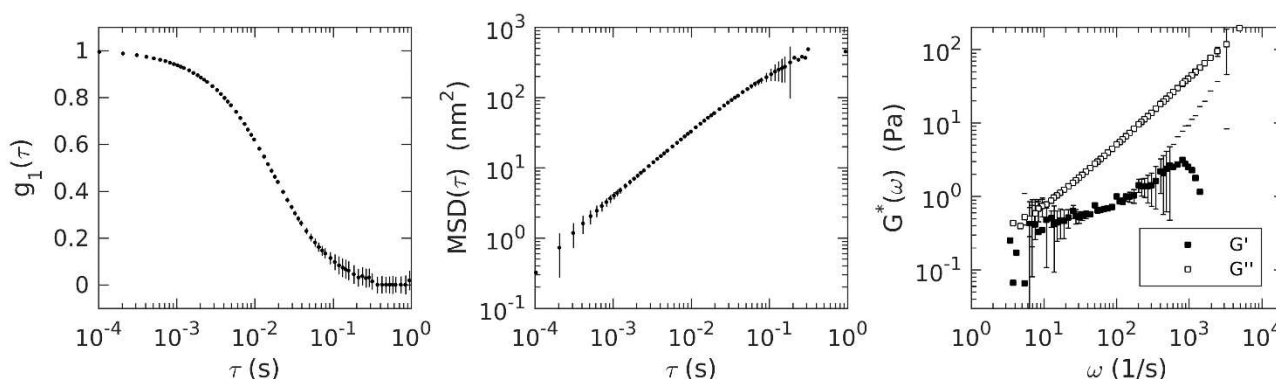


Figure 1. A typical DWS correlation function (left panel), from which MSD (central panel) and complex mechanical modulus $G^*(\omega)$ are deduced (right panel).

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Magnetic field influence on aqueous surfactant solutions

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Although the magnetic field (MF) effects are investigated for many years still some of the results are debatable. The published papers deal with the magnetic fields application in industry, agriculture, medicine, and others areas [1-4]. Initially the principal goal of MF application was protection against hard scale formation at elevated temperatures in industrial pipes or house heating installations. Successful application of MF eliminate usage of chemicals for water softness which are expensive and harmful for the environment. To our knowledge only a few papers dealing with investigation of magnetic field effects on surfactant solutions have been published. On the other hand, surfactants are present in the surface and waste waters, soil, and many industrial waters, sewage treatment plants, laundry, etc. Therefore it seemed us interesting to learn whether some effects would be observed also in a surfactant solution.

For this purpose a static MF (max. 0.5 or 0.65T) originating from a cylindrical Nd magnet or three N-S-N poles connected magnets was applied in which the sample of 10^{-3} M anionic sodium dodecyl sulfate (SDS) or cationic dodecyl three methyl ammonium bromide (DoTAB) solution (both concentrations below CMC, respectively) was placed for 2-3 h in an open plastic vessel. Every 30 min the vessel was weighed and evaporated amount of water was calculated. Simultaneously the same reference volume of the surfactant was left without MF which was also weighed. Some evaporation experiments were continued up to 2-3 days. First a significant increase in the evaporation rate was found for MF treated Milli-Q water (10-40 mg during 2h). Then, from the MF untreated SDS solution smaller amounts of water evaporated from MF treated water than from pure water. However, from MF treated SDS solution water evaporated faster than that from untreated one. In the case of cationic DoTAB surfactant if the solution was not MF treated the water evaporation rate was faster than that of pure water. Also from MF treated solution water evaporated faster than from untreated. Similar relationships were observed for the long time (2-3 days) MF treated solutions of these two surfactant solutions. Moreover, preliminary experiments showed that the static MF treatment of the anionic surfactant solution significantly decreased its surface tension if its concentration is below CMC. Similar experiments are under way with the cationic surfactant.

The classical magnetic field theory hardly can explain the observed effects. The latest theories developed to explain magnetic field effects claim that more important is the interacting MF gradient than its strength. Also the non-classical theory of nucleation mechanism and formation of dynamically ordered, so called liquid like oxyanion polymers are used to explain the magnetic field action. Possible mechanisms which would be helpful to explain the observed MF effects in the studied surfactants solutions will be presented.

Acknowledgements: This project was financed by The National Science Centre based on the decision number DEC-2016/21/B/ST4/00987.

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Thin Film Breakup in Densely Packed PEG-*b*-PnBA Films and their Composite Films with Iron Oxide Nanoparticles at the Air-Water Interface

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Poly (butyl acrylate), PnBA, readily spreads at the air/water interface and its basic properties are already well studied [1]. For intermediate pressures, the film thickness is found to be of the order of 1...2 nm [2]. We prepare Langmuir monolayers of PnBA homopolymers and its block copolymers with poly (ethylene glycol), PEG-*b*-PnBA, as a block partner. In this series the molecular weight ranges from 5...30 kg/mol while the PEG block in the block copolymers acts as a small hydrophilic anchor of constant size ($M_N = 0.3$ kg/mol). After investigating the general compression behaviour with the Langmuir technique, we develop a structural model based on in-situ Brewster-Angle-Microscopy (BAM), in-situ X-Ray reflectometry (XRR) and Langmuir-Blodgett measurements in the compressed state. Additionally, we investigate the ability of iron oxide nanoparticles of different sizes (5, 10 and 20 nm) to form monolayers and try to introduce them into the PnBA polymer films to create composite films.

In the semi-dilute regime, we find that the PEG block in the diblock copolymers can tune the air/water interface from approximately θ solvent to good solvent conditions using a power law analysis established by de Gennes [3]. In the concentrated regime, a phase transition from a 2D continuous water-free monolayer to more complex structure occurs. BAM imaging and off-specular surface scattering (XRR) provide a consistent picture of film breakup. The film is in an initial capillary instability stage of dewetting that can be described analogous to spinodal decomposition in fluid mixtures. Our results suggest a preferred length scale of 2.5 μm . However, the fluctuating quantity is the height of the surface instead of composition fluctuations. In addition, hysteresis experiment were performed indicating that polymer is removed from the film in the highly compressed state [4].

The iron oxide nanoparticles are able to form a monolayer of roughly 7 nm and 13 nm for the 5 respectively 10 nm large particles confirmed by specular reflectivity measurements. Our results from Langmuir experiments and XRR measurements show that the 20 nm particles do not form a monolayer at the air-water interface. First results on the composite films indicate that the 5 and 10 nm particles have been successfully introduced into a composite film with the PEG₆-*b*-PnBA₁₃₂ block copolymer. The compression isotherms of the composite films greatly resemble the pure polymer films especially for the 5 nm particles. For the 10 nm films stronger deviations are visible. XRR results indicate that the film thickness is significantly smaller compared to the pure iron oxide films, however, further analysis of the composite films is part of our current work.

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Self-assembled structures of water/glycerol/EO30PS system in bulk and on a solid substrate

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In pharmaceutical, cosmetics, detergency and painting applications, it is very important to understand the structural changes in bulk that occur during the drying process of formulations, as that is essentially happening during their practical application (mainly evaporation of water) because it is the key factor to control texture. Also, it is very important to understand the static and dynamic adsorption process of surfactants on a substrate and the structure of the adsorbed dried film because it is the key factor that controls function and properties of the formed film [1,2]. Therefore, we focused on the difference of self-assembled structures of water/glycerol/polyoxyethylene (30) phytosteryl ether (EO30PS) system in bulk and on a solid substrate because the interaction between substrate and surfactant has a substantial effect on the self-assembly which may be related to the bulk structure but in detail may also differ strongly from the bulk situation. In bulk, neutron small angle scattering (SANS) experiments show that with increasing loss of water, the degree of ordering was increased and changes of the aggregate structure only occurred at the highest water concentration. The results also indicated that spherical micelles of EO30PS are densely packed and become ordered during the drying process. On the other hand, neutron reflectometry (NR) revealed that EO30PS molecules adsorb onto a Si surface in form of bilayers and the resulting analysis indicated that for higher concentrations there are on average two bilayers on the substrate. However, off-specular neutron reflectometry also indicated that EO30PS molecules do not always cover all of Si surface. Hence the adsorbed membrane structure of EO30PS is probably not well-ordered. Atomic force microscope (AFM) images of the adsorbed film formed by EO30PS surfactant were consistent with the NR results. The combination of these experimental results then allows for a much deeper understanding of the structural properties of practical formulations as they are applied for instance in cosmetic lotions.

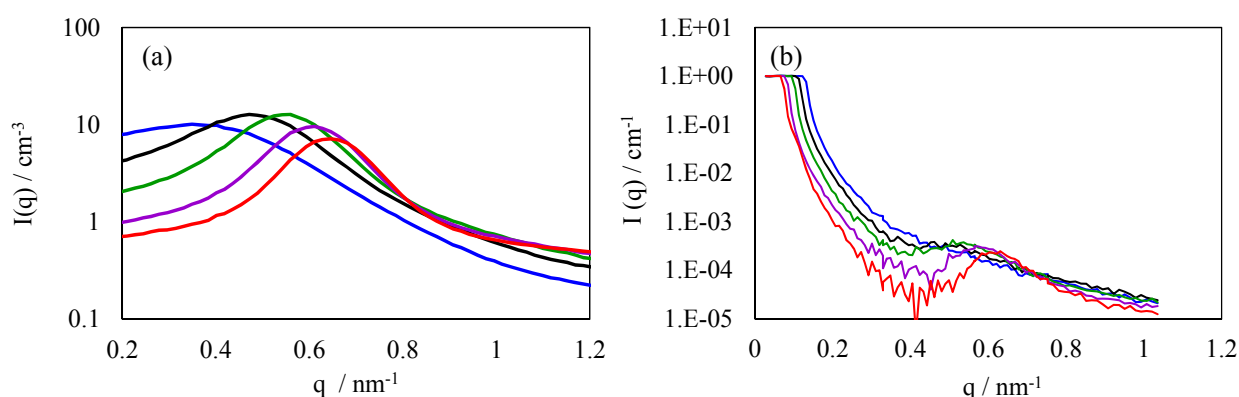


Figure 1. (a) SANS and (b) NR data of D₂O/glycerol/EO30PS solutions at 25 °C: D₂O/glycerol/EO30PS = 85.5/9.5/5 (blue), 72/18/10 (black), 59.5/25.5/15 (green), 48/32/20 (purple), and 37.5/37.5/25 (red). Sample compositions were based on light water.

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Study of structure of water droplets of sodium bis (2-ethylhexyl) sulfosuccinate reverse microemulsions in the presence of sodium cholate

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The analogous picture of normal membrane structure in cell is created by reverse micelles, besides water dissolved in the core of micelle represents the best model of the confined water in biosystems [1]. The doping of most widely used sodium bis (2-ethylhexyl) sulfosuccinate (AOT) reverse micelles interface by bile salts is used to increase enzyme catalytic activity [2]. Besides incorporation of the bile salts into AOT reverse micelles results in increasing of size of the water pool and in the lowering of the percolation temperature [3]. Moreover bile salts are biological surfactants with ability to enhance drug permeation through biological membranes [4].

The goal of the proposed work was to study the influence of additives of ionic biological surfactant sodium cholate introduced in the water nanodroplets of AOT reverse micelles on the: ratio of the bound, free and trapped water fractions, binding process of optical probes with reverse micelles, study of influence of amount of water additives on percolation of conductivity of mixed reverse microemulsions, etc. with infrared, UV-visible spectroscopy and conductivity measurements.

The microstructure of AOT reverse micelles in the presence of ionic sodium cholate was investigated using infrared spectroscopy in the range of water/surfactant molar ratio ($W=1\div 10$). Deconvolution of the O-H stretching vibrational absorption spectra in the region of $3000\text{--}3800\text{ cm}^{-1}$ into three subpeaks (free, bound and trapped water fractions) with a Gauss fitting program and Monte Carlo method was accomplished at the low values ($W=1\div 4$) of water/surfactant molar ratio (W).

The microenvironment of mixed reverse microemulsions (AOT+sodium cholate) was investigated with an ultraviolet-visible spectroscopy by using of ortho-nitroaniline and methyl orange as molecular probes. The values of binding constants and association degrees of ortho-nitroaniline and methyl orange with AOT reverse micelles at different concentrations of sodium cholate were determined.

Electrical conductivity of the reversed mixed micellar solutions (AOT+sodium cholate) was studied. Influence of concentration of sodium cholate on percolation of conductivity of AOT reverse microemulsions was investigated.

The obtained results are discussed based on the model of formation of primary and secondary micelles of bile salts at below and above the critical micelle concentration respectively [5].

Results may be useful in the investigations of the interface features of reverse micelles as models for biomembranes i.e. in the investigations of water structure, when it is confined to nanometer-scale cavities, viz. in biological systems.

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Chemical oscillations in three-phase systems using the quasi-elastic laser scattering method

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Non-linear phenomena in non-equilibrium systems have attracted significant attention in fundamental physico-chemical systems, such as biological membranes, chemical sensors and solvent extractions. A common feature in many of these phenomena is the presence of inhomogeneous interfacial tensions and solutal Marangoni convections that control the dynamics of the system. In our laboratory, we have recently developed a new technique, the so-called quasi-elastic laser scattering (QELS) method, to investigate several applications of these systems [1]. This technique allowed us to measure the interfacial tension between liquid-liquid or gas-liquid phases by measuring the frequency of the light scattered by the capillary waves. The great advantage of this method is that it is non-invasive, i.e. it does not require any mechanical probe to be inserted into the system. This property is critical to conduct accurate measurements when investigating the molecular behaviour at interfaces. Therefore, using this technique it is possible to systematically investigate the relationship between interfacial tension changes and non-equilibrium phenomena.

Here, we review and summarize our recent applications of the QELS method to the study of chemical oscillations in three-phase (donor/membrane/acceptor) systems consisting of immiscible liquids, such as water/oil/water [2, 3]. When surfactants such as cetyltrimethylammonium bromide (CTAB) were dissolved in the donor phase, recurring pulses in the potential difference between the aqueous phases were observed. This kind of oscillations are considered fundamental chemical approaches to biological phenomena [4] with potentially important applications, such as chemical sensors that can identify the molecular nature, because the oscillation pattern depends on the liquid phase.

Our QELS measurements revealed the presence of oscillations also in the interfacial tension of the acceptor phase and that these oscillations were synchronous with the donor-acceptor potential difference. This indicated that the oscillations were due to the inhomogeneous adsorption and desorption of the surfactants at the acceptor interface. In turn, this uneven interfacial tension distribution generated a Marangoni convection in the oil phase. In order to visualize this convection and clarify its role in the formation of the oscillations, we added a fluorescent molecule, rhodamine 6G, as the surfactant in the donor phase. We analysed the behaviour of these surfactant molecules during their diffusion in the bulk of the membrane phase and their adsorption and desorption at the acceptor-oil interface by observation of their fluorescence with a digital camera. This convection was found to be responsible for the continuous transports of rhodamine 6G to the acceptor phase interface during the potential drop.

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Temperature effects on the inert – aqueous electrolyte solution interface

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Hydrophobic materials, such as inert gases, hydrocarbon oils, ice, Teflon or diamond do not chemically react neither with water molecules neither with ions from aqueous electrolyte solution. Due to surface hydrophobicity water dipoles are repulsed from the surfaces and orientation of water molecules is less random than in the bulk of the solution. This ordering and distribution of the water molecules and ions in the vicinity of the surface causes the formation of the electrical interfacial layer [1]. It was found for all hydrophobic materials that the electrophoretic mobility, and thus the surface charge and surface potentials, are pH dependent [2]. The value of isoelectric point was found to be in the acidic region, between pH 2 and 4. The origin of electrical charge of the inert material/interface, and pH dependency, have been a subject of numerous debates in the recent years and is still not solved [3].

In this research we analyzed reactions and process within interfacial layer of inert (Teflon, diamond and graphite)/aqueous electrolyte solution. We defined hydronium (H^+) and hydroxide (OH^-) ion as potential – determining ions. The distribution of H^+ and OH^- ions between bulk and interface is described as separate accumulation of H^+ and OH^- ions at the interface. Total reaction is described as exchange of H^+ and OH^- ions between bulk of solution and the interface $[2\text{H}^+(\text{aq}) + \equiv\text{OH}^- \rightleftharpoons \text{H}^+ + \text{H}_2\text{O}(\text{l})]$ (Figure 1).

The thermodynamic parameters of the above mentioned processes are obtained indirectly from the temperature dependency of equilibrium parameters. Determining temperature dependence of electroneutrality points (isoelectric point or point of zero charge) enables the evaluation of the difference in standard distribution enthalpies of H^+ and OH^- . This data enables us to better understand the behaviour of the electrical interfacial layer and creation of the suitable mathematical and physical models [4]. Electroneutrality points were obtained in the temperature range from 10 °C to 50 °C by using variety of methods: Streaming potential, Electrophoretic mobility and potentiometric mass titration. Differences in standard distribution enthalpy of H^+ and OH^- ions on the Teflon, diamond and graphite surfaces was calculated and compared.

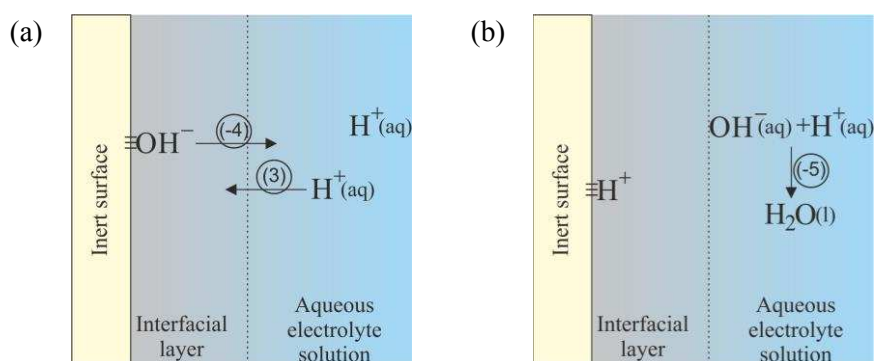


Figure 1. Exchange of H^+ and OH^- ions between interfacial layer and bulk of the solution and dissociation of water molecule in the bulk of the aqueous electrolyte solution.

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Measuring Attractive Interactions between Drops in Polymer Surfactant Systems via Microfluidics and Atomic Force Microscopy

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Attractive interactions between drops in which aggregation, rather than coalescence occurs, lead to the formation of aggregates, gels or microstructures that then control the phase behaviour, stability, rheology and most importantly function of formulated products (*e.g.*, food, personal care products, pharmaceutical formulations). These forces are often highly system specific and are a function of a number of additive components. This talk will focus on a new method using a microfluidic device to measure the attractive surface forces between drops that arise from multi-component complex fluids including polymers, polyelectrolytes or polymer-surfactant systems. The attractive interactions between oil drops in SDS and PVP measured through direct force measurements using an atomic force microscope (AFM) and through a novel microfluidic drop chaining device to measure surface forces will be compared. This presentation will also discuss aspects such as the effects of drop size and adsorption kinetics on the attractive behaviour observed in both measurement techniques.

Native cellulose as a powerful natural emulsifier

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Cellulose is the most abundant, biodegradable and renewable natural polymer on earth, and therefore a key source for sustainable materials in an industrial scale. During the last decade, researchers in the field paid attention to cellulose amphiphilic nature, giving a new perspective for cellulose insolubility in water [1-3].

Cellulose polar-nonpolar structural anisotropy along glucose ring planes raised questions regarding its adsorption behaviour at oil-water interfaces, as well as its ability of stabilizing oil droplets. Many cellulose derivatives are efficient polymeric emulsifiers, and have been widely used in commercial applications [4]. Other types of cellulosic stabilizers are particle-type celluloses, namely, cellulose microcrystalline powder, cellulose nanocrystals, cellulose micro-/nanofibrils and regenerated cellulose [5-7]. Particle-type celluloses behave as “Pickering” stabilizers, a mechanism that differs from flexible polymer stabilization [8]. Here, the key question is how does native cellulose behave at oil-water interfaces in its molecular state?

The purpose of this work is to demonstrate the amphiphilic character of cellulose by its ability to efficiently create emulsions. Preliminary results showed that molecular dispersed native cellulose is a powerful emulsifier being able to create nanosized emulsions with improved stability and optical properties, compared to cellulose derivatives and particle-types based emulsions.

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Biophysical and Functional Studies of two BP100 Analogues Modified by a Hydrophobic Chain and a Cyclic Peptide

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Antimicrobial peptides (AMPs) are ubiquitous compounds that work as a primary defense against pathogenic microorganisms. BP100, (KKLFKKILKYL-NH₂), a rationally designed short, highly cationic AMP, acts against many bacteria, displaying low toxicity to eukaryotic cells [1]. In previous work we found that its mechanism of action depends on membrane surface charge and on peptide-to-lipid ratio [2].

Here we present the studies of two BP100 analogs: BP100-alanyl-hexadecyl-1-amine (BP100-Ala-NH-C₁₆H₃₃) and *cyclo*(1-4)-D-Cys¹, Ile², Leu³, Cys⁴-BP100 (*Cyclo*(1-4)-cILC-BP100) (Figure 1). We studied their binding to large unilamellar vesicles (LUV) of palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) and 1-palmitoyl-2-oleoyl-*sn*-glycero-3-[phospho-*rac*-(1-glycerol)] (POPG) of variable lipid composition, as well as their conformational and functional properties, comparing them to those of BP100. The analogs bound to LUV of POPC:POPG with higher affinity and a lesser dependence on electrostatic forces than BP100. In the presence of LUV, BP100 and BP100-Ala-NH-C₁₆H₃₃ acquired α -helical conformation, while *Cyclo*(1-4)-cILC-BP100 was partly α -helical and partly β -turn. Taking in conjunction the light scattering determination of particle size and zeta potential, the redistribution of a probe initially located in the vesicles outer leaflet, the leakage of LUVs internal contents, and the optical microscopy of giant unilamellar vesicles, it was concluded that, at high concentrations, all three peptides acted by a carpet mechanism causing membrane disruption, while at low concentrations the peptides acted by disorganizing the lipid bilayer, probably causing membrane thinning. However, the analogs exhibited a higher degree of activity and lesser membrane surface charge dependence, probably due to their greater hydrophobicity. The MIC values of both analogs towards Gram-positive and Gram-negative bacteria were similar to those of the parent compound; in contrast, both peptides exerted a much greater hemolytic effect. Confocal microscopy showed Gram-positive *B. subtilis* killing with concomitant extensive membrane damage suggestive of lipid clustering, or peptide-lipid aggregation. These results were in agreement with those found in model membranes.

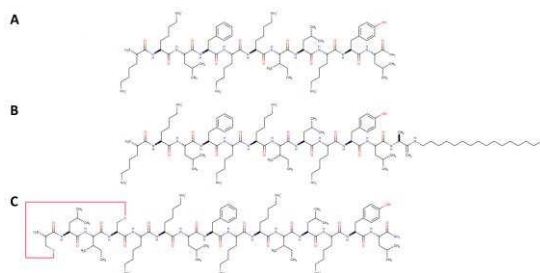


Figure 1. Structures of (A) BP100, (B) BP100-Ala-NH-C₁₆H₃₃ and (C) *Cyclo*(1-4)-cILC-BP100.

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Microencapsulation of active ingredient by polyelectrolyte complex formation

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This paper includes the results of investigations the polyelectrolyte complexes systems used for preparing microparticles by a W/O/W double emulsion technique for hydrophilic active agents delivery. By double emulsion method, the core droplets can be loaded with many substances to achieve various functions such as the encapsulation of nutrients, drugs, antibodies etc. [1]. The primary W/O emulsion consists of aqueous protein solution dispersed in an organic phase containing an oil-soluble surfactant, e.g., Dioctyl sulfosuccinate sodium salt (AOT) in soybean oil. For encapsulation and controlled release of active ingredients were used polyelectrolyte complexes formed by Chitosan and Xanthan gum, Chitosan and Alginate, that can be used to encapsulate proteins, enzymes etc.

Lipase from *Mucor miehei* was used as the active ingredient to be encapsulated by double emulsion technique. In order to establish the optimal conditions for NPs formation, different formulations were prepared by changing the concentrations of Chitosan, Xanthan gum, Chitosan and Sodium Alginate at different pH values while analyzing their effect on the size, surface change and association efficiency of the loaded agent.

Some of the formulation parameters were determined in previous works [2] and were used for enzyme encapsulation. Determination of microcapsule formula was evaluated by encapsulation efficiency, loading capacity, and release profile. In the first step, enzyme was loaded into oil with surfactant for obtainment O/W primary emulsion. In the second step, 3 ml of the primary W/O emulsions were then re-emulsified in 25 ml of 0.5%w/v, Chitosan solution at 3000 rpm for 1 min at room temperature. 5 ml of the secondary emulsion, produced by use of a Chitosan solution, then were incubated into 25 ml of 3% sodium alginate solution during 2 h., and then by injection was passed through 1% solution of CaCl₂, and washed by water, filtrated. Then microcapsules were passed through 0,7% of Sodium Alginate, and 1% of CaCl₂.

The mechanical strength of hydrogel networks obtained by the interaction between Chitosan and Xanthan Gum complexes also allowed obtaining microcapsules that can be used for drug delivery and controlled release.

For detecting of lipase activity was used the fluorescein dibutyrate and measurements were monitored by UV- -spectrophotometer [3].

The association efficiency of the resulted enzyme microcapsules reached 83,5%, after 2 h incubation in PBS solution, the total release reached 70%.

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Influence of the structure of organosilicon compounds on their colloidal-chemical properties

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One of the way to synthesize the stable polymer suspensions is heterophasic polymerization of vinyl monomers in the presence of water-insoluble organosilicon compounds. To explain the high stability of polymer suspensions, the influence of the structure of the organosilicon compound on its colloidal-chemical properties was studied.

It was shown that when the transition from the linear to the comb-like structure of the organosilicon compound occurs, the interfacial tension decreases from 28 to 4 mJ/m², while the surface activity of organosilicon compounds increases from 2.5 to 14 mN•m²/mol. It should be noted that organosilicon compounds are capable of forming of the interfacial layers with a thickness of 7.5-135 nm, which greatly exceeds the allowable levels of the interfacial layer for hydrocarbon surfactants.

Thus, it can be assumed that the high stability of polymer suspensions is related to the surface activity of their structure and time in their interfacial layers of the stability barriers. Interfacial adsorption layers on the surface of monomer droplets and subsequently polymer-monomer particles formed from a polymer in their surface layer during the creating and using of organosilicon surfactants adsorbed on the surface of monomer droplets from the bulk. The amount of surfactants in the interfacial layer of polymer-monomer particles increases with the polymerization due to its incompatibility with the formed polymer and its forced displacement onto the surface of the particles. In the process of displacement the surfactant conformation is changed, it can crystallize, become denser, i.e. the interfacial layer becomes more durable.

Electrically conductive long term stable ultrathin Gallium/Gallium(hydr)oxide layers

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Single Gallium/Gallium(hydr)oxide $\text{Ga}/\text{GaO}_x\text{H}_y$ layers were prepared by induced break-up after forced wetting. Multilayers were formed by repeating the deposition procedure. X-ray reflectivity shows a multilayer structure. The repeat unit consists of a Ga layer covered by a GaO_xH_y layer (thickness 2.9 nm). The multilayer thickness is proportional to the number of deposited layers. The multilayer-air roughness may be smaller than the substrate-multilayer roughness, which is attributed to the large surface tension of Gallium. The electric conductivity of a multilayer follows Ohm's law. The sheet resistance decreases with the number of deposited layers. We suggest that induced break-up after forced wetting is an environmentally friendly way to produce large ultrathin conductive layers from fluid metals [1].

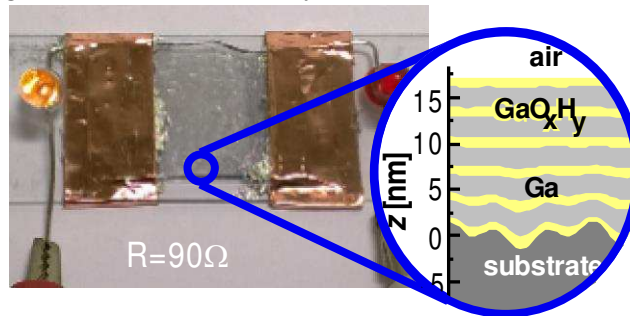


Figure 1. This is a comparison between theory and experimental data.

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Properties of water-in-oil microemulsions doped with thermo-responsive polymers

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By crossing the so-called volume phase transition temperature (VPTT), acrylamide based thermo-responsive hydrogel particles made of e.g. poly-*N-n*-propylacrylamide (PNNPAM) undergo a reversible micro-phase separation process. In the case of PNNPAM the VPTT is located at $T \approx 22$ °C [1]. Thus, by increasing the temperature and therefore crossing the VPTT, a reversible switching from a swollen hydrophilic to a collapsed hydrophobic particle is observed. In this study, we investigate the properties of non-ionic water-in-oil (w/o) microemulsions doped with these thermo-responsive polymers. While, on the one hand the PNNPAM-particles influence the phase behavior and the microstructure of w/o-microemulsions, the confinement given by the microemulsion affects the structure and the VPTT of the particles on the other hand. Thereby, both effects depend strongly on the number density and the size of microemulsion droplets and particles. To investigate the mutual influence, collapsed particles (0.25 wt% in D₂O) were solubilized in w/o-microemulsions of the type D₂O – cyclohexane(d12) – C₁₂E₆ in a first series of experiments. As it is seen in figure 1 left, the doping of the w/o-microemulsions with collapsed hydrogel particles have almost no influence on the phase behavior. Small angle neutron scattering (SANS) experiments were performed to elucidate the structure of the doped w/o-microemulsions. Figure 1 right shows the recorded SANS-curves of the collapsed hydrogel particles in D₂O (0.25 wt%), the hydrogel-free microemulsion (film contrast) and the hydrogel doped w/o-microemulsions (hydrogel/film contrast) at $T = 29.5$ °C. Comparing the scattering curves, an increase of the scattering intensity at low q and a less pronounced oscillation at intermediate q can be observed for the doped microemulsion. The analysis of the scattering curves by appropriate models [2-4] suggests that sphere to cylinder transition is induced by doping spherical w/o-microemulsions with collapsed hydrogel particles.

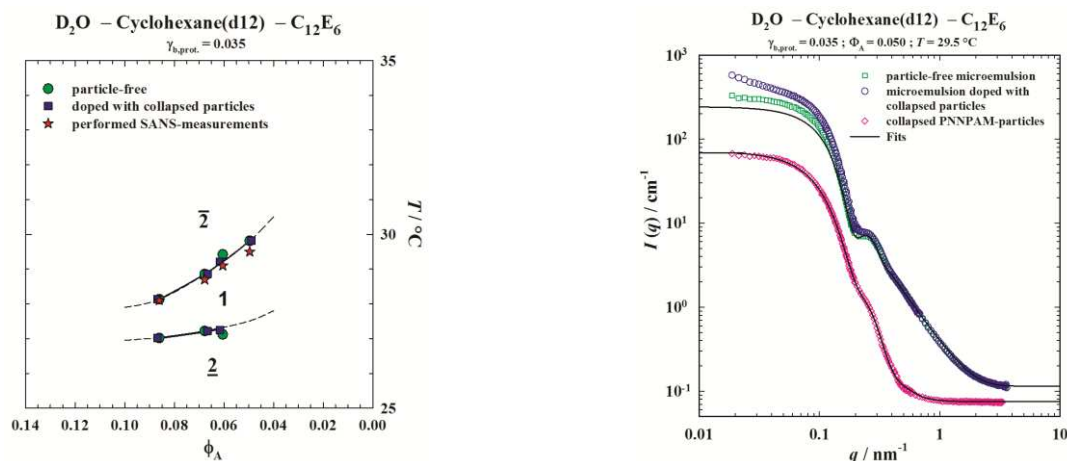


Figure 1. (Left): Phase diagrams of the system D₂O– cyclohexane(d12) – C₁₂E₆ with and without PNNPAM-particles. (Right): Exemplary scattering curves of the collapsed PNNPAM-particles, the pure w/o-microemulsion and the doped w/o-microemulsion.

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PNIPAM microgel-stabilised aqueous foams

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Aqueous particle stabilized foams can be found in many technical applications and food products. In these systems the particles adsorb at the air-liquid interfaces of the foam and stabilize them. When altering the properties of the particles like their hydrophobicity, the properties of the produced foams can be changed. Typical particles are modified silica nanospheres, but also soft colloidal particles like proteins, especially in food-related systems [1].

Another class of soft colloidal particles are cross-linked, short-chained poly-N-isopropylacrylamide (NIPAM) polymers, which have attracted much attention during the last years and were studied with various techniques and in the context of multiple possible applications. Since these microgels are responsive to external stimuli like temperature, materials made from them can be considered “smart” materials. A prominent example are thermo-responsive emulsions stabilized by microgel particles adsorbed at the water-oil interface. In these systems the emulsion stability can be controlled by changing the temperature [2,3].

In this contribution we exploit the interfacial activity of PNIPAM microgels to stabilise aqueous foams. These foams are very stable at temperatures below the volume phase transition temperature (VPTT) of NIPAM and can be destabilised by increasing the temperature above the VPTT. Furthermore we shine light on the relationship between the properties of individual microgels (e.g. size, elasticity, particle concentration) and the properties of foams, prepared with them.

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Corresponding state description of CO₂-microemulsion systems stabilized by a new fluorinated surfactant

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Over the past decade the fundamental research on CO₂-microemulsions has gained increasing interest. Especially, the possibility to tune the phase behavior and nanostructure via the pressure is one outstanding property of these systems. Often non-biodegradable, fluorinated surfactants are used to formulate well-structured CO₂-microemulsions [1]. From the application point of view, well-structured CO₂-microemulsions stabilized by biodegradable hydrocarbon surfactants are of utmost interest. Consequently, a number of research groups focused on the synthesis of such surfactants, which solubilize scCO₂ efficiently [2,3]. Here the properties of the microemulsion system H₂O/NaClO₄ – CO₂ – Capstone® FS-3100 was studied as a function of composition, temperature and pressure. Capstone® FS-3100 is a F-(CF₂)_i-(CH₂CH₂O)_j-H surfactant with a short perfluorinated alkyl chain, i.e. a low bio accumulation and toxicity. To the best of our knowledge, this is the first time the phase inversion of a CO₂-microemulsion is fully evidenced by studying the water-rich, balanced and CO₂-rich part of the phase diagram. The analysis of the SANS curves, recorded close to the respective emulsification failure boundaries and the efficiency point, clearly show a transition from CO₂-swollen micelles in water via bicontinuous structures to water swollen micelles in CO₂. Furthermore, as found for the oily counterparts [4], the length scale of the structure runs through a maximum at the phase inversion temperature. These results indicate that the corresponding state description for classical state of the art microemulsions, found by Sottmann and Strey [4], is also applicable to CO₂-microemulsion systems.

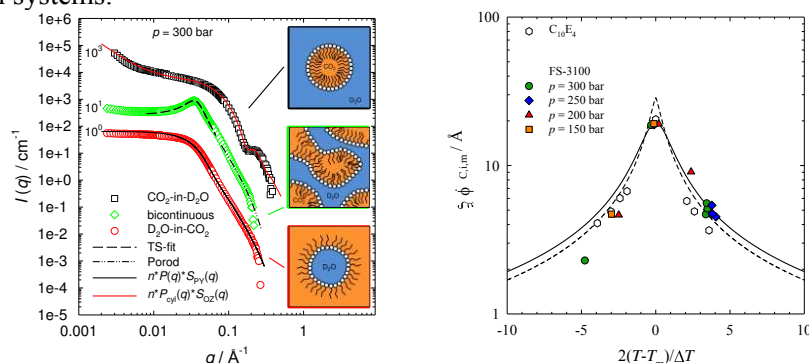


Figure 1. *Left:* Exemplary SANS curves of balanced, CO₂-in-water and water-in-CO₂ microemulsions made from D₂O/NaClO₄ – CO₂ – FS-3100. The data were described using the *Teubner-Strey* model and the form factor for polydisperse spheres/cylinders combined with a hard-sphere/*Ornstein-Zernike* structure factor [5], respectively. *Right:* Scaled characteristic length scale $\xi\phi_{C,i,m}$ as a function of the reduced temperature $2(T-T_m)/\Delta T$ for H₂O – *n*-octane – C₁₀E₄ [6] and D₂O/NaClO₄ – CO₂ – FS-3100.

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Stabilization of oil-in-water emulsions containing hydrophobically modified xanthan: role of the chain conformation

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Polysaccharides are widely employed in many industries such as food or cosmetic mainly to stabilize oil-in-water emulsions. Indeed, the rheological behaviour of the aqueous phase can be controlled by increasing the viscosity, thus slowing down or inhibiting the phenomenon leading to instability (creaming, flocculation and coalescence). Among them, xanthan gum is the most used due to its outstanding thickening properties. Moreover, xanthan can adopt two different conformations^[1], with distinct rheological properties^[2] depending on the experimental conditions: an ordered semi-rigid helical structure or a disordered flexible coil. However, because of its poor interfacial properties, the addition of an emulsifier remains necessary to disperse and stabilize the oil droplets. Unfortunately, the use of low molecular weight surfactants has many disadvantages related to toxicological and environmental considerations. To overcome this problem, we developed amphiphilic xanthan derivatives by grafting alkyl residues onto the polysaccharide backbone.

The objective of the present work is to describe how the structure and the stability of oil-in-water emulsions containing amphiphilic xanthan, modified under both conformations, can be controlled. In solution, modified xanthan present much better bulk rheological properties than pristine xanthan^[3]. In addition, shear interfacial viscoelasticity has been strongly improved compared to unmodified xanthan^[4], hence confirming the potential stabilizing properties.

Finally, as expected, unmodified xanthan cannot stabilize the emulsions as phase separation occurred within only few hours while emulsions obtained with modified xanthan remain stable over months (see figure 1).

These results clearly demonstrate the high potential for hydrophobically modified xanthan as emulsion's stabilizer which has been studied as a function of polymer conformation, concentration, grafting density and hydrophobic chains length.



Figure 1. Photographs of oil-in-water emulsions containing pristine xanthan one day after preparation (left) and containing modified xanthan after 3 months (right).

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Ultra low crosslinked microgels are ordered in bulk and disordered in two-dimensions

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The interplay between softness and liquid-to-solid transition is one of the more general problem in nature, for example in the kinetic of protein folding [1] or for living cells [2]. In this contribution, we present the phase behavior of water suspensions of ultra low crosslinked poly(*N*-isopropylacrylamide) microgels studied in three and two-dimensions. In three-dimensions the phase behavior is comparable to the one of regular crosslinked microgels: Coexistence between crystals and liquid and fully crystalline samples are observed (Fig. 1A) [3,4]. Small-angle neutron scattering measurements of the single particle form factors show no failure of the spherical shape, both in crystalline and disordered, overcrowded samples.

At the oil-water interface, a rich phase behavior for regular crosslinked microgels with a solid-solid phase transition is reported [5]. We monitored the compressions isotherms and analyzed atomic force microscopy images of depositions at different concentrations of ultra low crosslinked microgels. It is revealed that in two-dimensions their crystallization is suppressed (Fig. 1B). The reason for this is the wide variation of the microgels bulk moduli together with the reduced mobility of the microgels due to the confinement. Furthermore, the degree of compression can be used to switch the property of the depositions from the linear polymer-like to the one of a suspension of colloidal particles.

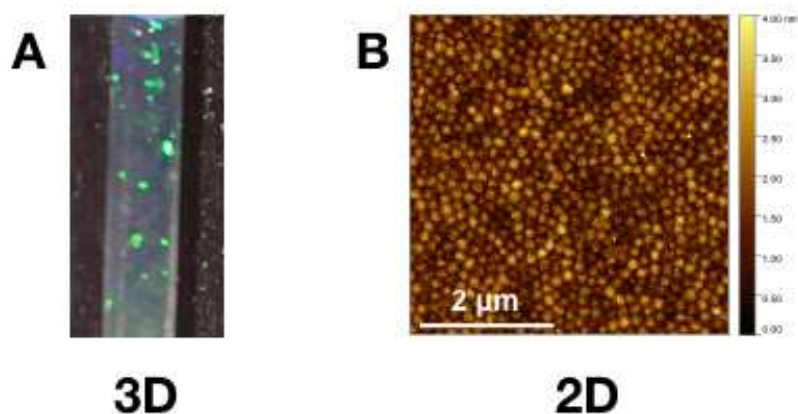


Figure 1. A) Crystals formed by the ultra low crosslinked microgels in water suspensions, three dimensional. B) Disordered arrangement of microgels imaged with atomic force microscope after deposition, two dimensional.

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Designing responsive foams with an adjustable temperature threshold of destabilization

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Responsive aqueous foams that refer to foams for which the macroscopic stability with time can be switched between a stable and an unstable state have recently attracted a growing interest [1]. The optimization of many processes such as washing or material recovery processes require at the same time the formation of a stable foam, as well as the need to destabilize it in another step of the process. Such ability to rapidly destroy the foam on demand is however a difficult goal to achieve, because the more stable the foam is, the more difficult it is to destabilize. In view of the numerous applications, the design of responsive foams is a new and important issue. However, up to now, there was no system for which the threshold temperature of destabilization can be precisely chosen within a wide range of temperatures limiting their potential for applications. Our approach to design thermoresponsive foams with a widely adjustable temperature threshold of destabilization is based on a green formulation: 12-hydroxystearic acid (12-HSA) mixed with counterions (alkanolamine) of different chain lengths, and at different molar ratio R between the fatty acid and the counterions [2-3].

First, by coupling microscopy techniques, small angle neutron & X-ray scattering and DSC, we investigated the bulk structures, from the molecular to the mesoscopic scale. For all the counterions and depending on the temperature T and R , either micron-size tubes or micelles were formed. We showed that tubes transitioned into micelles at a precise temperature. This temperature transition depended on both R and the alkyl chain length of the counter-ion and could be precisely tuned from 20°C to 75°C. We highlighted that the transition at the supramolecular scale came from the chain melting phenomenon at low R and the surface melting process of the hydrogen bonds at high R [2].

Second, at the macroscopic scale, we demonstrated that there was always a range of T for which stable foams can be produced, whatever the counterion and R [3]. All these foams had a neat critical temperature of destabilization, above which they rapidly collapsed. Remarkably, this critical temperature can also be continuously set between 20°C and 75°C, by changing the counterion and T (Figure 1). We demonstrated that the foam stability was directly correlated to the supramolecular scale: the foam stable/unstable transition was controlled by the topological change of the fatty acid self-assemblies from micron-size tubes to micelles.

Thus, a proper choice of R and of the counterion length enables to set the temperature transition over a range that almost covers the one for which water is liquid. It is the first time that, by using the same surfactant, responsive foams are made with a threshold temperature varying over such a wide range of temperatures [3].

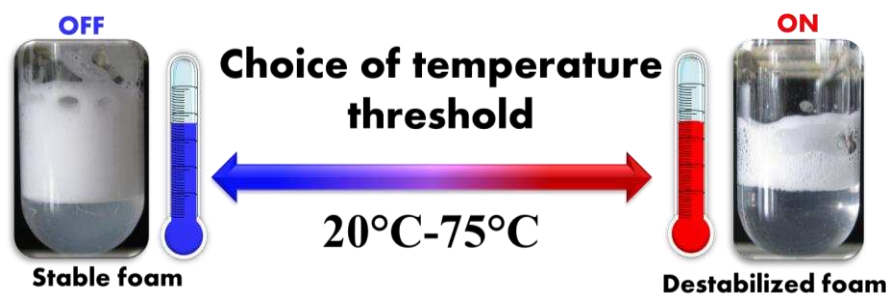


Figure 1: Illustration of the thermoresponsive foams with a threshold temperature between 20 to 75°C.

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Modelling phase transfer of electrolytes in emulsified microemulsions

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Recycling of metals in hydrometallurgy is based on liquid-liquid extraction and desextraction between complex fluids [1]. These are concentrated acidic or basic aqueous solutions in contact with organized organic phases containing extractant molecules (which selective affinity to extracts metal ions) in the form of water-poor microemulsions. Winsor II regime with excess aqueous solution is required for efficient electrolyte transfer. The free energy of electrolyte transfer between phases is much lower than the free energy of complexation in all industrially cases.

Here, we combined a general model based on thermodynamics equations [2] taking into account the microemulsion structures for which the free energy is calculated using a Gaussian random fields model [3-4] in order to calculate the ion free energy of transfer between an aqueous reservoir and an organized organic phase. We show that taking into account extensive values for the complexation, the extractant adsorption at the interface, and the active area variation allows for predicting the free energy of extraction. This is also confirmed by small angle scattering as a signature of the type of water-poor self-assembly. Furthermore, we demonstrate that the apparent selectivity is really different from the complexation energy differences between ions.

To our best knowledge, this is the first theory proposed to link complexation with nearest neighbour and free energy of phase equilibria from first principles. We will show the strength as well as the weaknesses of this emerging modelling method using Gaussian random waves.

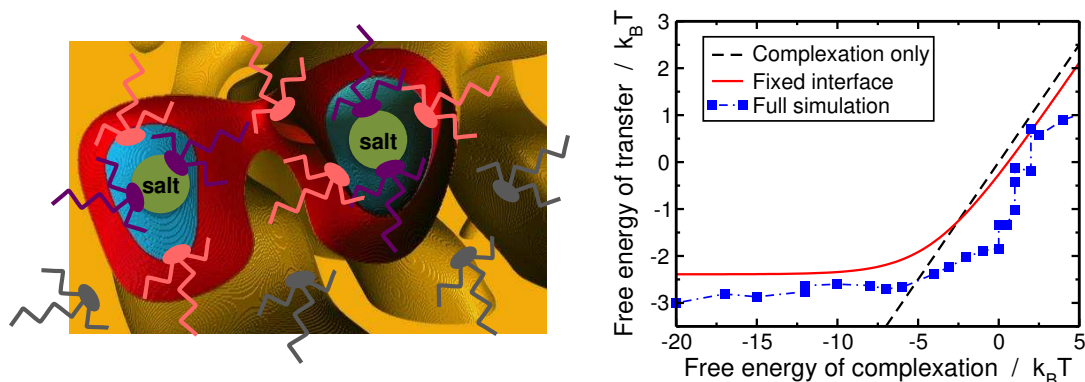


Figure 1. (Left) Schematic representation of water-poor microemulsion. (Right) Free energy of ion transfer to water poor-microemulsion calculated as a function of the free energy of ion complexation using different levels of approximation.

Acknowledgements: The authors acknowledge financial support from the European Research Council under the ERC Grant Agreement no. [320915] REE-CYCLE: Rare Earth Element reCYCling with Low harmful Emissions.

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Unusual immersion stability of ultrathin polycation/graphene oxide layer-by-layer structures in electrolyte solutions

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Ultrathin multilayers containing graphene oxide (GO) nanosheets hold a great promise in diverse applications involving energy storage, electronics, water purification by filtration or deposition of antireflective coatings. Many of these applications require that the film assembled in a layer-by-layer (LbL) manner is in direct contact with a liquid phase, most often water or an aqueous solution. Obviously, the multilayer must retain its integrity in a given solution and temperature interval in order to be practically useful for e.g. water-solute separation. Although the mechanical stability of GO LbL structures have been characterized by tribological test methods in dry state [1], there has been much less emphasis on the investigation of chemical stability of polymer/graphene oxide composite nanofilms in contact with water and in solutions of potentially reactive chemical substances. Low stability of LbL films in certain solutions (e.g. due to disintegration or chemical modification) is one of the possible limiting factors for their potential applications.

This presentation focuses on the LbL assembly of hybrid nanofilms composed of alternating layers of graphene oxide colloidal particles and a cationic polyelectrolyte (poly(diallyldimethylammonium chloride, PDDA)) and their deconstruction. Although it has been demonstrated long time ago that oppositely charged colloidal species of GO and PDDA are capable for the alternating assembly over charged surfaces such as glass or quartz [2,3], the effect of the type and composition of the dispersion medium both on the multilayer build-up has just been scarcely studied. Herein, we show the effect of the solution pH conditions on the optical thickness and structure of films containing few hybrid (PDDA/GO) bilayers. The second part of the presentation will concern with the immersion stability of the ultrathin assemblies in different types of electrolyte solutions involving dilute and strong acids and bases [4], which show anomalous behaviour as compared to the stability behaviour of the “traditional”, all-polyelectrolyte multilayers [5].

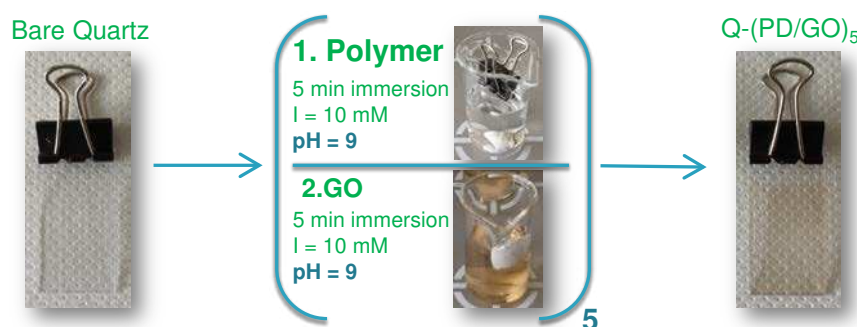


Figure 1. LbL build-up of graphene oxide multilayers aided by polyelectrolytes on quartz support.

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Interactions between dendritic nanoparticles and lipid multilayers: Implications to fundamentals of nanotoxicity

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Nanoparticles are widely found in modern technologies, ranging from biosensors to food additives [1]. However, the cytotoxic effects of nanoparticles are not well understood, stimulating a new research area dubbed ‘*nanotoxicity*’. Nanotoxicity has been found to depend upon the size, shape and surface chemistry of nanoparticles, and can be imparted via a multitude of toxicity pathways [2]. The most common method for determining the cytotoxic effects of nanoparticles has been through dye-based cytotoxicity assays that can provide information such as cell proliferation, glucose consumption and membrane permeability [3]. However, these assays give little information about the *fundamental interactions* between nanoparticles and cells that lead to cellular entry (endocytosis) and resulting toxicity. An understanding of nanoparticle interactions with membranes is key to understanding endocytosis, membrane fusion and nanotoxicity, as well as improving drug-delivery-vector design. Due to the complex nature of cells, this is difficult to examine *in vitro* and so using membrane models represents a promising and important alternative approach.

This project aims to explore how the physicochemical properties of nanoparticles influence their interactions with various membrane models. Many self-assembled lipid systems can be used to model cell membranes [4], including monolayers, bilayers, lipid mesophases, and liposomes. Whilst lipid multilayers have also long been recognised as bearing structural resemblance to cell membranes, they are conventionally prepared by using spin-casting from a volatile organic solvent [5]; thus, it has been difficult to study the interactions between such lipid multilayers with biomedically relevant nanoparticles often dispersed in aqueous media. Here we use a recently developed method for preparation of lipid multilayers and bilayers *via* drop-casting aqueous phosphatidylcholine (PC; a common eukaryotic membrane lipid) liposome dispersions on mica substrates, which have been characterised using synchrotron X-ray reflectivity (XRR) at the ESRF in Grenoble [6].

We have investigated how polyamidoamine (PAMAM) dendritic nanoparticles (dendrimers) of varying size (or generation), dosage, and terminal groups (NH₂ or hydrophobic C₁₂ chains), influence *d*-spacing in PC bilayers, as well as coherence length (*L_a*) and paracrystalline disorder (*g*) in PC multilayers. The composition and thus fluidity of the membranes was altered by the addition of varying ratios of cholesterol and by using saturated and unsaturated lipid tail groups (DOPC/DPPC). Atomic force microscopy (AFM) was used to investigate the topology of lipid multilayers. Interestingly, multilayer structural disorder is promoted not only by the dendrimer size and functionalisation, but also by the method of dendrimer addition in the liposome preparation. This is evident from the shift in the Bragg peak positions, ΔQ , as well as the peak broadening (*i.e.* widening in the peak full width at half maximum) in the XRR curves. Co-assembly of the dendrimer with the lipids during the early stage of the liposome formation led to dendrimer intercalation in the ultimate stacked lipid bilayers. We will discuss the implications of our results to the energetic considerations in nanoparticle cellular entrance.

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Miscibility of cationic and zwitterionic surfactants in adsorbed film and micelle studied by X-ray reflection and XAFS

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The structure and property of adsorbed film at soft interfaces are affected by molecular interaction closely related to molecular packing which is affected appreciably by the geometrical shape of molecules as well as that of interface. Since molecular assemblies of surfactants are of importance as a fundamental model for complicated molecular organized systems such as biological membrane, systematic studies on adsorbed films at soft interfaces as well as aggregates in surfactant solution are crucial to understand the structure-function relation of molecular organized system. In this study, we aim at discussing the miscibility of cationic surfactant, tetradecyltrimethylammonium bromide (C14TAB) and zwitterionic one, tetradecylphosphocholine (C14PC) molecules in surface adsorbed film and micelle on the basis of X-ray reflectivity (XR) [1] and X-ray absorption fine structure (XAFS) [2] measurements coupled with surface tensiometry.

Phase diagram of adsorption and that of micelle formation showed negative deviation from ideal mixing of molecules both in the adsorbed film and micelle. The excess Gibbs energy is more negative in the micelle than in the adsorbed film, indicating that the interaction between C14TAB and C14PC is stronger in the micelle than that in the adsorbed film. This is mainly due to the fact that the critical packing parameters (cpp) of both C14TAB and C14PC molecules are close to 1/3 because of their large head groups and therefore the packing of molecules is energetically more favorable in spherical micelle than at planar adsorbed film.

Electron density profile normal to the surface indicated that in the pure films the charged head groups of C14TAB and C14PC take staggered arrangement to reduce electrostatic repulsion between them. In the mixed system, on the other hand, the mixing of C14TAB and C14PC relaxes staggered arrangement due to an attractive ion – dipole interaction between cationic trimethylammonium (TMA) and zwitterionic phosphocholine (PC) groups. This was supported by lower Br ion binding in the mixed adsorbed film than in the pure C14TAB film determined by total reflection XAFS analysis. Another noticeable point was that Br ion binding is higher in the adsorbed film than in the micelle. This induces an enhancement of ion – dipole interaction in spherical micelle compared to that at planar adsorbed film, and eventually the interaction between TMA and PC groups becomes favourable in addition to that between hydrophobic chains in mixed micelle than in the adsorbed film.

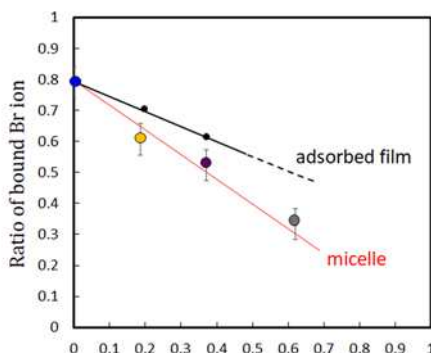


Figure 1 Fraction of bound Br ion vs. film and micelle compositions.

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Location of small molecules in lipid bilayers: insights into cryoprotective mechanisms

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When cells or organisms are subjected to dehydration and/or freezing, a key factor in survival is the interaction between membranes and cryoprotective molecules. These molecules fall into two categories: those found in nature (e.g. sugars manufactured inside cells which cannot permeate membranes); and molecules used in laboratory cryopreservation (membrane penetrating molecules, such as DMSO and glycerol). Both classes of molecules can alter membrane structure, but the mechanisms differ.

Previously we have studied the structure of synthetic membranes in the presence of sugars using SAXS and SANS [eg 1-2]. More recently, we have conducted membrane diffraction experiments on stacked multilamellar membranes which provides higher order diffraction information, allowing the Fourier reconstruction of the bilayer structure [3-4]. By deuteration of various components, and adjusting neutron contrast by changing the D₂O/H₂O ratio, the positions of these molecules within the bilayer may be determined with high precision.

In this talk we will present recent results on DMSO, and compare these with previous results on non-penetrating cryoprotectants, highlighting the different modes of action of these two types of molecules. The relevance of these results to our understanding of cryopreservation will be discussed.

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Selective Deposition of Polystyrene Nanoparticles on Glass Fibers

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Depositing particles on fibers has been long standing with wide-ranging applications in diverse areas such as sensors, solid-state devices, and high-performance composite materials [1]. It has been shown that textile surfaces when modified with colloidal particles result in more durable fibers with features such as water and dirt repellency, and anti-fouling characteristics.

Besides, recently, there has been much interest in directing particles to specific locations by patterning flat substrates [2] through a surface functionalization by chemically modifying the substrate to contain active sites guiding the particles to desired locations.

In the current work, we bridge the gap between uniform particle depositions on fibers and directed assembly of particles on flat surfaces, which, to the best of our knowledge, has not yet been done. We demonstrate a proof of concept for the selective deposition of nanoparticles on chemically modified micrometer size glass fibers (GFs), referred to as “patterned” GFs containing hydrophilic and hydrophobic segments. We then localize polystyrene nanoparticles onto the hydrophilic segments of these fibers deposited via a dip-coating method. To achieve a contrast in wettability, cleaned hydrophilic GF segments were treated with Octadecyltrichlorosilane (J&K Scientific GmbH, Germany) (OTS treated). The nanoparticles used in this study were commercially available Polystyrene (PS) latex nanoparticles (Microparticles GmbH, Germany) with a mean particle diameter of 99.0 ± 0.4 nm suspended in milliQ water at a particle concentration of 1 wt%. Dynamic contact angle measurements by the Wilhelmy technique and deposition of PS nanoparticles via dip coating were conducted using a force tensiometer (K100SF, Kruss GmbH Germany) at room temperature.

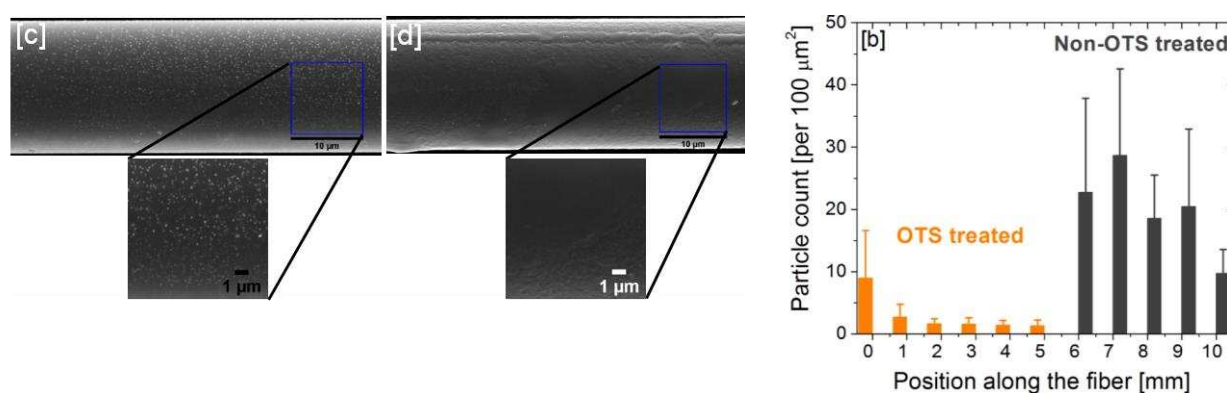


Figure 1. (Left) SEM images of the non-OTS and OTS treated segments of a glass fiber. (Right) Particle counts along the length of patterned GFs (withdrawal velocity of 500 mm/min)

By comparing the advancing and receding contact angle values of the different GF surfaces, we can conclude that the non-OTS treated segments are nicely hydrophilic while for the OTS treated segments, the angles tend more towards the hydrophobic regime. This sharp contrast in wettability facilitates to selectively drive the deposition of the nanoparticle on the non-OTS treated segments as evidence by Figure 1.

Thus, this approach demonstrates the possibility for the controlled localization of particles on fibers. In perspective, we will create consecutive patterns of varying surface functionalities to direct the deposition of particles on fiber surfaces for potential application in composite materials.

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Effect of SiO₂ nanoparticles on droplet stabilization in emulsions: a simulation study

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Langevin dynamics method was used for modeling Pickering emulsion stabilization. The influence of nanoparticle and droplet parameters on the kinetics of SiO₂ nanoparticle adsorption on the surface of oil droplets was numerically determined.

The tendency toward reducing the stability of emulsions with a decrease in the diameter of oil droplets was observed. Drops with a diameter of 1000 nm and higher were resistant to flocculation and coalescence at the ionic strength of the aqueous phase lower than 0.05 mol/l. The distance between oil droplets increased at all stages of modeling due to electrostatic repulsion between oil drops with adsorbed SiO₂ nanoparticles.

Drops with a diameter of 700 nm were unstable to flocculation. Aggregation of droplets started after $\approx 1 \cdot 10^{-4}$ s. The time of flocculation beginning decreased with decreasing oil droplet diameters and it was equal $0.35 \cdot 10^{-4}$ s in emulsions with 300 nm droplets. Moreover, droplets with diameters lower than 300 nm were unstable toward coalescence.

Fractions of flocculated drops and the number of drops in flocs were determined for different parameters of the emulsions. Emulsion stability diagram with regions of emulsions unstable and stable toward flocculation and coalescence was obtained.

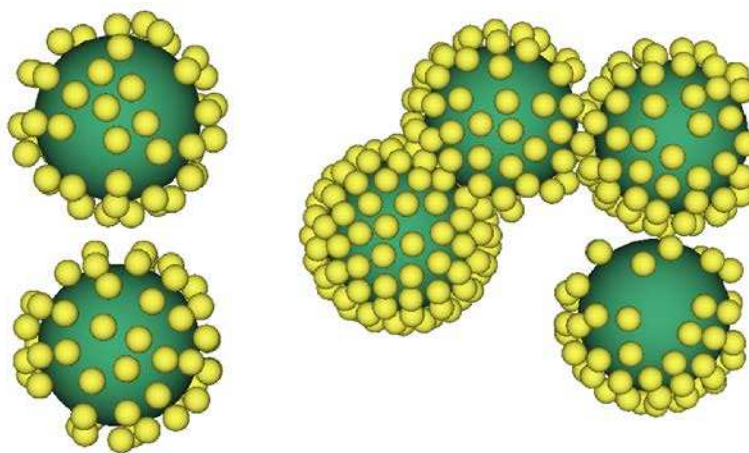


Figure 1. Individual droplets and floc formed as a result of SiO₂ nanoparticle adsorption on the surface of oil droplets. ζ -potential of SiO₂ nanoparticles -50 mV, oil droplets - -10 mV. Ionic strength of the aqueous phase - 0.05 mol/l.

Acknowledgements: This work was supported by the Ministry of Education and Science of Russia through the government assignment 10.4650.2017/6.7 and Russian Foundation for Basic Research grant 16-03-00658.

Syntheses and Surface-Active Properties of N-(Azobenzene-4-Oxy-2-Hydroxypropyl)-N-(Alkyloxy-2-Hydroxypropyl)Aminopropyl Sulfonate as Photoresponsive Surfactants

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New photoresponsive surfactants, N-(azobenzene-4-oxy-2-hydroxypropyl)-N-(alkyloxy-2-hydroxypropyl)aminopropyl sulfonate (GnAZOAS), have been designed by incorporating alkylglycidyl ether derivatives by the attack of a nucleophilic reagent with photochromic property as a azobenzene. G12AZOAS surfactant solution was converted to 93 % *cis* isomer by UV irradiation at 350 nm and the *cis* isomer mixture was reconverted again to 74% *trans* isomer by irradiation in the visible region ($\lambda > 445$ nm). The critical micelle concentration (CMC) of the *trans* form was about 1.45×10^{-3} mole/l and the value of the 93% *cis* form was 2.84×10^{-4} mole/l. In the region between these two CMC values the surface activity can be photocontrolled. And the difference in cmc for *cis* and *trans* isomers of GnAZOAS surfactants increased proportionally with the chain length of the alkyl group. The minimum average area per molecule, which may be attributed to the effect of structure between planar and bent, the area for the *trans* and *cis* isomers of the surfactant is 1.14 and 2.19 nm², respectively. The emulsifying ability of the *cis* isomer was less active than the *trans* one. Also, the studies on physical properties such as critical micelle concentration, emulsion stability and foaming test of the synthesized surfactants have been carried out with respect to changes before and after the UV/vis light irradiation.

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Adsorption of hyperbranched arabinogalactan-proteins from plant exudate at solid-liquid interfaces

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Plant exudates like Acacia gums are made of glycosylated hydroxyproline-rich proteins, with a high proportion of heavily branched neutral and charged sugars in the polysaccharide moiety. These hyperbranched arabinogalactan-proteins (AGPs) display high added-value functionalities in particular their ability to adsorb at solid-liquid and liquid-liquid interfaces. Industrial applications of these AGPs concern mainly stabilization of dispersed food systems and as adhesive. However, even if applications of these AGPs are widely spread, little is known about the molecular mechanism underlying the adsorption properties of these hyperbranched AGPs [1,2].

The present study focus on the adsorption of *Acacia* gums (*A. senegal* and *A. seyal*), and its molecular fractions isolated by chromatography at solid-liquid interfaces, onto gold surfaces characterized with a quartz crystal microbalance with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR). Those are powerful methods that allow highly sensitive, quantitative, real-time, in situ and noninvasive detection of molecules adsorption on a solid surface. QCM-D probes the variation of shear of an oscillating piezoelectric sensor, caused by changes in the total mass of the adsorbed molecules, while SPR allows the determination of the mass of the adsorbed species from the change of refractivity of the gold film. Combining those two techniques can provide information on the sorption mechanisms, structural changes and obtained the state of hydration of the adsorbed film. Comparing protein-rich and polysaccharide-rich molecular fractions will allow the determination of their respective contribution in the formation of surface interactions in AGPs. The effect of pH and ionic strength in solution on the adsorption behavior, the maximum coverage and the thickness of the layer were investigated, and the fraction of water in the gums film was estimated.

A. senegal and *A. seyal* gums present different adsorption behavior depending on experimental conditions. While both gum forms an interfacial viscoelastic film, *A. seyal* gum generally presents a more rigid and homogenous film on the gold surface at weak adsorption. There are specific pH conditions where strong or weak gum adsorption occurs, but *A. seyal* gum always presents a weaker adsorption on the gold surface than *A. senegal* gum (Figure 1). Both gums present, a very hydrated film (70-90%), with low adsorption near the isoelectric point of the whole gum the adsorption increasing however with ionic strength in solution. Interestingly, it was observed a slow decrease of the degree of hydration near the isoelectric point. These results show a relationship between the protein content in AGPs and its adsorption capacity. Gold surface after adsorption of gums and fractions were characterized by AFM and XPS spectroscopy to map the film after drying (thickness, structure) and provide chemical information.

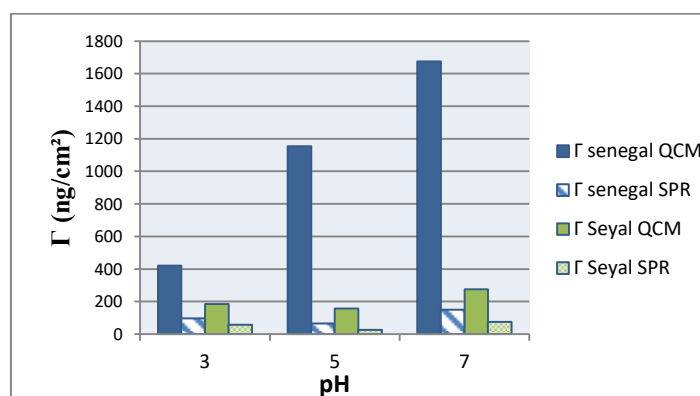


Figure 1. Acacia gums adsorption on gold surface with 10 mM acetate in solution

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Study of features of emulsion stabilizers at the water/liquid interface

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A new approach for the microencapsulation of active ingredients used for the targeted delivery of functional reagents and its controlled release in the necessary medium is the use of various types of emulsions stabilized by synthetic and natural systems. Managed delivery means, such as micro- and nano-capsules, can protect active substances from the effects of the external environment and ensure their prolonged action.

In this regard, the development of a smart encapsulation technology based on direct, double, multiple emulsions is interesting. For this it is needed to carry out a study to identify the colloidal chemical features of the formation of interfacial adsorption layers at the liquid interfaces and to establish the features of emulsification with synthetic and natural composite materials.

The aim of this work is to study the mixed adsorption layers of emulsion stabilizers (synthetic and natural systems) at the water / liquid interface. Interfacial tension, dilational rheology of sodium caseinate and its mixture with xanthan gum were studied. From the obtained features the optimal concentration of studied objects were determined which further were used for the capsulation of polyphytic oil and Vitamine E by direct emulsification. The optimal conditions (concentration ratio, pH) were determined. It was shown, the perspectives such systems as emulsion stabilizers and for the capsulation of active ingredients.

Investigation of the properties of micro- and nanocontainers with biocide

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Biocides are chemical substances that can deter or kill the microorganisms responsible for biofouling. A bright representative of a new class of "green" biocides, it is possible to name compounds of the isothiazolinone group and among them, especially 4,5-dichloro-2-n-octyl-4-isotriazolin-3-one (DCOIT).

The main advantages of the biocide DCOIT are of its broad spectrum of antimicrobial activity at very low concentrations, self-regulation of the concentration in aqueous media due to its poor water solubility, and rapid biodegradability and therefore low environmental harmfulness.

In this work the properties of nanocontainers with biocide DCOIT, such as size, electrokinetic potential, polydispersity and the possibilities of using Pickering emulsions in the system TPM+DCOIT/SiO₂ were investigated, for the obtaining of organic protective coatings containing containers.

Suspensions of final nanocontainers showed a very high degree of monodispersion.

Due to the fact that the nanocontainer shell was formed partially by hydrophobized silica nanoparticles, the zeta potential of the final containers had a sufficiently high negative charge at pH=7.

The content of biocide in nanocontainers with included in it DCOIT varied from 10 to 30% by weight.

The possibility of encapsulating the biocide DCOIT was experimentally established using silica nanoparticles.

Optimal parameters of the encapsulation process in the TPM + DCOIT/SiO₂ system were determined and the composition was determined by conducting a full-scale series of experiments, which provides a fundamental scientific basis for this technique.

A positive effect of the encapsulation of the biocidal DCOIT in nanocontainers was established, which was confirmed by statistically reliable tests of biological activity.

One step formation of controllable complex emulsions

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Emulsion is a dispersion of droplets of one fluid in a second fluid. Conventionally, it is formed by simple mixing of two immiscible fluids and thermodynamically stabilized by surfactant for specific period. Recently, emulsions with complex geometries including multiple emulsion, Janus emulsion, or multilayered emulsion have been interested because of their significant potential in many applications including foods, pharmaceuticals, cosmetics, functional materials, and chemical separation. Contrary to the tremendous importance, unfortunately, the preparation method remains one of the most challenging issues from a colloid perspective.

Here, we report that novel scientific finding of generation of complex emulsions based on phase separation of droplet. The basic principle of phase separation of emulsion droplet can be induced from mass-transfer of separating agent triggering control of the formation of multiple emulsions in confined microfluidic system and novel approach generating complex multiple emulsions in a single step mediates precision control of the size of droplets, efficient encapsulation as well as compartment of active ingredient into desired position in a emulsions droplet.

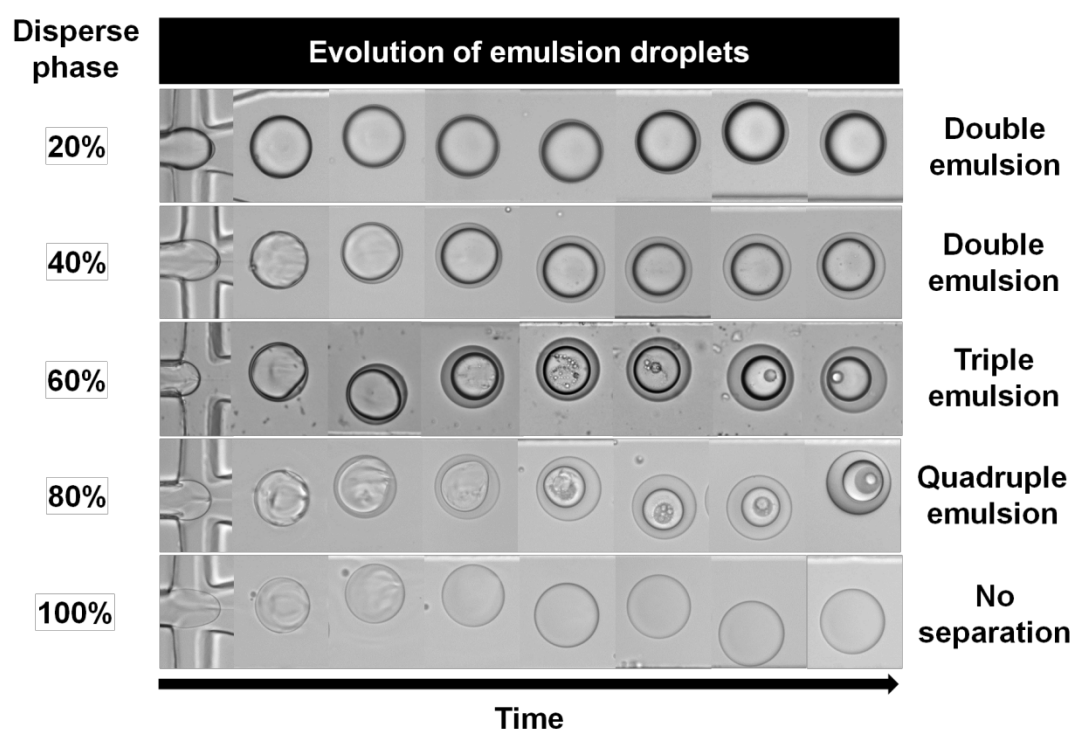


Figure 1. Generation of multiple emulsions from single droplet in a microfluidic channel

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Trans-cinnamaldehyde nanoemulsions stabilized using hydrophobically modified inulin with a powerful stability against stress conditions

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Recently, there has been an increasing interest within the food industry to employ natural ingredients as an alternative for synthetics due to the consumer demands. Synthetic food preservatives can be potentially replaced with naturally occurring compounds known as essential oils. In this study, cinnamaldehyde with outstanding properties such as antimicrobial, antioxidant, and anticancer was utilized to formulate nanoemulsions with hydrophobically modified inulin (HMI) and the outcomes were compared with a commonly used Tween 80 surfactant. The cinnamaldehyde oil-in-water nanoemulsions were successfully produced with no considerable particle size changes during long-term storage (30 days) at 20°C. Surprisingly, the formed nanoemulsions showed no evidence of physicochemical instability when exposed to a very high salt content (2M) as well as to thermal processing at 90°C for 30 min with a constant droplet size (<150 nm). Cryo-SEM confirmed the morphology and droplet size distribution of the fabricated nanoemulsions. Antimicrobial tests exhibited that only 1-2% of these nanoemulsions was enough to entirely suppress the growth of *E. coli* and *S. aureus*. Agar well diffusion assays presented that these colloidal dispersions were more effective against *S. aureus* than *E. coli*.

The results obtained from this study have invaluable implications for the fabrication of a natural colloidal dispersion with potential antimicrobial applications in not only food industry, but also pharmaceuticals and beauty products.

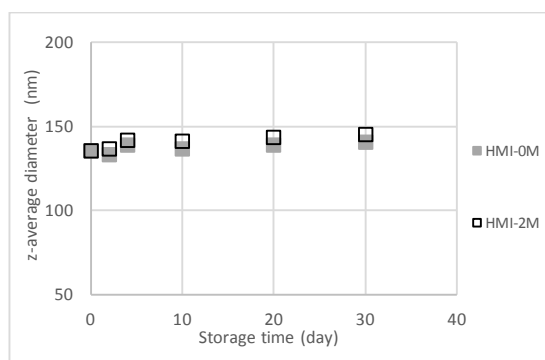


Figure 1. Droplet size changes of nanoemulsions in the absence and presence of high salt content.

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Double layer electrostatics of heterogeneous surfaces with circle phase contours

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A system composed of two semi-infinite bulk phases (air/electrolyte solution) divided by a flat charged surface is studied. The particular considered surface is modelled as a Langmuir type monolayer consisting of two surface sub-phases, divided by a circle contact line (see Fig.1). The charge distribution in the liquid phase (g_B) as well as on the surface (g_S) is assumed within the framework of the Gouy-Chapman theory. The gas phase is supposed electro neutral. This system defines a non-trivial 3D-2D-1D boundary value problem, formulated and solved for a straight line (1D) phase elsewhere [1,2]. The novel element here is that the line phase is a charged circle (rim). The rim curvature effect includes the appearance of additional potential difference inside/outside the circle. Basic analytical relations are obtained and evaluated for the surface potential. The role of the potential is discussed with respect to the bio- membrane pore permeability. Another effect, the so-called Maxwell stress is analyzed. Special attention is paid on its radial component at the rim. Aside of the mentioned above effects, some electrical parameters, specific for 2D, 1D phases, are discussed. Such parameters are the respective surface dielectric constants, ϵ_S (2D) and ϵ_L (1D). Formally defined within the generalized Maxwell equations, they are evaluated and shortly discussed as excess quantities (within the framework of *Gibbs'* theory).

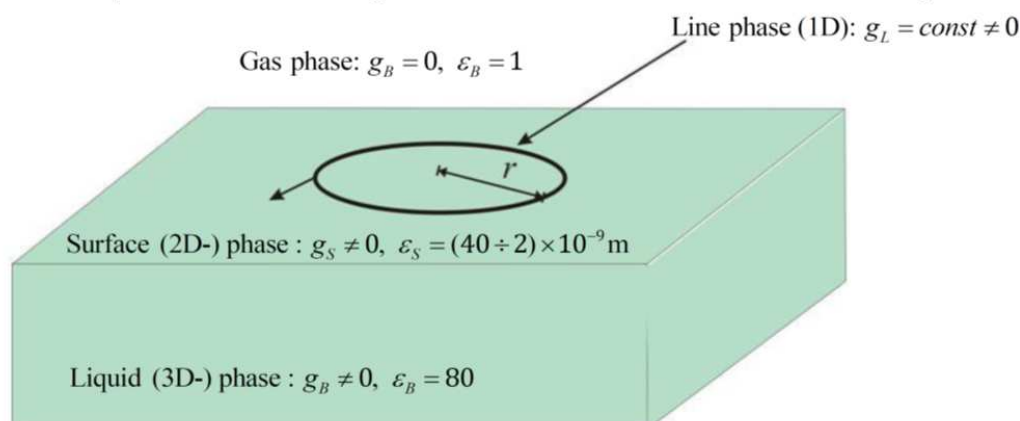


Figure 1. A sketch of the studied system, with all substantial physical parameters.

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Surface properties of partially perfluorinated alcohol with F-DPPC at the air-water interface

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A fluorocarbon chain is lower cohesiveness and higher rigidity than hydrocarbon chains. In addition, a fluorocarbon has hydrophobicity and lipophobicity simultaneously. These properties are useful for applications in various fields such as biomedical and industry fields [1]. We had already investigated the binary monolayer properties of the fluorinated compounds and DPPC system [2]. Herein, in this study, the binary monolayer properties of the fluorinated compounds and 1-palmitoyl-2-[16-fluoropalmitoyl]-phosphatidylcholine (F-DPPC) were investigated to understand the interaction and an aspect of biomembrane interaction on their interfacial behaviour.

Partially fluorinated alcohol of (perfluorohexyl)nonanol (F6H9OH), was synthesized [2]. 1-palmitoyl-2-[16-fluoropalmitoyl]-phosphatidylcholine (F-DPPC) was obtained from Avanti Polar Lipids (Alabaster, AL). The surface pressure (π -molecular area (A) and surface potential (ΔV) – A isotherms were measured for two-component monolayers made of and partially fluorinated alcohol of (perfluorohexyl) nonanol (F6H9OH) on the substrate solution of 0.15 M NaCl at 298.2 K. The Wilhelmy method and the ionizing electrode method were used. Brewster angle microscopy (BAM), fluorescence microscopy (FM) were also employed.

We have investigated that the binary Langmuir monolayers of F-DPPC and F6H9OH behaviour. The data for the binary system were analysed using an additivity rule. The excess Gibbs free energy of mixing for the present system were calculated from the π -A isotherms. Two-dimensional phase diagrams were constructed on the basis of the disordered/ordered phase transition pressure and the monolayer collapse pressure versus the molar fraction of F6H9OH. The transition pressures and which allows description of the collapse pressure of a monolayer made of two miscible components, was used to establish the miscibility within the monolayer. An interaction parameter and an interaction energy were calculated. These analyses suggested that the binary F-DPPC/F6H9OH monolayers were miscible with each other. The phase diagrams of the two systems were classified into the positive azeotropic type. Furthermore, morphological observations with Brewster angle microscopy (BAM) and fluorescence microscopy (FM) were carried out to support the binary miscibility. These results suggest that F6H9OH fluidizes F-DPPC monolayers.

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Synthesis and characterization of solution processable semi-alicyclic homo- and co-polyimide membranes and their gas separation properties

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Aromatic polyimides are promising membrane materials for gas separation because of their outstanding gas separation properties, thermal stability and mechanical properties. Despite their excellent membrane properties, most existing polyimides containing aromatic backbone are generally insoluble in common organic casting solvents, leading to restricted membrane modification such as asymmetric membrane and thin-film composite to give high gas permeation flux. The solubility of aromatic polyimides can be improved by incorporating alicyclic structure into the aromatic polyimide backbone and by impeding the formation of intermolecular charge-transfer complex between nitrogen and carbonyl group. Among various alicyclic dianhydride, 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DOCDA) was selected because it is a cheap chemical and can be easily synthesized by Ene Synthesis. In this study, we synthesized the soluble polyimides that prepared by a one-step thermal imidization process in the presence of DOCDA and various aromatic diamines. Also, we synthesized DOCDA-based copolyimides by adding various dianhydrides and diamines with different chemical structure to improve the gas permeation properties. Thin dense membranes were prepared by solution casting method to investigate their gas separation properties. All synthesized polyimides were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The thermal properties of the polyimide membranes were observed with differential scanning calorimeter (DSC) and thermogravimetric analyser (TGA). The gas permeabilities and ideal selectivities for H₂, CO₂, N₂, and CH₄ of the prepared polyimides were tested using a time-lag based gas permeation apparatus. The gas permeation properties of the polyimide membranes were measured for six representative gases (H₂, CO₂, O₂, CO, N₂, and CH₄). The gas permeabilities and selectivities of polyimide membranes were significantly influenced by the chemical structure of the diamines, which could be explained reasonably by the kinetic diameter of gases, the fractional free volumes and d-spacing values of the polyimides. DOCDA-based polyimides also showed very high selectivities for H₂/CH₄ and CO₂/CH₄ and slightly low permeabilities for H₂ and CO₂, which performances were comparable to the commercial polyimide materials, P84[®] and Matrimid[®] used in gas separation field.

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The role of magnesium ions in the creation of nanocomposite materials based on polytetrafluoroethylene modified by natural silicates

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Nanocomposite materials based on polytetrafluoroethylene are used for the manufacture of sealing parts in the friction units of various machines. The main influence on the properties of the polymer matrix is exerted at the interface between the polymer base and nanomodifier particles, which are often represented by natural silicates. The modifier undergoes mechanical activation before addition. As a result, different ions are released into the medium, including magnesium ions, which are capable of electrostatic and donor-acceptor interaction with other components of the medium. This may be one of the main reasons for the marked improvement in the properties of composite materials.

The surface properties of the nanomodifier were studied using the example of bentonite. The method of adsorption from aqueous solutions of methylene blue was used to study the properties of the initial bentonite (**B**), the bentonite activated by grinding (**B_{act}**) or by the action of hydrochloric acid (**B_{acid}**). The methylene blue adsorption isotherms on all samples (fig. 1) correspond to the Langmuir adsorption equation. The specific surface area of bentonite decreases approximately three times for mechanically activated bentonite and almost twice for acid activated. It was found that the fraction of the fine suspension in the aqueous extracts becomes smaller by the acid-activation and even smaller by the mechanically activation of bentonite. In the latter case, a significant fraction of the fine fraction remains on the walls of the mill. The loss of fine suspension during acid activation is explained by its washing out during the sample preparation.

The adsorption constant for the activated bentonite samples almost doubles for acid-activated bentonite and for mechanically activated bentonite. Analysis of aqueous extracts from the samples showed that the number of mobile magnesium ions increased substantially after activation by both methods (fig.2). They can form a strong the donor-acceptor bond with extensive conjugated system of electrons of the methylene blue, as well as the ions of aluminum released during activation.

Thus, the activation of bentonite used as a modifier of polytetrafluoroethylen can lead to an increase in the interaction of the polymer with the nanoparticles of additive due to the donor-acceptor interaction of fluorine atoms having unshared electron pairs with the magnesium ions on the surface of the silicate particles. Even for chloroform, the share of donor-acceptor interaction in the energy of adsorption on magnesium oxide is as high as 46.7% [1]. Apparently, the same nature of interaction underlies the regulation of decomposition of polytetrafluoroethylene waste in the presence of oxides and hydroxides of alkaline earth metals [2]. A refinement of the above assumption can be obtained only after studying the adsorption on bentonite samples of fluorine-containing hydrocarbons from their solutions in an indifferent organic solvent.

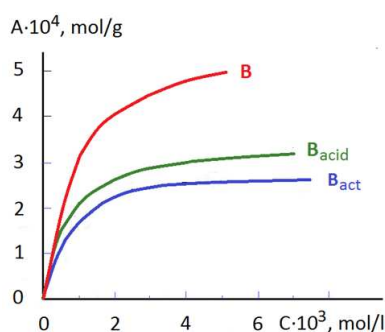


Figure 1. Isotherms for the adsorption of methylene blue on bentonite initial (**B**) and activated mechanically (**B_{act}**) or by the action of acid (**B_{acid}**)

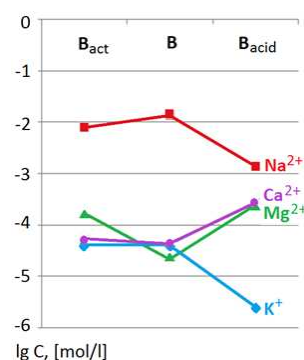


Figure 2. The contents of exchangeable cations in aqueous extracts from bentonite samples: **B**, activated (**B_{act}**) and (**B_{acid}**). Solid:liquid = 1:10.

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Sorption interaction of a non-autonomous quasi-liquid film of ice with acetic and chloro-acetic acids

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Ice is an important component of the natural environment. In natural conditions, its presence is due to negative temperatures existing in the moisture-containing systems. Ice is present as inclusions in permafrost rocks or an independent component in glacial systems. Soluble indicator chemicals move to the surface from different depths in permafrost due to migration through unfrozen water films. Taking into account the composition of permafrost, it is possible to distinguish water films that exist due to the adsorption properties of mineral and organic rock components and the so-called quasi-liquid films on the surface of ice inclusions. If a noticeable degree of salinity is, unfrozen films can include a layer of a bulk aqueous solution substances.

Until quite recently, the quasi-liquid film of ice was envisaged to be a unique phase state of water, which could only exist in the presence of a volume ice phase, therefore it was called non-autonomous. To estimate its influence on migration processes, it was necessary to study the physico-chemical properties of the film. By sorption from solutions in hydrophobic solvents, it was established that organic substances (methanol, ethanol, carboxylic acids with the low molecular weight) having a high partition coefficient between water and the phase of the organic solvent pass into the quasi-liquid film from the solution [1].

The presence of a transition layer was also established at the ice-water interface when studying sorption molybdate anions from an aqueous solution [2]. They are indicators of the behavior of a quasi-liquid ice film under changing conditions. The addition of a magnesium salt facilitated the sorption of molybdate anions [3, 4], while the addition of ethanol lowered it [4]. In the latter case, the authors hypothesized the influence of the hydrophobic part of the alcohol molecule on the "strengthening" of the water structure in the film, as well as the adsorption of polar molecules of ethanol on the surface of ice particles. The latter was confirmed by the aggregation of ice particles in aqueous solution if ethanol was added. The assumption of such behavior in a system of organic matter with polar molecules required experimental verification.

Acetic and chloroacetic acids were selected for sorption experiments. Three sections are evident on the isotherms of sorption of these acids (fig. 1). The first, similar to experiments with solutions in hydrophobic solvents, should be associated with the transition of acid molecules from the aqueous solution into a quasi-liquid film of ice. The subsequent increase in sorption may be due to the thickening of the transition film due to the additional melting of the layers of the solid phase of ice adjacent to the quasi-liquid film. If the acid concentration increases further, the acid molecules are adsorbed on the surface of the ice particles. The difference in adsorption isotherms for two acids can be due to their different relation both to the components of the solution and to the quasi-liquid film itself.

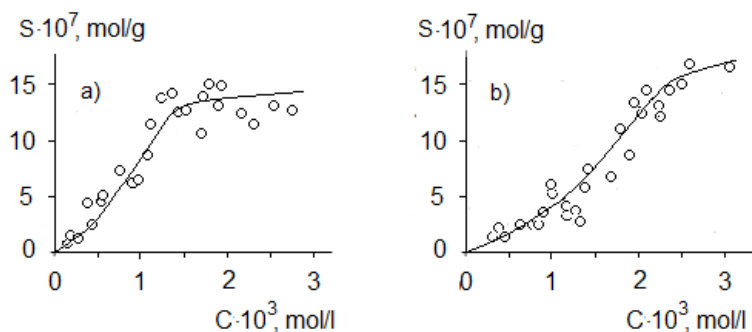


Figure 1. Sorption (S) of acetic (a) and chloroacetic (b) acids on the surface of dispersed ice from aqueous solutions with KCl at -4 (a) and -4.2 °C (b).

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The potential of improving oral health with liposomes and polymer-coated liposomes

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Dry mouth is a common but often overlooked condition. Dry mouth is due to systemic and chronic diseases such as Sjögren's syndrome and radiation towards the head and the neck region. Last but not least, dry mouth is a common side-effect of many different medications [1]. Taking into account the increasing amount of elderly in the population, problems related to dry mouth is likely to explode in the future. Dry mouth is not a dangerous disease in itself, but can lead to both painful and more serious diseases such as wounds, fungal infections, dental caries and erosion of the teeth. People diagnosed with dry mouth are likely to have problems with eating and swallowing. In addition dry mouth gives a considerably reduced quality of life.

One of the most important aspects of having good oral health is saliva. Saliva is composed of 99% water and 1% of inorganic and organic constituents. In saliva, micelle-like globules of proteins can be found, with a size of 50 nm – 1 µm. These micelles form the acquired enamel pellicle at the teeth and are also lubricating the oral cavity. Liposomes are spherical entities in the same size area as the micelles of saliva. Liposomes could have a potential as a salivary substitute, acting by a biomimetic approach. In order to increase the bioadhesive properties of the liposomes, the liposomes can be coated with a biopolymer.

In this study liposomes (from Egg PC or Soy PC combined with Egg PG or DOTAP) were prepared by the thin film method and extruded 200 nm. The hydration medium used was 5 mM phosphate buffer pH 6.8. The liposomes were coated with 0.1 wt % alginate, low methoxylated pectin or chitosan. The size and the charge of the prepared formulations were characterized according to size, polydispersity index (PDI) and charge.

The formulations were investigated with respect to the interaction with artificial saliva and the adhesive properties towards hydroxyapatite (a model substance of the teeth) and towards mucous producing cells. In addition the lubricating properties and the toxicity towards buccal cells (TR146 cells) and mucous producing cells (HT29-MTX) were studied. Finally, the water adsorption/desorption properties by the use of dynamic vapour sorption measurements (DVS measurements) were investigated.

The study showed that stable polymer coated liposomes could be prepared [2]. This was verified by an increase in size and a shift in the zeta potential. The coating process seemed to be driven by electrostatic deposition. Some of the formulations showed strong interaction with artificial saliva and also adhesion to both hydroxyapatite and the mucous producing cells [3]. These interactions were mainly dependant of the charge of the formulation itself. The formulations with positive charge interacted strongest. However, also the formulations with a negative charge interacted to some degree. Interestingly, some of the formulations had lubricating properties (preliminary data). Almost all the investigated formulations tended to be non-toxic towards the two types of cells investigated. The water adsorption/desorption properties of the formulations revealed results of great interest. The polymer coated liposomes turned out to adsorb more water than both the uncoated liposomes and the biopolymers dissolved in phosphate buffer [4].

This study has shown that liposomes and polymer coated liposomes may have great potential in improving oral health, and in special, improving the oral condition of dry mouth patients.

Acknowledgements: The author would like to thank The Research Council of Norway Grant 231324/F20 for financial support.

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Mesoporous silica nanoparticles for smart drug depot nanocarriers

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Nanomedicine has become one of the most exciting challenges of the present century with peculiar attention to innovative nanocarriers for the drug delivery of specific biomacromolecules, such as anticancer proteins, antibacteria peptides and peculiar polysaccharides used to address specific molecular recognition. However proteins and peptides need a stealth carrier to improve their self-life in biological fluids. Due to their good biocompatibility and possibility of functionalisation, ordered mesoporous silica nanoparticles (MSN) are receiving great attention as drug depot carriers. Here an overview of recent results related to preparation, drug loading and stability of functionalised MSN in the presence of physiological fluids will be presented [1-8]. It will be shown that electrostatic interactions, ionic strength and specific ions effects at the functionalised MSN charged surfaces address the stability of the system and the cell internalization. Results related to the use of the biopolymers hyaluronic acid and chitosan as stimuli-responsive agents, and the proteins lysozyme and bovine serum albumin as an antibacteria model protein and an important component of serum, respectively, will be discussed. Besides the usual characterizations through SAXS, DLS and Zeta potential, TEM image techniques, based on different strategies to prepare the samples, were used to give evidence of the protein location inside or at the surface of the MSN, whereas fluorescence confocal microscopy and TEM allowed to investigate the biocompatibility and the role of the biopolymers on the internalization into different kinds of cells (see Fig. 1).

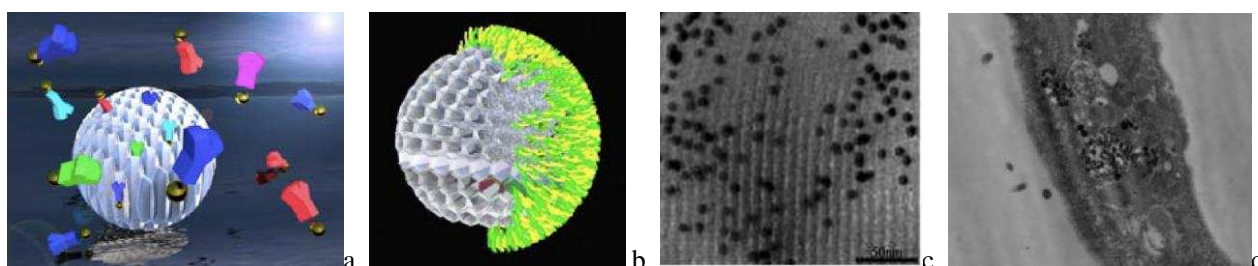


Figure 1. (a)-(b) Loading and functionalization of MSN; (c) TEM image of proteins in the MSN pores; (d) Internalization of functionalised MSN.

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DNA/RNA oligonucleotides detection using upconverting nanoparticles

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The advances in PCR sequencing techniques have facilitated the discovery of noncoding nucleic acids, such as microRNAs (miRNAs), that are being used as biomarkers for cancer or viral infections facilitating their early diagnostics [1,2]. However, proper diagnosis of disease requires the analysis of multiple sequences (multiplexing) by qRT-PCR. This type of sequencing is valid only in wealthy regions since these techniques require specific labs, trained personnel, and expensive reagents. In this work, we report the application of upconverting nanoparticles (UCNP), made of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$, for the development of a novel oligonucleotides detection technique that could overcome some of the aforementioned drawbacks. We have developed two different methods able to detect picomolar concentrations of specific oligonucleotides.

The first method is based on a homogenous assay that uses fluorescence resonance energy transfer (FRET) between the UCNP and graphene oxide (GO). In this case, monodisperse UCNPs were functionalized with single strand DNA (ssDNA) that allows the interaction between the nucleobases of the DNA and the GO inducing luminescence quenching due to the FRET between the donor UCNP and acceptor GO. The presence of the complementary DNA provokes the hybridization and the formation of double strand DNA that does not interact with the GO surface reducing the luminescence quenching.

The second method is based on a heterogeneous assay with high specificity for the detection of miRNA that is expressed during the infection of dengue fever. On this occasion, the UCNP is functionalized with a ssDNA that contains an azide group. In the presence of a specific target sequence, inter-strand ligation is possible via a click-reaction between the azide of the UCNP probe and dibenzo-cyclooctyne (DBCO)-ssDNA- biotin probe present in the solution. As a result of this specific and selective process, biotin is covalently attached to the surface of the UCNP. The biotin presence allows the selective capture on a streptavidin-coated support, giving a luminescent signal proportional to the amount of complementary miRNA present in the sample. The limit of detection (LOD) of this technique allows its direct comparison with a PCR technique with a LOD of 10^{-17} moles [3].

Acknowledgements: We acknowledge the Spanish MINECO MAT2014-55065R and MAT2017-83111R for the support, Comunidad de Madrid B2017/BMD-3867, and Santander-UCM PR26/16-12B-3.

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How polymers affect protein adsorption

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Nanoparticles and liposomes are used as versatile drug nanocarriers. Upon injection into the bloodstream a protein layer will immediately coat the nanocarrier surface forming the so-called protein corona. This alteration of the nanocarrier surface chemistry can induce changes of the drug carrier properties and interfere with the carrier's targeting mechanism. In order to prevent this non-specific protein adsorption, drug nanocarriers are often coated with protein repelling polymers. By far the most widely used protein repelling polymer is poly(ethylene glycol) (PEG), but new and more biodegradable non-fouling polymers have been recently proposed. It has also been shown that the adsorption of certain proteins can be beneficial and promote specific cellular uptake.

A deeper understanding of protein adsorption to surfaces modified with non-fouling polymers is therefore desirable to control the protein corona composition and possibly its orientation and determine how these polymers interact with the proteins. We use monolayers at the air/water interface as model systems for differently functionalized surfaces. We study the influence of interaction between the polymer and the proteins by means of surface sensitive vibrational sum-frequency generation (SFG) spectroscopy to probe the polymer/water and the protein/polymer interaction. Our results on PEG suggest that, for certain proteins, the PEG density not only influences the amount of adsorbed protein but also the ordering at the surface [1] while for other new non-fouling polymers the interactions seem altogether more complex [2]. These findings will help in designing new polymers for biomedical applications.

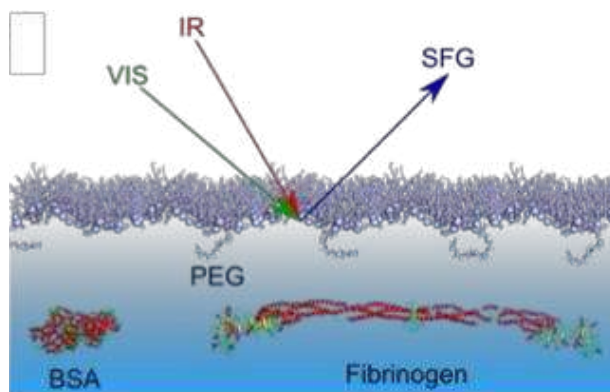


Figure 1. Interaction of Blood Proteins with non-fouling polymeric surfaces.

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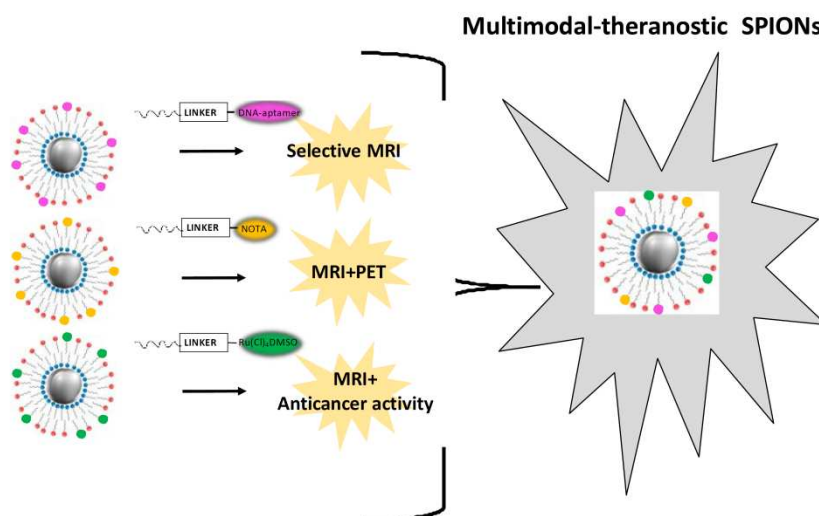
Functionalized Iron-Oxide Nanoparticles: from Design to in vivo Applications

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Theranostic multimodal nanoparticles (TNs) have been synthesized and characterized to obtain effective and selective vehicles that combine therapeutic and diagnostic capability. In particular superparamagnetic iron-oxide nanoparticles (SPIONs) have been exploited as magnetic resonance contrast agents for biomedical imaging. Besides their intrinsic physico-chemical properties, such nanoparticles (NPs) are valuable platforms able, when suitably functionalized, to deliver imaging and/or therapeutic agents in a selective way to a cellular target. Here, Fe_3O_4 NPs have been decorated with hydrophobically-modified molecules in order to address additional tasks: probes for positron emission tomography/computed tomography (PET/CT), anticancer agents. Recently, we optimized a versatile functionalization strategy based on decorating NP surface with biocompatible amphiphiles, such as lipophosphocholines, through hydrophobic interaction [1]. In principle, the method allows amphiphilic molecules with different functions to be easily lodged in the lipid layer. For the PET/CT applications, the surface of both NPs have been functionalized with suitably designed amphiphilic NOTA derivatives as chelating agents for ^{68}Ga complexation. The anticancer activity have been achieved using the amphiphilic Ru(III) complex-based molecules we have recently synthesized and proved to have high antiproliferative activity against several tumor cells through tests in vitro [2]. Aptamers, short single-stranded oligonucleotides, and peptides have been used as targeting molecules able to recognize tumor markers specifically, discriminating between health and sick cells, to overcome the severe issue of the lack of selectivity of the typical agents for cancer treatment and diagnosis. We have focused on oligonucleotide sequences bearing a hydrophobic tail in 3' or 5' position, which should be lodged in the lipid shell of NPs. An anti-VEGF DNA aptamer known to adopt a G-quadruplex structure since VEGF, being involved in the development and progression of several cancers, have been exploited both in diagnostics and as a drug target. Here we will present a comprehensive work from the design and physico-chemical characterization to the in vivo applications [3].



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Study of insecticide-loaded multilamellar liposomes diffusion through artificial skin membranes : effect of key parameters.

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Controlled drug delivery is one of the major research topics in the pharmaceutical field. Drug delivery through the skin is one of the preferred routes of administration for animal health. Depending on the drug to be delivered to the animal, either topical (minimal transversal diffusion) or systemic (transdermal diffusion) delivery pathway must be privileged. Formulation must then be adapted to each drug in order to control and select the skin penetration pathway.

Among all the possible drug delivery systems, liposomes have been highly developed because of their lipid-based composition which makes them biocompatible. The barrier nature of the skin makes it difficult for most drugs to penetrate by this route and liposomes have been shown to improve delivery through the skin [1]. However, many questions remain to be answered on the mechanism of action of these vesicular formulations [2-3] notably because the comparison between the different published studies is hardly feasible. It is indeed admitted that three parameters play a major role in liposomes diffusion through the skin: their size, their surface charge and their elasticity. In most studies, all three parameters are varied at the same time thus no conclusion on the real impact of each parameter can be drawn [4].

We propose here to analyse the influence of each individual parameter on the penetration of drug-loaded liposomes. Onion-type liposomes were chosen for drug encapsulation. Their multi-lamellar structure, succession of concentric phospholipid bilayers alternating with aqueous layers, allows the encapsulation of both hydrophilic and hydrophobic drugs, and also high storage ability [5]. Moreover, as will be shown, the key parameters can be independently controlled by vesicle composition. Dinotefuran, an insecticide of the neonicotinoid class, was chosen as the model drug. For ethical, practical and economic reasons, artificial membranes are used as a simple and reproducible alternative to animal skin. The *in vitro* penetration kinetics of onions differing in their formulations is followed using a non-invasive optical technique: confocal Raman microscopy (Figure 1). Conclusions on the importance of each parameter will be given from the comparisons of penetration depth profiles.

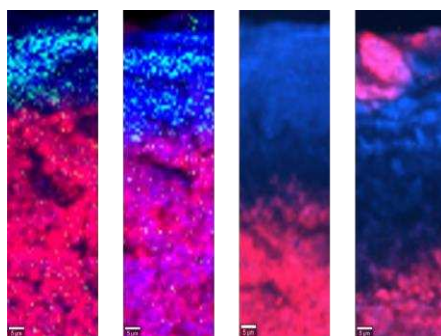


Figure 1. Imaging of onion-type liposomes (pink colour) diffusion front through artificial skin membrane by confocal Raman microscopy.

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SAXS Characterization of liposomal formulations to treat Fabry Disease

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Fabry disease is a lysosomal storage disorder, where a mutation in the α -Galactosidase A (GLA) gene causes accumulation of glycosphingolipids leading to damage of the kidneys, heart and nervous system. The disease is currently treated by intravenously injection of free GLA in the patient causing instability of GLA, high immunogenicity, low bioavailability and in the end high medicine prices. To overcome this, the first steps to develop liposomes that can encapsulate GLA and improve the performance has been begun. More work with the liposomes is necessary and currently being done to archive perfect control of the assembly process and even better performance. The liposomes can be formed of several different components that can alter the size, polydispersity and structure of the liposomes, and characterization of different formulations is therefore important in the improvement of the liposomal formulations. We have used small-angle X-ray scattering (SAXS) to get structural information of the system in presence of different liposomal components. We use a para crystalline model [1] with a finite number of layers and disorder between layers, with a set of Gaussians to describe the cross-section profile of the lipid bilayer. Scattering from GLA contributes to the total signal and is in the model added to the scattering from the bilayers, so that an estimate of the amount of GLA can be obtained. With our model, we can track GLA in the liposomes as well as changes in bilayer thickness, amount of multi-lamellar structures and bilayer ordering. With cryo-TEM, we can get an estimate of the number of bilayers which correlates well with the number obtained with SAXS and at the same time the GLA concentrations determined with SAXS fits well with the absolute GLA concentrations. Increasing distance between layers correlates well with incorporation of larger molecules and generally the model parameters fits well with those found with other techniques. Overall, the SAXS data can give us a lot of information on the structure, composition and polydispersity of the liposomes. To complement SAXS we used static and dynamic light scattering to obtain information on the size and polydispersity of the samples. This information was used for the SAXS model as well as for characterization of the homogeneity of the samples. All this information is an important step for further development of new liposomal drug formulations and will help in the design of new liposomes with desirable characteristics which in turn might help improving the treatment of Fabry Disease and other diseases where liposomal drug delivery can improve treatment.

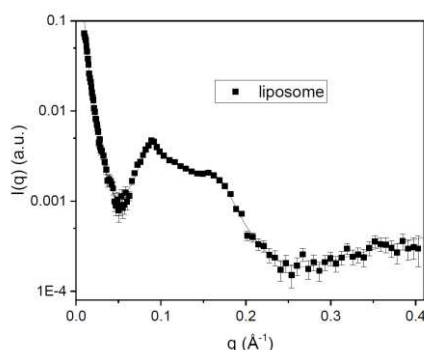


Figure 1. Small-angle X-ray scattering data of a liposomal drug formulation and a model fit

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the grant agreement No 720942.

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Unravelling interaction mechanisms between lipoproteins and nanocarriers: the biomolecule corona

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In the field of nanomedicine, colloidal nanocarriers receive increasing attention to be developed for applications in diagnostics and therapy. It is now well accepted that those developed nanocarriers systems need to be well characterized in biological media in order to assess their biological fate after administration to an organism. In this regard, the so-called ‘protein corona’ that forms when blood proteins adsorb onto nanocarriers surfaces has received much attention [1]. Interestingly, in the protein corona of many different colloidal nanocarrier systems a significant amount of apolipoproteins was found and their concentration was enriched in comparison to blood levels [2,3]. However, the reason for this enrichment has not been understood yet. Therefore, we aimed at getting further insight into the interaction mechanisms between lipoproteins, which present the natural occurring form of apolipoproteins, and model nanoparticles.

In this study, we analysed the formation of a corona after incubation of polystyrene nanoparticles with different types of lipoproteins (high density lipoproteins – HDL, low density lipoproteins – LDL and very low density lipoproteins – VLDL) as well as the complex blood plasma mixture [4]. For detailed characterization, isothermal titration calorimetry (ITC), liquid chromatography-mass spectrometry (LC-MS), cholesterol and protein assays and transmission electron microscopy (TEM) were applied. It was found that indeed complete lipoproteins interacted with the nanoparticle surface and this interaction was not purely driven by the adsorption of apolipoproteins. From ITC and TEM it was concluded that lipoproteins disintegrated upon surface contact and the lipoprotein molecules (such as lipids, cholesterol, triglycerides etc.) formed a layer around the nanoparticles until saturation was reached. This was supported by the fact that significant amounts of cholesterol and cholesterol esters were found in the corona, even in concentrated plasma where additionally a high amount of proteins was present.

In conclusion, we can support the idea of a ‘biomolecule corona’ formation – a term that recently came up in literature – rather than a pure ‘protein corona’. Regarding the design of such nanocarriers surfaces this implies that many more factors need to be taken into account to achieve a controlled behaviour in a biological environment.

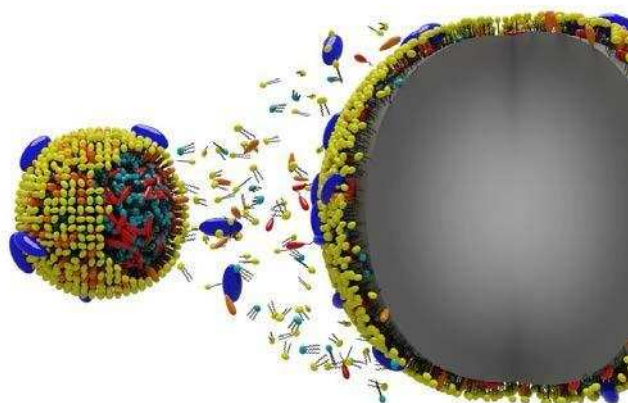


Figure 1. Schematic illustration of lipoprotein-nanoparticle interaction: Lipoproteins disintegrate and lipids cover the nanoparticle surface.

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Membrane interactions of nanoclay particles as carriers of antimicrobial peptides

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Membrane interactions are critical for the successful use of inorganic nanoparticles as antimicrobial agents and as carriers of, or co-actives with, antimicrobial peptides (AMPs). In order to contribute to an increased understanding of these, we investigated the effects of particle size and charge on nanoclay interactions with both bacteria-mimicking, mammalian-mimicking lipid membranes as well as Gram-negative and Gram-positive bacteria.

The first project focused on cationic charged layered double hydroxide nanoparticles (LDH) and the effect of particles size (42-208 nm) [1]. It was found that with decreasing particle size increased binding to bacteria-mimicking membranes, extractions of anionic lipids and resulting membrane destabilization was seen. This also translated into size-dependent synergetic effects with the antimicrobial peptide LL-37. Due to possible strong interactions with anionic lipopolysaccharide and peptidoglycan layers, direct membrane disruption of both Gram-negative and Gram-positive bacteria is suppressed. However, LDH nanoparticles cause size-dependent charge reversal and resulting flocculation of both liposomes and bacteria, which may provide a mechanism for bacterial confinement or clearance.

A follow up study on nanoclays was conducted focusing on the membrane interactions of anionic charged laponite nanoparticle in the absence and presence of LL-37. Because of the net negative charge of laponite nanoparticles, LL-37 loading capacity increases with increasing charge contrast. Peptide binding to laponite nanoparticles was demonstrated to occur primarily at the outer surface of the nanoparticles in a largely helical conformation, causing charge reversal, effects again increasing with pH.

Bare as well as peptide-loaded laponite nanoparticles caused bacteria flocculation of *E. coli*, originating from the interaction of laponite with bacterial lipopolysaccharide (LPS), present in the outer *E. coli* membrane. This effect seems to be limited to Gram-negative bacteria as laponite did not cause flocculation of *Bacillus subtilis* (*B. subtilis*), nor did it bind to lipoteichoic acid in such bacterial membranes.

As such, the present investigation reports on several novel phenomena by demonstrating that size of the nanoparticle, in this case of LDH nanoparticles, affects membrane interactions and that nanoparticle charge does not invariably control membrane destabilization and bacteria flocculation, by identifying the ability of anionic laponite nanoparticles to effectively flocculate Gram-negative bacteria through LPS binding, the latter offering a promising approach for confinement of infection and inflammation caused by such pathogens.

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Study of membrane phase transition in bacterial vesicles

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In the last few years, it has been discovered that the majority of eukaryotic and prokaryotic cells release small lipid vesicles. These vesicles, generally called micro-vesicles or exosomes, are becoming the object of a great scientific interest, because of their role as carrier of information about progenitor cells, through their cargo of proteins and nucleic acids and the biochemical composition of their membrane [1]. Here we present a study of the temperature-induced phase transitions in the membrane of bacterial Outer-Membrane-Vesicles (OMVs). In particular, we study the OMVs produced by *Escherichia Coli* because they are considered a model system for biological studies. Indeed, as known from the literature [2], *Escherichia Coli* membrane presents different temperature phase transitions due to structural changes in the organization of the lipid bilayer. In our study, we have studied the phase transition behaviour of the OMVs membrane by Light Scattering measurements at varying temperature [3]. OMVs were characterized by the presence of phase transitions similar to those revealed for *E. Coli* membrane but occurring at slightly different temperatures. In order to better understand the membrane behaviour at the transition temperature, SAXS measurements have been made and will be analysed in the next future.

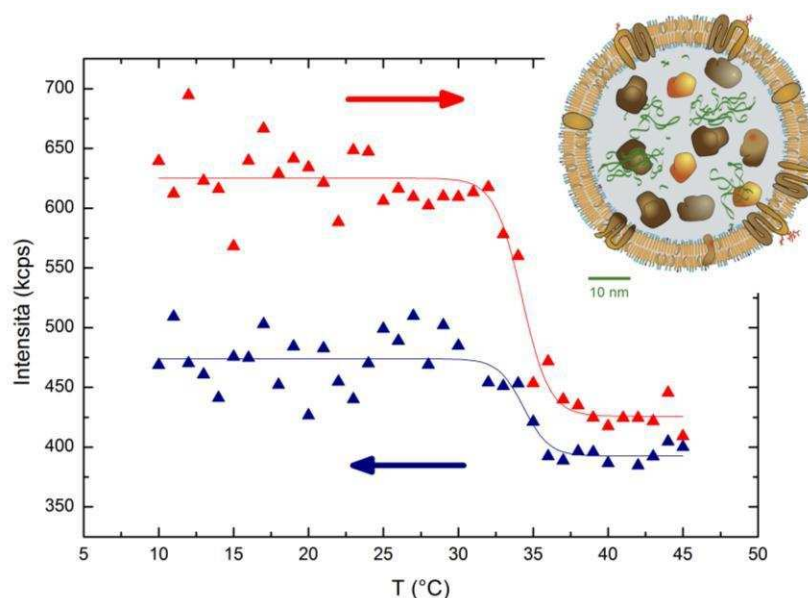


Figure 1: Light scattered intensity as function of temperature. For both increasing (red) and decreasing (blue) temperature it is clear that a membrane phase transition occurs.

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pH-responsive mesoporous silica nanoparticles dual-modified with “gatekeeper” biopolymers for drug delivery

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Advance drug delivery carriers with potential of personalized medicine include stealth and targeting components. Building up of such functionalized components is realized via specific coating. Promising design (Scheme 1) of a long-circulating, highly dispersed and pH-sensitive mesoporous silica nanoparticles (MSNs) carrier includes the surface modification with polymers: polydopamine (PDA) and polyethylene glycol (PEG) i.e. MSNs@PDA-PEG nanoparticles [1].

Small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) measurements confirmed that the MSNs of hexagonal structure with the layer of PDA and PEG of thickness ~ 20 nm can be successfully prepared. Bovine serum albumin (BSA) adsorption experiments showed that less protein was absorbed to MSNs@PDA-PEG nanoparticles after the anchoring of PEG, which supports the stealth properties of prepared carriers. Doxorubicin hydrochloride (DOX) was used as model drugs to be encapsulated into MSNs@PDA-PEG nanoparticles (DOX/MSNs@PDA-PEG nanoparticles). DOX/MSNs@PDA-PEG nanoparticles exhibits proper entrapment efficiency and drug loading up to 94.2% and 31.4%, respectively. The in vitro release profile of DOX/MSNs@PDA-PEG nanoparticles exhibited pH-responsive and gradual drug release. Cytotoxicity assay showed that DOX/MSNs@PDA-PEG nanoparticles had comparable cytotoxicity to A549 cells compared to pure DOX. The intracellular distribution of DOX/MSNs@PDA-PEG nanoparticles was displayed by using confocal laser scanning microscope. It points that PDA and PEG can play “gatekeeper” and stealth roles for MSNs as promising nanocarriers for cancer treatment.

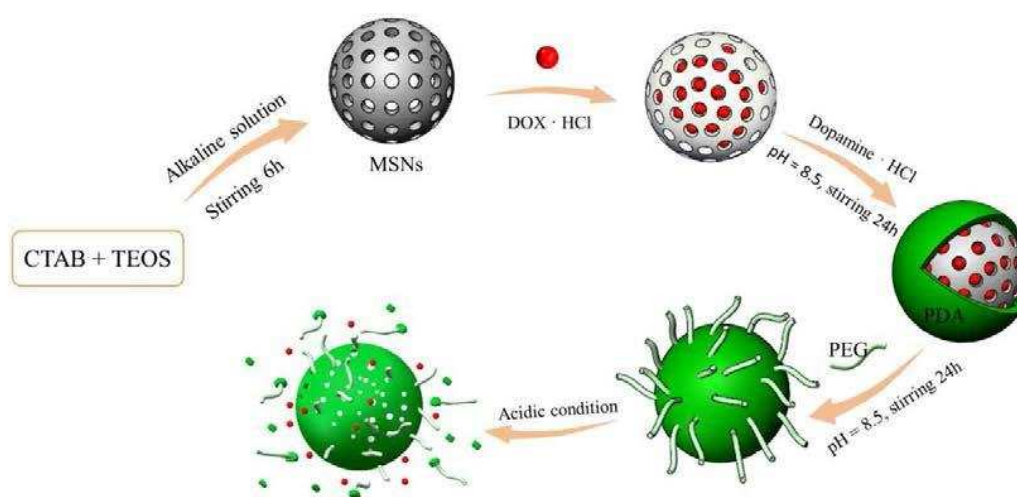


Figure 1. The preparation process of MSNs@PDA-PEG and DOX/MSNs@PDA-PEG nanoparticles.

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Nanoparticle-Cell Interactions: Surface Chemistry Effects on the Cellular Uptake of Biocompatible Block Copolymer Assemblies

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The development of nanovehicles for intracellular drug delivery is strongly bound to the understating and control of cellular uptake mechanisms. We have recently demonstrated that the cellular uptake of block copolymer nanoparticles is substantially influenced by the length (or molecular weight) of PEO stabilizing shells and by the chemical nature of the hydrophobic core. [1] We further focused on the cellular uptake of block copolymer assemblies consisting of a pH-responsive poly[2-(diisopropylamino)ethyl methacrylate] (PDPA) core stabilized by three different biocompatible hydrophilic shells: zwitterionic type poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC), highly hydrated poly(ethylene oxide) (PEO) and an also proven non-toxic and non-immunogenic poly(N-(2-hydroxypropyl)methacrylamide) (PHPMA). All particles had a spherical core-shell structure. The largest particles with the thickest hydrophilic stabilizing shell obtained from PMPC₄₀-b-PDPA₇₀ were internalized to higher level than those smaller in size and stabilized by PEO or PHPMA and produced from PEO₁₂₂-b-PDPA₄₃ or PHPMA₆₄-b-PDPA₇₂, respectively. Such a behavior was confirmed among different cell lines with assemblies being internalized to a higher degree in cancer (HeLa) as compared to healthy (Telo-RF) cells. The behavior was attributed to the preferred affinity of PMPC to cell membranes and particularly to scavenger receptors.[2] Therefore, cellular uptake of nanoparticles at the sub-100 nm size range may be governed by the chemical nature of the stabilizing layer rather than particles size and/or shell thickness.

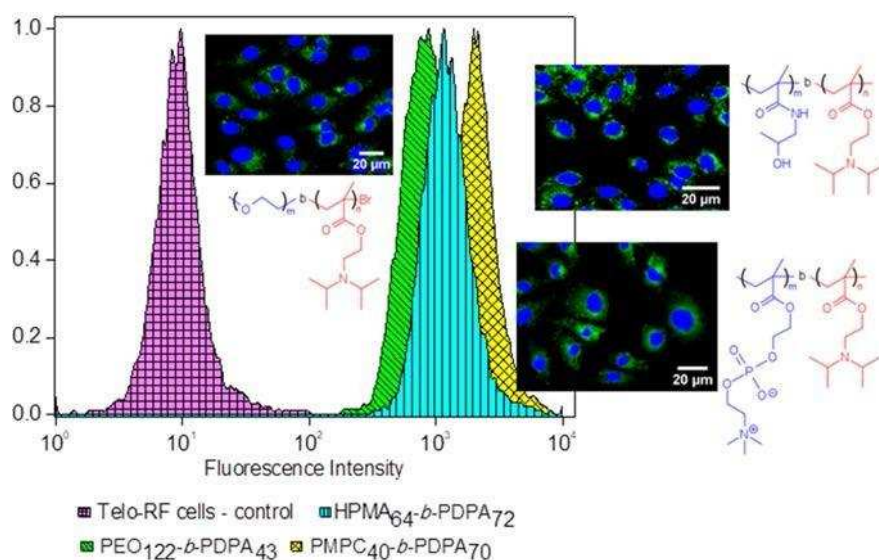


Figure 1. The flow cytometry and fluorescence microscopy data demonstrate that the PMPC₄₀-b-PDPA₇₀ nanoparticles are internalized to higher extent as compared to PEO₁₂₂-b-PDPA₄₃ or PHPMA₆₄-b-PDPA₇₂.

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Silver nanoparticle monolayers of tunable structure, stability and charge

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The preparation of silver nanoparticle layers characterized by controlled coverage, structure, stability and surface charge is in the centre of scientists dealing with nanomaterials. Taking into account biological applications, one should remember that highly dense nanoparticle coatings gradually released silver nanoparticles and ions are more efficient in the prevention of the development of pathogens. It was proven that the toxicity of positively charged nanoparticles is larger than that of negatively charged particles due to attractive electrostatic interactions with phospholipid cell membranes of microorganisms. Considering the deficit of reliable experimental data the aim of this work was to develop robust methods for preparing monolayers of positively charged silver nanoparticles applying the colloidal self-assembly process.

Cysteine-functionalized silver nanoparticles of an average size of 22 ± 4 nm (DLS, TEM), applied in the studies, were synthesized in chemical reduction method using sodium borohydride and silver nitrate. The functionalization of nanoparticle surface by cysteine was confirmed by surface enhanced Raman spectroscopy (SERS) and inductively coupled plasma optical emission spectrometry (ICP-OES). The electrophoretic mobility measurements allowed to determine the isoelectric point of nanoparticles, which appeared at pH 5.1.

Deposition mechanisms of nanoparticles on bare and polyelectrolyte-modified substrates (mica, silica) was investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM) and streaming potential measurements (SP). The influence of ionic strength and pH was studied in detail. It was found that the diffusion-controlled deposition of nanoparticles on bare silica at acidic conditions allowed to obtain positively charged silver monolayers of coverage up to 34%. The negatively charged monolayers of coverage up to 30% were formed at basic conditions on poly(allylamine chloride) (PAH) or poly(diallyldimethylammonium chloride) (PDADMAC) modified surfaces. The density and structure of monolayers were tuned by changing ionic strength of silver suspensions used in deposition experiments. Additionally, the streaming potential measurements allowed to determine the acid-base characteristics and the stability of silver nanoparticle monolayers. The desorption of nanoparticles from the monolayers was noted for ionic strength above 10^{-2} M. Also the influence of pH on the desorption kinetics of nanoparticles was quantitatively evaluated. Using the random sequential adsorption model (RSA) and 3D electrokinetic model for the interpretation of experimental data, the equilibrium adsorption constant and binding energies between the nanoparticles and surfaces were calculated.

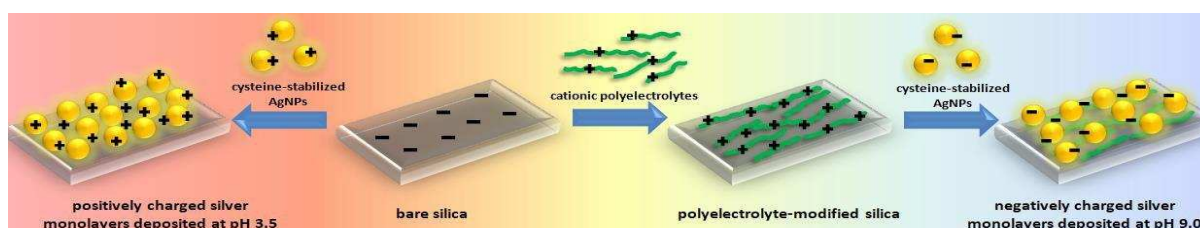


Figure 1. pH-dependent deposition mechanisms of cysteine-functionalized silver nanoparticles.

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Oximes-loaded lipid nanoparticles for brain protection and treatment of organophosphorus poisoning

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One of the most important problems for treatment of severe neurological diseases is the delivery of drugs to the central nervous system (CNS) due to inability of certain molecules to pass through the blood-brain barrier (BBB). To overcome this problem different colloid nanocarriers can be used. The encapsulation of drugs into nanocontainers improves bioavailability, reduces administered doses, insures prolonged release, and facilitates delivery to targets.

The treatment of acute organophosphorus poisoning consists of administering a combination of acetylcholinesterase (AChE) reactivator (quaternary oximes), atropine as anticholinergic drug, and an anticonvulsant to prevent irreversible brain damage [1]. However, current quaternary oximes are unable to reactivate phosphorylated AChE in the CNS because they do not cross significantly the BBB [2]. Strategies for designing nanocarriers for drug delivery to the CNS and screening for BBB permeability showed that nanoparticles based on natural and biodegradable materials are promising. Lipid nanoparticles are biocompatible and biodegradable and have very low toxicity, thereby fulfilling the requirements of preclinical safety [3].

We report the preparation of pralidoxime chloride (2-PAM)- and a new efficient hydrophobic uncharged 3- hydroxy-2-pyridine aldoxime-loaded solid lipid nanoparticles. These encapsulated oximes are suitable for intravenous (*iv*) administration, and *in vivo* efficient therapy of rats poisoned by paraoxon. To realize the potential of combination therapy, design of formulation delivery systems for delivery of two oximes with different physiochemical properties was investigated. Several tasks were solved: i) overcoming BBB for 2- PAM and its reactivating action of brain AChE; ii) increasing the bioavailability (solubility) of 3-hydroxy-2- pyridine aldoxime; iii) to achieve sequential release of both oxime and prolongation of the time window of oxime therapy.

In addition, new mixed cationic liposomes based on L- α -phosphatidylcholine and cationic surfactant administered via the intranasal route were found to overcome the BBB, allowing oximes to reach directly central AChEs. This last approach provides evidence that reactivation of central AChEs can be achieved by a non-invasive approach.

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Probing surfactant membrane interactions with molecular dynamics simulations

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Understanding the selective permeability of biological membranes is important when designing novel molecules for a wide variety of applications. Examples of these molecules are penetration enhancers such as sucrose monolaurate (SML), a chemical that interferes with the integrity of the stratum corneum of the skin. Experimental studies using quartz crystal microbalance suggest that adding sucrose monolaurate to a model bilayer of DOPC and DOPS will lead to spontaneous membrane disruption [1]. An understanding of the mechanism and factors underpinning the observed membrane disruption process will help us design better functioning formulations with SML for potential applications in drug delivery and consumer care. In this talk, molecular dynamics simulations of the interactions between SML and a model membrane bilayer will be presented. We used the CHARMM36 [2] family of force fields to develop the parameters for sucrose monolaurate with the initial atom typing performed using ParamChem [3,4]. Our model membrane was constructed using the portal CHARMM-GUI. Simulations were performed using Gromacs [5]. The results of our simulations indicate the SML parameters we developed adequately describe the behaviour of SML molecules in an aqueous solution. SML molecules would transiently insert into the model membrane and leaving it, which is in good agreement with experimental data [1]. We have also considered the interactions of SML micelles with the model membrane to simulate concentrations above CMC. Our simulations shed lights on how the membrane integrity can be affected by the presence of SML.

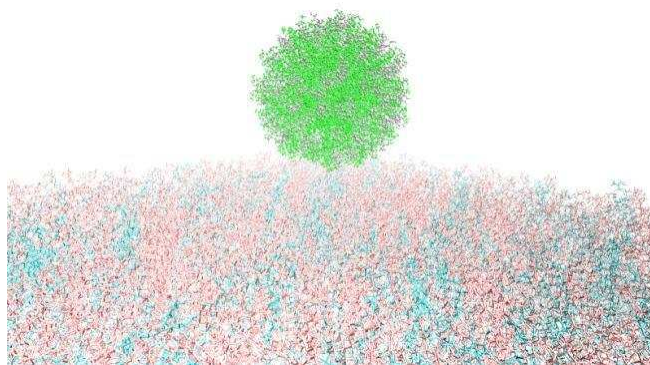


Figure 1. SML micelle interacting with model membrane.

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Sub-micrometer sized roughness suppresses bacteria adhesion

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Pathogenic bacteria cause millions of infections annually and billions of dollars are spent on decontamination of equipment and cleaning of tubes, pipes or ship hulls. Biofilm formation is battled with antibiotics, biocides or specific surface modification. However, proven toxicity and increasing resistance of bacteria raises the issue how to prevent adhesion of bacteria to surfaces [1]. Superhydrophobic surfaces have been proposed to delay biofilm formation [2]. Their efficiency was related to the reduced anchoring area caused by entrapped air. Here we challenge this assumption by testing the adhesion of *E. coli* bacteria to surfaces of different topography and wettability. Surprisingly, surface topography can outweigh wettability. An irregular three-dimensional layer of silicone nanofilaments suppresses bacterial adhesion, both, in the presence and absence of an air cushion. Our results suggest that every 3D topography will delay biofilm formation, (i) if bacteria do not fit into the pores of the coating or (ii) if bending of the bacteria is required to adhere [3]. Thus, such a 3D topography offers a hitherto underestimated possibility to design antibacterial surfaces which do not require biocides or antibiotics.

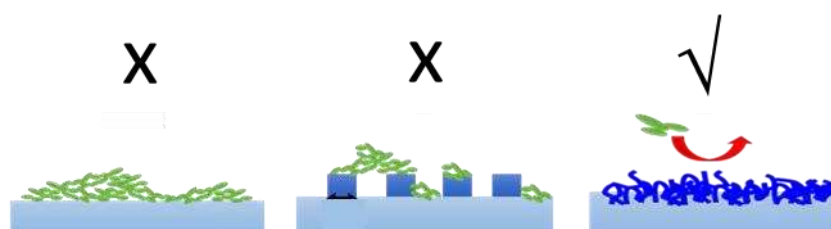


Figure 1. To design surfaces that suppress biofilm formation, we investigated surfaces of different topography and wettability. Surprisingly, surface topography can outweigh wettability. Surfaces, including superhydrophobic surfaces, suppress biofilm formation if their 3D topography and characteristic length scales require that bacteria need to bend. The presence of an air cushion is of minor importance.

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Antimicrobial peptide/glycerol monooleate self-assemblies

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Dispersions of glycerol monooleate (GMO) in water, so called cubosomes, have a self-assembled self-assembled bicontinuous cubic structure in their interior. The low-viscous cubosomes are formed by use of a suitable dispersion methods and stabilizing agents from the highly viscous bulk liquid crystalline phase. They have the capacity of carrying both hydrophilic, lipophilic as well as amphiphilic molecules. These colloids can form an ideal carrier system for molecules such as antibacterial peptides (AMPs), keeping them in a solubilized state in water and even protecting them against degradation in the biological environment [1, 2].

Here, we report the preparation and characterization of GMO-peptide self-assemblies based on the interaction of cubosomes and the amphiphilic α -helical AMP LL-37, a host defense peptide that is found in humans. Small angle X-ray scattering (SAXS), dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM) were used to characterize and visualize the colloidal structures. The impact of stabilizer and LL-37 loading on the self-assembled structure will be discussed. LL-37 was found to integrate spontaneously into the interfacial layer of the cubosomes, where it actively and critically contributes to the packing of the molecules gradually transforming the cubosomes to micelles, see Fig. 1a. [1,3] Additional antibacterial assays on a broad range of both gram negative and positive bacteria strains, together with toxicity assays bridge the colloidal structure and composition to the biological activity[3]. The nanostructural transformations in the GMO-LL-37 self-assemblies and the impact on their corresponding biological activities, may guide the further development of these nanocarriers for the targeted delivery of poorly water-soluble AMPs and may form an alternative system to conventional antibiotics.

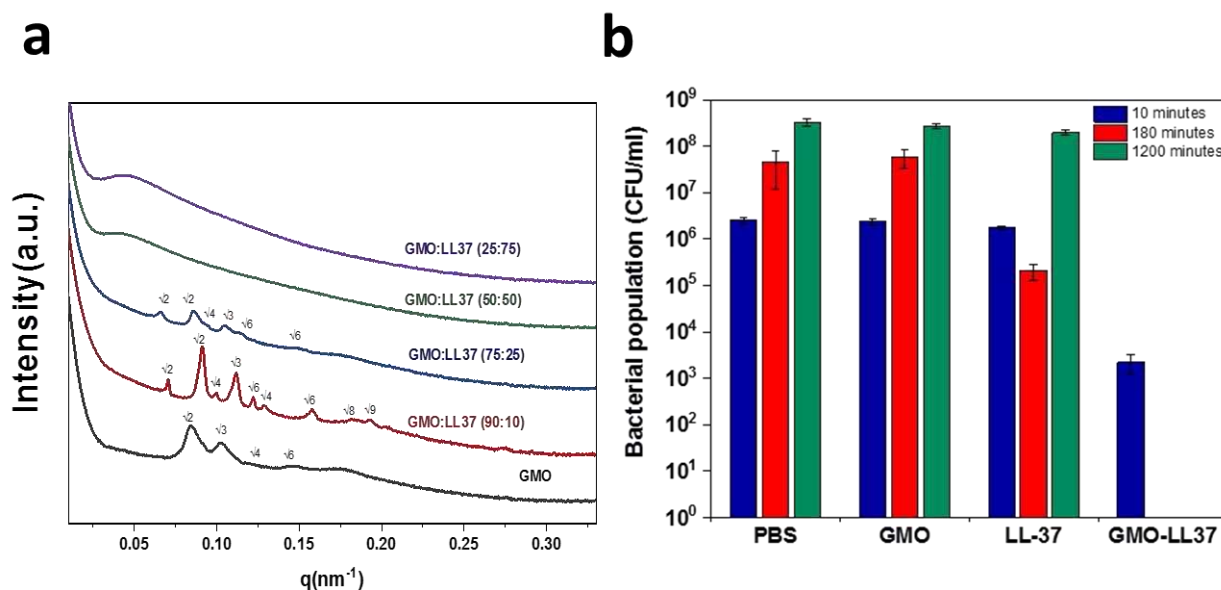


Figure 1. a) SAXS patterns of GMO-based dispersions with varying GMO: LL-37 w/w ratios at 25 °C **b)** Antibacterial performance of selected self-assemblies against *E. coli* with corresponding controls. The bacterial culture was treated with 64 μ g/mL of LL-37 in the form of a free solution (positive control) or as part of a selected self-assembled nanostructure.

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How are salivary pellicles affected by surfactants of different ionic character?

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Surfactants are often used in oral health products such as toothpastes and mouthwashes. The use these compounds has been related to exacerbation of periodontal disease, initiation and progression of gingival recession and recurrent oral ulceration [1]. However, oral care products without surfactants have been unsuccessful as these components fulfil several functions [2]. They serve as solubilizing, dispersing, emulsifying and wetting agents. Moreover, they promote foaming, which is preferred by consumers since it provides a perception of cleanliness. Thus, it is of high interest [1, 3] to identify and use surfactants with the lower adverse effects. In this context, it is of great value to understand how surfactants interact with the first interfacial layer that they encounter i.e., the salivary pellicles. Salivary pellicles are (mostly) proteinaceous nm-thick films that form on any type of surface upon exposure to saliva. The role of the pellicle is manifold. Among its functions, hydration and lubrication of the underlying tissues is often listed [4]. Along with others, we have performed previous studies on surfactant-pellicle interactions e.g., [5]. However, at present there are no systematic investigations on how these interactions are affected by properties of the surfactants, such as their ionic character, or on how they alter functions fulfilled by the pellicle like hydrating and lubricating the underlying surfaces. Here we present such a study with a focus on amphoteric and nonionic surfactants, which are seen as potential substitutes for ionic surfactants i.e., those more often used in oral health products, but are also known to specially cause adverse reactions to oral tissues [6]. We have performed ellipsometry, QCM-D and neutron reflectometry investigations in order to elucidate how amphoteric and nonionic surfactants alter structural properties e.g., thickness and hydration, of salivary pellicles. Moreover, we have also investigated how these interactions alter the lubrication properties of salivary pellicles as measured with an Atomic Force Microscope.

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A Microfluidic Approach to Model Deep Vein Thrombosis

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Deep vein thrombosis (DVT) is a dangerous and painful condition in which blood clots form in deep veins (e.g. femoral vein). If these clots become unstable and detach, they can be delivered to the lungs resulting in a life threatening complication called pulmonary embolism (PE) [1]. Mechanisms of clot development remain unclear, however researchers suspect that the specific flow patterns in veins, especially around the valve flaps play a fundamental role [2].

In order to study DVT, we fabricate valves made of polyethylene glycol diacrylate (PEGDA) in-situ in a microfluidic device achieving control over geometry and elasticity using stop flow lithography [3,4]. By tuning PEGDA and photoinitiator concentration we independently varied the elasticity of each valve's leaflet in order to obtain symmetrical or asymmetrical characteristics. To analyse the velocity profiles we exploit ghost particle velocimetry (GPV) [5,6] and we study particle accumulation, mimicking clot formation, by flowing polystyrene particles. Here we show the results we obtained. In particular, we found that particles tend to accumulate at the tip of symmetric leaflet valves whereas in an asymmetrical valve a predominant accumulation behind the more flexible valve leaflet happens. We were also able to describe, experimentally and computationally, the vorticity developing at the tip of the flexible valves that might be linked to the formation of thrombi.

Elasticity of valve and flow conditions are important factors when looking at clot formation in DVT as they will influence residence time behind the valve and thus increase likelihood of thrombus formation and this is important as a major risk factor for DVT in the elderly is a reduced elasticity of their valves.

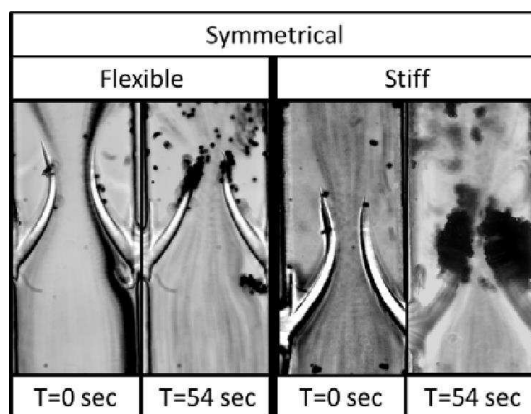


Figure 1. Visual representation of how the stiffness of the valve influences particle build up.

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Liquid crystalline phases as phantoms for validation of *in vivo* diffusion MRI methods

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Diffusion magnetic resonance imaging (MRI) can be applied for non-invasive probing of the microstructure of biological tissue. This possibility has motivated the development of several MRI protocols capable of identifying and quantifying microstructural changes in human organs, including the brain, to be used as tools for fundamental research as well as diagnostics [1]. In the development of new such MRI protocols, access to reference objects, phantoms, with well-defined microstructures is crucial for optimization and validation. In a typical desired application, it is necessary to establish that the methods developed can accurately distinguish between microstructures of different local anisotropy. More specifically, the key point is the ability to separate different structures with respect to anisotropy in the diffusion of water.

Aqueous surfactant mixtures can form liquid crystalline phases with anisotropic structures of different symmetry, e.g. lamellar and hexagonal structures, and dimension on a length-scale appropriate for MRI phantoms. In this talk, the development of useful MRI phantoms from aqueous surfactant mixtures will be discussed [2]. It appears that a good understanding of surfactant phase behaviour may indeed be useful for helping us to better understand the brain.

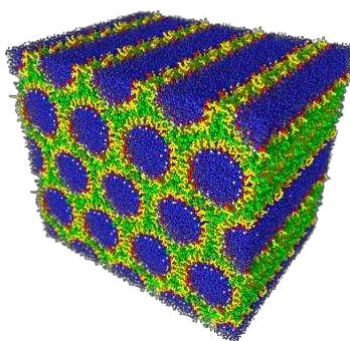


Figure 1. Illustration, rendered from molecular dynamics simulation data, of a reverse hexagonal liquid crystalline phase of sodium dioctyl sulfosuccinate AOT (white sodium ions, red hydrophilic headgroups, yellow hydrophobic tails), isooctane, and water (blue). A liquid crystalline phase of this type has been found to be successfully applicable as a MRI phantom.

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Characterization of protein aggregation in biopharmaceuticals

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In the last decades, therapeutic proteins and monoclonal antibodies (mAbs) in particular are increasingly used for treatment of various adverse conditions such as cancer, autoimmune diseases and life-threatening infections with growing success, which is projected well into the future. However, proteins are inherently labile molecules that often undergo unwanted chemical or physical degradation during manufacturing and storage. In particular, aggregation is a commonly observed degradation pathway of therapeutic protein drug products. Aggregates of all sizes were shown to increase the risk of unwanted immune response during treatment. Prevention of their formation is thus crucial in determining the formulation stability and safety [1].

Protein aggregation depends on many factors, such as temperature, pH, solution composition and container type. Many different aggregation pathways are known and described by models in literature [2]. In addition to that, every protein exhibits different aggregation properties due to its unique amino acid sequence to a point that even monoclonal antibodies of the same subclass have to be treated individually during production process development. Pharmaceutical companies therefore employ broad screenings to determine stability of each therapeutic protein molecule under different conditions.

Our work is the design of these screenings to obtain the most physio-chemical stability properties of the protein molecule from the minimum amount of sample. In addition to aggregation, other degradation pathways such as oxidation and fragmentation are also considered. Size exclusion chromatography, affinity chromatography, capillary electrophoresis, dynamic light scattering, flow image microscopy and differential scanning calorimetry are the main methods used in the screening. Different stability parameters, such as denaturation temperature and dynamic interaction parameter, are linked to degradation under various conditions [3]. Basic mass action models of aggregation are applied to get a better understanding of concentration dependence of aggregation. Because proteins are surface active molecules, the influence of interfaces on aggregation are also studied.

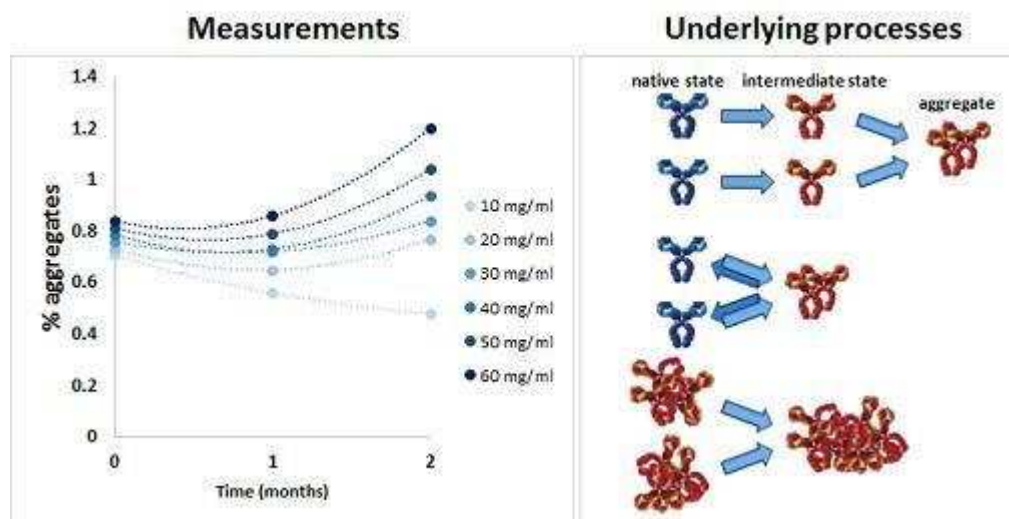


Figure 1. Effect of protein concentration on aggregation dynamics and a schematic representation of the underlying processes.

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Gone fishing: Using Atomic Force Microscopy for a height-dependent capture of bacterial fimbriae under specific and non-specific conditions

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The role of bacteria fimbriae in the formation of biofilms (e.g. at the urinary track) has been studied under different conditions. Fimbriae, which cover the entire surface of bacteria, are highly coiled peptide chains of just few nanometers in diameter that can be up to several micrometers long. They are used by bacteria to adhere to other bacteria as well as to interact with their environment [1]. In addition, they carry *adhesins* which attach them firmly to the substrate, so that the bacteria can withstand shear forces and obtain nutrients. In the specific case of *E. coli*, *type 1* fimbriae are known to attach to mannose via the so-called *catch-bonds* by means of the receptors located at their end-region, while the rest of the structure is known to be dominated by hydrophobic moieties, responsible for nonspecific interactions [2].

In this work, a novel Atomic Force Microscopy (force spectroscopy-based) methodology for capturing *E. coli* fimbriae at different bacteria-to-tip/cantilever distances will be presented [3]. The “fishing” of fimbriae was performed under varying measuring conditions (i.e. cantilever chemistry, tip geometry, contact time, environmental bulk solutions, and number of fimbriae), which influenced the success and strength of the final bond formation. Subsequently, a controlled retracting motion of the cantilever enabled the recording of physical magnitudes such as the maximum tip/fimbriae adhesion, or even to monitor the appearance of unfolding events of the coiled fimbriae chains. The inter-relation of these magnitudes provides an insight about the structure and the functional role of fimbriae.

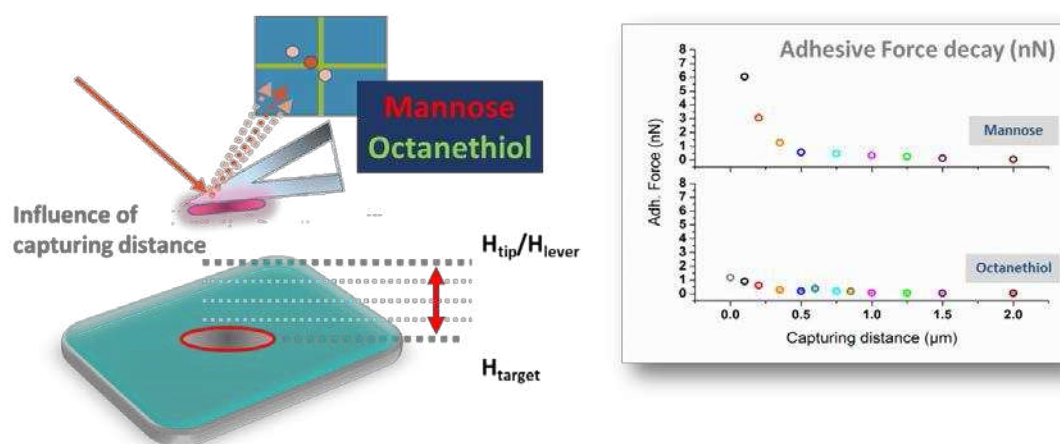


Figure 1. (Left) Sketch of the measuring setup. Dashed lines indicate the different heights at which the cantilever is located. (Right) Adhesive force values as obtained from the minimum in the retraction plot..

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A Chemical Synthesis Paradigm for *in utero* Repair of Spina Bifida

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Spina Bifida - literally meaning “*split spine*” in Latin - is the most common birth defect with 0.2 % occurrence worldwide [1]. It is due to foetus' spine failing to close during the first month of pregnancy, resulting in the exposure of nerves to the amniotic fluid, with permanent consequences affecting both cognitive and psychometric capacities [2]. To date no treatment exists and the damage to the nerves is irreversible. However, a possible solution could lie in the so-called “double hit hypothesis”, which conjectures that covering the opening in the spinal cord with a material non-permeable to then amniotic-fluid would protect the nerves and therefore prevent the induced life-long complications [3].

This project aims to design, synthesise, and characterise biocompatible hydrogels and microgels which would adhere to the spina bifida opening to form tough and highly flexible protective wound dressing that seals the nerves from the amniotic fluid. Hydrogels appear as a material of choice in tissue engineering because of their elasticity and tensile strength very close to human tissues [4,5]. Recent research in wound healing has highlighted the potential of polysaccharides as adhesive, biocompatible materials [6].

To this end, chitosan was derivatised with carbic anhydride to provide a range of functionalised polymers that could be crosslinked *via* thiol-ene photoclick chemistry. The mechanical properties of the resulting hydrogels could be varied by controlled and preliminary cell studied highlighted their potential applications in tissue engineering. Alternatively, microgels with a diameter varying between 150 and 300 nm could be successfully prepared by using water-in-oil nanoemulsions as templates, with gelation facilitated by *in situ* photo-initiated cross-linking. The microgel particles were then isolated and characterised by dynamic light scattering (DLS), Zeta potential measurements and electron microscopy. The outer shell of the microgels was successfully functionalised by click chemistry to allow further generation of complex wound healing materials.

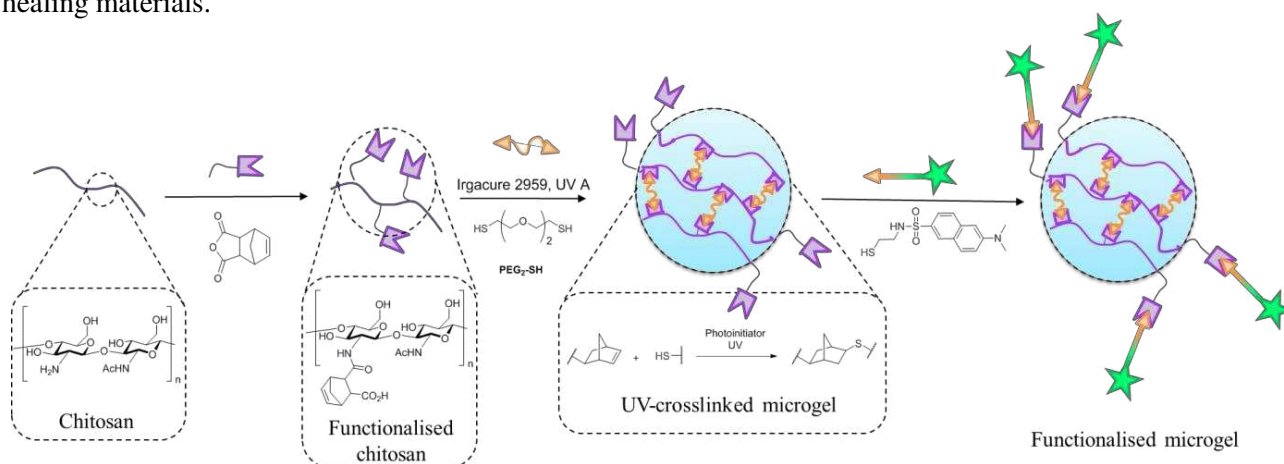


Figure 1. Synthesis of chitosan-functionalised microgels.

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Feeling young – Tactile ability and skin-tribological properties of young and elderly

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Existing methods to measure tactile spatial acuity under static touch are criticized to have low sensitivity failing to detect or underestimating sensory deficits [1]. This study reports on a new method to quantify tactile discrimination ability based on blinded active exploration of systematically varying micro-textured surfaces and a same-different paradigm. The developed method was employed to compare tactile ability of young and elderly women using active touch [2]. Wrinkle-patterned surfaces were made in-house at RISE as previously described in Skedung *et al.* [3]. Surfaces S0 (blank), S20 (~20µm), S40 (~40µm), S60 (~60µm), S80 (~80µm) were repeatedly and randomly compared against a reference (~100µm). Sixty female participants, 30 young (age 18-25) and 30 elderly (age 65-85) judged whether presented pairs of surfaces were perceived as *same* or *different*. Biomechanical properties were measured by means of a finger hydration (Corneometer CM 825), finger elasticity (Cutometer MPA580) and tactile friction (ForceBoard). The results reveal that elderly participants show significantly reduced fine texture discrimination ability. The young group successfully differentiated S20 and S40 from Ref100 with average correct responses of 97% and 87%, respectively. The drop in tactile ability was seen with S60 (55% correct responses). The drop in discrimination ability for the elderly group is observed already with S20 (63% correct responses). Both groups successfully distinguish the blank S0 and showed similar results on S80 and Ref100 (compared against itself where the correct answer is *same*). The elderly group also displays statistically lower finger friction coefficient, finger moisture and finger elasticity, suggesting a link. The tactile perception test and biomechanical properties were measured in dry state as well as 30 min after application of two humectant formulas on the index finger (containing 5% and 7% glycerol tested randomly and in blind on two different days). The ability to distinguish S20 significantly improved with both 5% and 7% of humectant, as has been observed also during static touch [4]. The increase in finger hydration and elasticity indicate that skin-tribological properties play a role in the immediate but temporary remediation of dynamic tactile discrimination. With this new method, not only the deterioration can be quantified, but its remediation by training or treatment can also easily be assessed.

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Novel aqueous formulations based on the encapsulation of ceramide-like molecules with cosmetic interest

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Ceramides consist of a sphingosine covalently bound to a fatty acid by an amide linkage. They are involved in the regulation of diverse cellular functions such as cell growth, differentiation, senescence, apoptosis and immune responses [1]. Ceramides are also structural elements of many cells and tissues.

The outermost layer of the skin, the stratum corneum, is formed by a broad range of lipids, proteins and cells called corneocytes [2]. Among the intercellular lipids, ceramides are the main one, accounting for 40-50% of total intracellular lipids [3]. Human hair also contains ceramides but in this case, in trace amounts. Ceramides are highly hydrophobic molecules which play a major role in the water-retaining property and barrier function of hair as well as skin [1, 4]. However, the ceramide layer can be partially degraded due to environmental effects such as radiation or pollution. This has stimulated the research on the development of new formulations enabling for the reparation of ceramide barrier. However, its poor solubility may be seen as an important drawback for the preparation of platforms for encapsulation and controlled release of ceramides in skin repairing application. On the other hand, the insolubility of ceramides can become an advantage to increase the deposition of ceramide onto the skin because it is expected that skin repairing formulation must allow a maximization of both the adsorption and the absorption of ceramide in the skin. In recent years, several formulations have been tested for the encapsulation of ceramide-like molecules for the fabrication of formulations with applications in the cosmetic field, e.g. vesicles, elongated micelles, or emulsions. However, the main drawback of such formulations is their low effectiveness for ceramide encapsulation (below 2 wt%). This has been recently improved using microemulsions and lamellar phases as platform for ceramide encapsulation, with the latter allowing us to enhance the encapsulation yield.

In this communication, we discuss our recent advancements on the fabrication of platforms for the encapsulation of ceramide-like molecules, focusing our interest in those cases in which a significant enhancement of the encapsulation yield is obtained. It is expected that aqueous formulations containing high amounts of encapsulated ceramide-like molecules can present important advantages on skin care cosmetics.

Acknowledgements: This work has been funded by MINECO and L'Oréal S.A.

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Preparation, Stabilization and Characterization of Microbubbles Decorated by Dendronized Iron Oxide Nanoparticles for Medical Applications

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Microbubbles (i.e. gas particles of less than ten microns in diameter dispersed in an aqueous medium) are being used as contrast agents for ultrasound imaging, targeted drug and gene delivery.[1-3] The shell of the microbubbles can be built from surfactants, lipids, polymers, nanoparticles, or from combinations of these materials.[4, 5]

We report the preparation and characterization of stable fluorocarbon-stabilized microbubbles with a shell of phospholipids that incorporates iron oxide nanoparticles grafted by dendrons fitted with pegylated chains [6]. We first present an investigation of Langmuir monolayers made from mixtures of phospholipids and dendrons (Fig 1a). The results show that the dendrons form microdomains within the mixed monolayers, as assessed by compression isotherms and atomic force microscopy after transfer on silicon wafers (Fig 1b).

Fluorocarbon gases, when introduced in microbubbles act as osmotic agents [7] and as cosurfactants to phospholipids [8, 9]. In a second part dedicated to microbubbles, we show that introducing the fluorocarbon in either the gas phase or the aqueous phase strongly impacts the size and stability characteristics of phospholipid-shelled microbubbles. We also found that small and stable microbubbles with dendronized iron oxide nanoparticles in their phospholipid shell can be obtained, as assessed by optical microscopy and an acoustical attenuation method. These new functional microbubbles can be used as contrast agents for both magnetic resonance and ultrasound imaging.

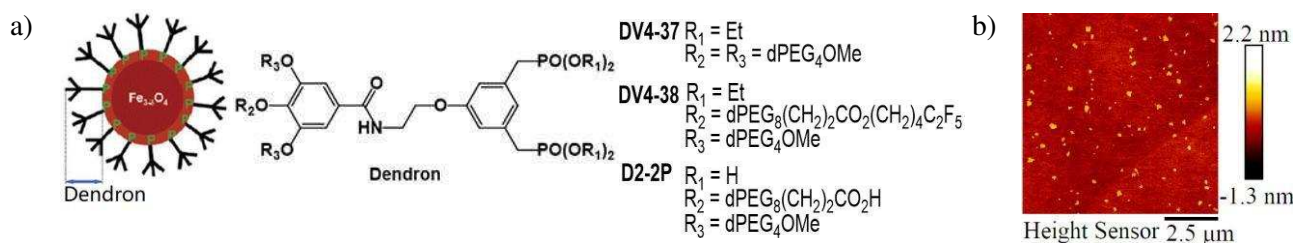


Figure 1. a) Schematic representation of a dendronized iron oxide nanoparticle and structure of dendrons; b) height AFM image of a LB film of a mixture of DMPC and dendron DV4-38 transferred on a silicon wafer at 16 mN m⁻¹.

Acknowledgements: DS thanks the NanoTransMed INTERREG V Upper Rhine project for a Ph.D fellowship.

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Formation of colloidal phase after dissolution of supersaturable dosage forms and its impact on oral absorption

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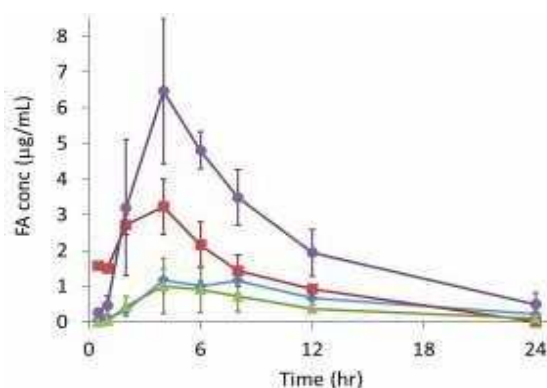
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Supersaturable dosage forms such as amorphous solid dispersions (ASD) are used for developing poorly soluble drugs for oral delivery. Supersaturated solution may cause phase separation into concentrated and diluted phases, and, the former may be stabilized as a colloidal phase due to surface stabilization by polymers in the case of ASD [1]. Impact of formation of the colloidal phase to the oral absorption has not been clarified yet. In this study, supersaturation followed by phase separation was evaluated for fenofibrate (FEN), and attempts were made to clarify relationship between phase separation behavior and oral absorption using three excipient polymers, vinylpyrrolidone-vinyl acetate copolymer (PVPVA), poly(methacrylic acid-co-methyl methacrylate) (Eudragit), and hydroxypropyl methylcellulose acetate succinate (HPMCAS).

For comprehending the supersaturation and phase separation behaviors, FEN was first dissolved in ethanol and added to 0.5 wt% polymer solution prepared by phosphate buffer. The solutions/dispersions were subjected to turbidity measurements to determine the phase separation concentration. As shown in the table, FEN dissolved molecularly in the phosphate buffer up to ca. 1 µg/mL at 25 °C, and it was rarely influenced by the presence of polymer. This concentration is approximately 10-fold of the equilibrium solubility. Above this concentration, the particle with ca. 400 nm in size was obtained for HPMCAS and Eudragit solutions, but the particle grew to the micro-scale in the phosphate buffer and PVPVA solution. ASDs were prepared using three polymers and also used as starting materials to acquire similar phase separation concentrations with those found for the artificial supersaturation system. Addition of 0.1% Tween 80 raised the phase separation concentration, where its dependency on the polymer species became evident likely due to difference in the crystallization inhibitory effect of each polymer.

ASDs were orally administered to fasted rats at a dose of 7.5 mg/kg. As FEN is metabolized almost completely in the liver during the first-pass metabolism, fenofibric acid (FA), active metabolite, was evaluated in the HPLC analysis. As shown in the figure, oral absorption was the most enhanced by Eudragit ASD, followed by PVPVA ASD. Absorption from HPMCAS was not improved relative to that from physical mixture, most likely due to limited absorption by the dissolution rate. The phase separation concentration seems to be a good predictor of order of the in vivo absorption, if it is solubility-limited. Thus, it should be important to comprehend the free solute concentration after the phase separation for predicting absorption from ASDs.



Phase separation concentrations of supersaturated FEN solutions (µg/ml)

	No polymer	PVP VA	Eudragit	HPMC-AS
25°C, 30 min	1.0	1.3	1.2	1.1
w/ Tween	17	20	25	30
37°C, 30 min	0.9	1.6	1.6	1.4
w/ Tween	32	35	50	60
ASD-25°C, 30 min	—	1.6	0.8	1.2
w/ Tween	—	11	18	22
ASD-37°C, 30 min	—	1.0	0.8	1.1
w/ Tween	—	30	35	40

Figure. (Left) Plasma FA concentration profile after oral administration of FEN formulations: Eudragit ASD (circles), PVPVA ASD (squares), HPMCAS ASD (triangles), and physical mixture with mannitol (diamonds). (Right) Phase separation concentrations of supersaturated FEN solutions.

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Casein probe–based fast plasmin determination in the picomolar range by an ultra-high frequency acoustic wave biosensor

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Detection of residual plasmin activity in milk represents a difficult challenge for the dairy industry. Conventional methods are either too expensive or incapable of providing enough data from UHT treated milk. Acoustic wave–based biosensors operated in the thickness shear mode (TSM) showed potential for the detection of proteolysis of β -casein, a milk protein, by protease plasmin. An ultra-high frequency device, the electromagnetic piezoelectric acoustic sensor (EMPAS), designed to enhance the sensitivity of TSM, was tested for detection of plasmin at low concentration. β -casein layers immobilised on the hydrophilic or hydrophobized surfaces of EMPAS quartz discs were used as substrate for the enzyme. On both surface types, the adsorbed β -casein mass and the stability of the layer was compared, with the result that hydrophobic surfaces provide superior conditions for immobilisation than the hydrophilic case. Consequent proteolysis measurements of these substrate layers were carried out in a broad plasmin concentration range (32 pM – 10 nM) in flow mode. Initial reaction rates measured at different enzyme concentrations have been used to construct a calibration curve based on an inverse Michaelis–Menten type equation. The sensitivity of the EMPAS allowed measurements of as low as 32 pM concentration of plasmin, reaching (and often exceeding) levels comparable to state of the art techniques like ELISA. The presented method however, unlike ELISA, is effective on a timescale of minute.

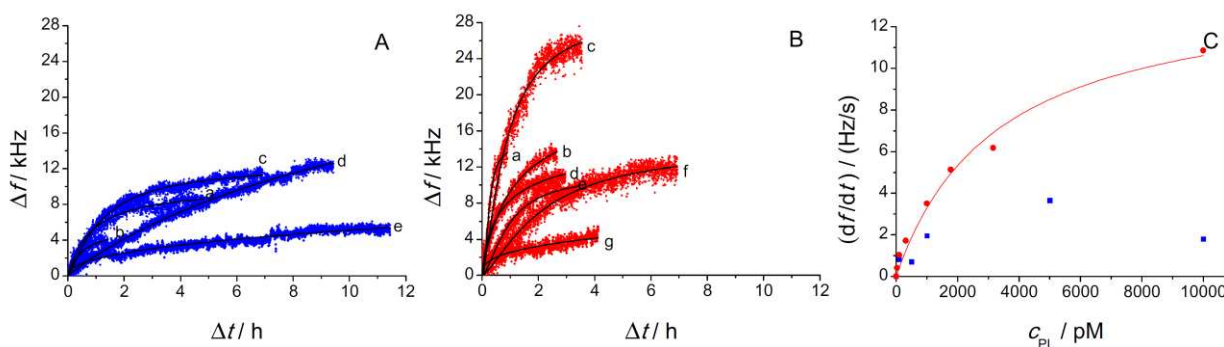


Figure 1. A and B: Time course curves of plasmin activity on β -casein at different plasmin concentrations, plotted on identical scales (measurement points and fitted Hill curves). A) hydrophilic, native quartz crystal: a) 10 nM; b) 5 nM; c) 1 nM; d) 500 pM; e) 100 pM; B) hydrophobic, silanized quartz crystal: a) 10 nM; b) 3.16 nM; c) 1.78 nM; d) 1 nM; e) 316 pM; f) 100 pM; g) 31.6 pM. C: Rates of df/dt initial frequency change determined at different c_{PL} plasmin concentrations for hydrophilic (■) and hydrophobic (●) quartz crystal surfaces, respectively.

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Novel insights into crucial properties determining the performance of polysorbate 80 as a pharmaceutical excipient

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Polyethoxylated sorbitan fatty acid esters (polysorbates) are non-ionic surfactants used for numerous applications within biochemistry, food production, cosmetics and pharmaceuticals as e.g. excipients in vaccines, emulsifiers, and for stabilization of proteins against unfolding [1-2]. Polysorbate 80 contains a hydrophilic headgroup with polyethylene oxide (PEO) oligomers (on average 20 EO units) attached to a sorbitan ring and esterified to a hydrophobic oleic acid ester chain (see insert in Figure 1). However, the synthesis of such macromolecules is not straightforward and does not provide a pure product, but rather a very diverse and heterogeneous mixture comprising of a variety of PEO isosorbide- and sorbitan-(mono- di- and tri-)-esters, PEO-esters, and free fatty acids etc. (see an example of a MALDI-TOF spectrum of polysorbate 80 in Figure 1). Different molecules present in the surfactant mixture affect properties relevant for the excipient performance in e.g. pharmaceutical formulations. The performance of this excipient is largely taken for granted despite the fact that raw material batch-to-batch variations can be large while still within specifications of the pharmacopoeias. Due to the extensive use of this surfactants in health and food science its chemical stability and aggregation behavior is extremely important to assess in order to avoid adverse biological effects.

By isolating individual component groups from the mixture, their abundance and individual physical properties have been characterised. Each group of isolated molecules, characterised with e.g., calorimetric techniques, MALDI-TOF and ¹H/¹³C-NMR, provides a piece of the puzzle to understand the behaviour of the mixture. It also provides novel insights into opportunities to improve the performance of the widely used excipient polysorbate 80.

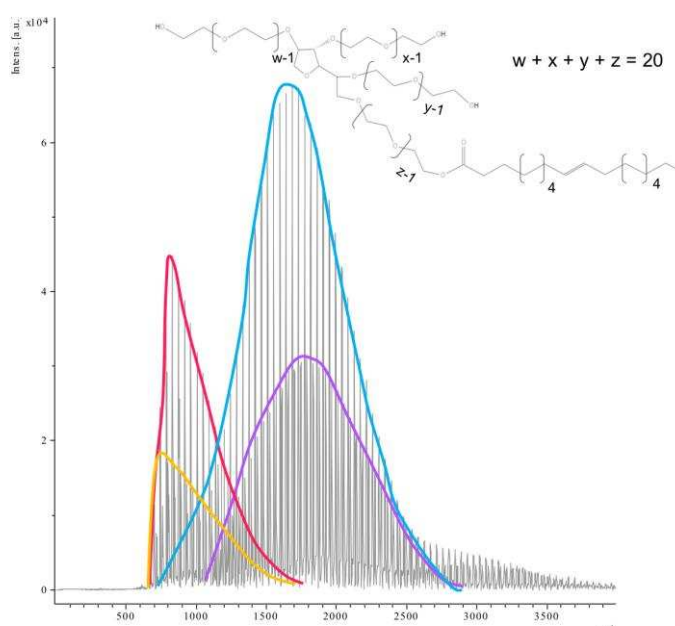


Figure 1. MALDI-TOF MS spectrum of the diverse molecular mixture of a polysorbate 80 sample. The mixture contains several subspecies (highlighted mass distributions) and the regular peak spacing corresponds to 44 Da, which equals one EO unit. Insert: Molecular structure of polysorbate 80.

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Protein loading by stimuli-sensitive tubules based on lysine surfactants

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Smart drug delivery vectors improve the efficiency of the delivery on the target cells, thereby minimizing the associated side effects in the treatment of patients. This type of vectorization can be achieved by nanostructured colloidal systems, such as micelles, liposomes, microemulsions, nanocapsules, dendrimers and polymers. When constituted by amphiphilic molecules, these vectors present considerable advantages, namely versatility in physicochemical properties and sensitivity to stimuli. Amino acid-based surfactants, in particular, are rather promising systems [1], because of their high biodegradability and reduced human cytotoxicity. In addition to forming micelles and liposomes, they can self-organize into other complex supramolecular structures, such as fibers, twisted ribbons, helical tapes and nanotubes [2,3].

In this work, we have studied a family of novel anionic double-chained lysine-based surfactants, with variable degree of chain length mismatch, comprising compounds 8Lys n and m Lys8, and 10Lys n and m Lys10, with $n, m = 12, 14$ and 16 ; and the compounds 12Lys16/16Lys12, where the numbers represent the number of C atoms in each alkyl chain. These compounds are able to form tubules with different morphologies in water, at room temperature. To obtain structural insight on these assemblies, microscopic techniques such as video- enhanced light microscopy (VELM), scanning electron microscopy (SEM), cryogenic scanning electron microscopy (cryo-SEM), cryogenic transmission electron microscopy (cryo-TEM) and atomic force microscopy (AFM) were used (figure 1). Interactions of the tubules with the protein lysozyme, under varying experimental conditions, was investigated by DSC microcalorimetry and UV/VIS spectroscopy, with the main goal of assessing the efficiency of the tubules as pH- and temperature-sensitive nanocarriers for a model biomolecule. Furthermore, a systematic study on the stability of these aggregates when in contact with different fluids was carried out (serum, artificial saliva, artificial sweat, blood). Results on the toxicity of the tubules *per se* and the tubule/lysozyme aggregates in human cells will also be presented.

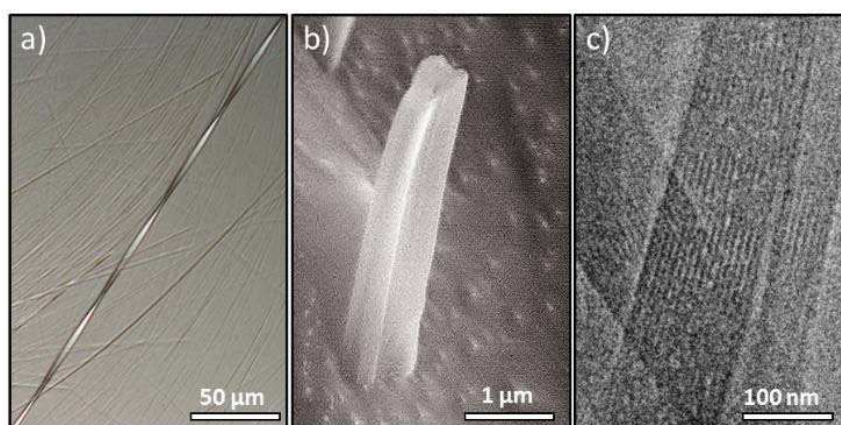


Figure 1. Tubular nanostructures of 8Lys16 in water (0.5% w/w) as observed by: a) VELM, b) cryo-SEM, c) cryo-TEM.

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Incorporation of Gadolinium based compounds into polyelectrolyte nanocarriers for theranostic application

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Nanotechnology is an interdisciplinary and multidisciplinary research field involving chemistry, physics, material science, biology, and medicine. Especially, nanotechnology is currently offering various exciting possibilities in biomedical fields and this application is referred to as ‘nanomedicine’. It is the field of research with huge expectations for the development of personalized therapies based on new nanoparticles as nanoscale materials effectively interact with biological systems. Therefore, the use of nanodiagnostics imaging and nanotherapeutics for use in targeted drug delivery may overcome many intractable health challenges.

The term “theranostic” is defined as a material that combines the modalities of therapy and diagnostic imaging. Thus, theranostics deliver therapeutic drugs and diagnostic imaging agents at the same time within one dose. Because of multifunctional properties, theranostic nanocarriers possess huge application potential in the personalized nanomedicine which is focused on developing therapies, that are tailored and optimized for the medical treatment of the individual characteristics of each patient.

The aim of our work was to develop of the method of preparation polyelectrolyte nanocarriers containing anticancer drugs (e.g. Taxol) and gadolinium based MR contrast agents. The theranostic polyelectrolyte nanocarriers were formed by sequential adsorption technique (layer by layer). The polyelectrolyte shell was formed from biocompatible polyelectrolytes poly-L-Lysine (PLL), polyglutamic acid (PGA) and Gadolinium based compounds: Gadolinium labelled-PLL or/and Gadopentetic acid. The formed nanocarriers were modified for passive targeting by pegylation. The size of formed nanocarriers was ~150 nm. The nanocapsules were tested as the MRI detectable drug delivery system. The results show the high activity of encapsulated drugs and they may be a promising platform for future personalized targeted therapies (e.g. cancer) or other biomedical applications.

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Hierarchically structured emulsions for brain tumors therapy

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Targeted drug delivery using stimuli-responsive carriers has provided a new approach for addressing the limitations of the conventional chemotherapy (high toxicity, poor tumor selectivity, multidrug resistance) but still faces many challenges. In this study, we proposed coupling a hierarchically structured double emulsion-based doxorubicin hydrochloride (DOX) delivery systems with specific pH-triggered drug release mechanism in the treatment of brain cancer (glioblastoma multiforme-GBM). The pH-triggered release- is regarded as one of the general strategies in targeting the acidic microenvironment of solid tumors.

In this study, two stable (water-in-oil-in-water) double emulsions DE-1 and DE-2 with pH stimuli-responsive biomaterial (sodium carboxymethylcellulose (Na-CMC)) in the external phase and encapsulated DOX in the internal droplets were prepared using a Couette-Taylor flow contactor [1]. For both emulsions, the DOX encapsulation efficiency over 95% was reached. The sizes of the internal drops of DE-1 and DE-2 were 5.3 and 3.7 μ m respectively. Three surfactants (Poloxamer 407, Tween80, Pluronic P-123) were located in the external phase of emulsions DE-2 to promote the formation of smaller droplets (8.9 μ m) compared to the emulsions DE-1 without Poloxamer 407 (19.8 μ m) which significantly reduces the surface tensions at the interfaces. To study the release behavior, the emulsions were diluted in phosphate buffered saline (PBS) at pH 6.3 (simulation of tumor tissue environment) and pH 7.4 (normal tissue). The volume ratios of the emulsion to PBS were 1:10, 1:100. Dilution of the emulsions did not affect their stability. For all emulsions, the release rates at pH 6.3 were higher than those at pH 7.4 (Fig. 1), demonstrating an obvious pH-responsive controlled release performance. At pH 6.3, the Na-CMC shows pH-dependent changes in the polymer network cause viscosity reduction and faster release of DOX. For DE-2 the release rate of DOX was faster than for DE-1 which is related to their different internal structure. The study confirmed that the releasing the DOX from double emulsions can be modified through the morphology/structure, composition and physicochemical parameters of emulsions. The results showed that the DOX-loaded emulsion might be classified as a potential hierarchically structured carriers for programmable pH-triggered drug delivery. These systems may also be suitable for targeting specific sites after the emulsion surface activation by deposition on the surfaces of the drops appropriate antibodies against the receptor that recognize the receptors of GBM cancer cells.

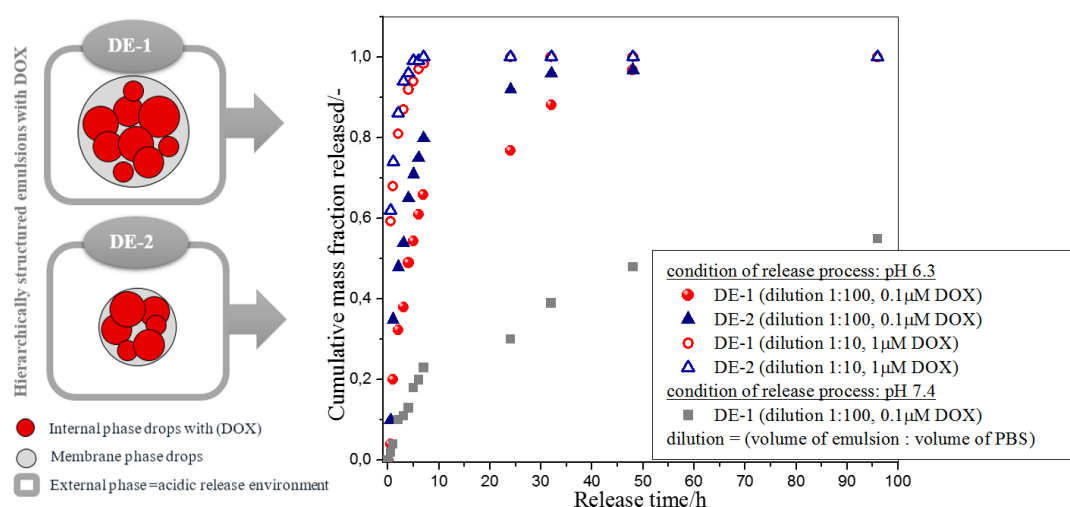


Figure 1. The cumulative release profiles of DOX from hierarchically structured emulsions DE-1 and DE-2.

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Neutron reflectometry in applied research of interfaces with liquid and soft media at the IBR-2 reactor

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In present-day studies of surfaces and interfaces at the submicron level, thermal neutron reflectometry is increasingly being used. In this connection, the development of neutron reflectometers with a horizontal sample plane for experiments on neutron scattering on free surfaces of liquids and soft media, as well as on hidden interlayers in solid-liquid interfaces, especially in applied research, is of current interest. Thus, at the IBR-2 pulsed reactor (JINR, Dubna), investigations were started on a new GRAINS neutron reflectometer [1] of this type. The reflectometer operates in the time-of-flight mode (wavelength range of 0.05 – 1 nm) taking advantage of a broad wavelength band of the cold moderator at the IBR-2. The inclined incident beam of thermal neutrons (grazing angle of 3 – 25 mrad, flux at the sample of $2 \times 10^6 \text{ s}^{-1} \text{ cm}^{-2}$) is formed by special deflecting neutron mirrors. The report presents the results of the first experiments on the reflectometer employing the analysis of specular reflectivity and diffuse scattering, which demonstrate the capabilities of the instrument with respect to studies of planar interfaces containing colloidal phases related with different applications. They include adsorption layers from nanoparticles suspensions and polymer solutions and electrochemical interfaces with liquid lithium-containing electrolytes. Steps are indicated for the further development of the reflectometer.

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Encapsulation of carvacrol in zein/resin composite nanoparticles

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Zein is renewable, non-toxic, digestible plant protein extracted from corn. It is prolamine, which is soluble in concentrated aqueous-ethanol mixtures and it precipitates and forms nanoparticles when its alcohol solution is added to bulk of water. Because of its hydrophobicity zein was already investigated for encapsulation of different essential oils and other non-polar compounds. Natural resins can be added to zein solutions in order to prepare composite nanoparticles, with different characteristics and encapsulation efficiency.

In this paper, carvacrol loaded zein and composite zein/resin nanoparticles were prepared by antisolvent precipitation. Firstly, zein/resin mixtures with varying mass ratio of the biopolymers were dissolved in 90% aqueous ethanol in order to obtain 2% wt. solutions. Thereafter, carvacrol oil is added to the aqueous ethanol solutions in amount of 5% w/w based on the biopolymers mass. Such solutions of biopolymers and carvacrol were then drop-wise added into a bulk of water in order to prepare loaded nanoparticles. Influence of zein/resin mass ratio on the encapsulation efficiency of thus prepared nanoparticles was investigated spectrophotometrically. It was shown that encapsulation of carvacrol is possible in both zein and zein/resin composite nanoparticles. The zein/resin mass ratio influences the encapsulation efficiency.

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Routes of synthesis single and gemini sulfobetaine type surfactants

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Sulfobetaine type surfactants are electroneutral salts carrying both a positive and a negative charge in the same molecule. Sulfobetaines possess two ionic centers of different sign, cationic one is usually quaternary nitrogen while anionic sulfonate moiety. The differences in the structure such as the length and presence of hydroxyl group of the spacer separating the quaternary ammonium center from the sulfonate group divides them into several subgroups. Sulfobetaines, whose hydrophilic polar headgroup carry both a positive and a negative charge in the molecule are interesting in several aspects. They exhibit good surface properties, good solubility in water and detergency. As reported in the literature they can be mild to eyes and skin. Moreover they are not toxic and can produce high and stable foam. Additionally sulfobetaines are hard water and degradation by oxidizing and reducing agents resistance compounds while comparing to many ionic surfactants. Sulfobetaines are insensitive to pH change. The effect of temperature changes and addition of electrolyte on sulfobetaines has been found to be minimal. They are also interesting compounds due to their biocidal activity [1,2].

The sulfobetaine type surfactants can be obtained in the quaternization reaction. The tertiary amines in which one of the group bonded to the nitrogen atom is long alkyl chain reacts with sulfate salts or sultones. However the significant step of synthesis is nucleophilic substitution reaction in which tertiary amines are obtained.

In the reaction which scheme is presented in fig. 1 both single and gemini sulfobetaines can be obtained. However the right selection of conditions of reaction is very significant. Slight changes in the reaction conditions can cause the reaction to proceed in a different direction. This is especially important when considering synthesis of both homo- and heterogemini surfactants [3].

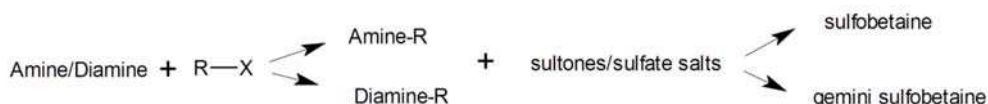


Figure 1. General route of synthesis of sulfobetaines and gemini sulfobetaines

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Sulfobetaine type surfactants as antimicrobial agents

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Sulfobetaine surfactants are electroneutral salts possessing, in the same molecule, two ionic centers of different sign. Sulfobetaines are compounds structurally similar to alkylbetaines. However they contain a sulfonate group instead of carboxylic one. Compounds belonging to this group can be divided into several subgroups differing from each other with the length and presence of hydroxyl group of the spacer separating the quaternary ammonium center from the sulfonate group [1].

They have no net charge. They are pH-Insensitive thus in neutral, alkaline and cationic solutions they exist in the form of internal salts. Together with the pH-dependent alkylbetaines, they are classified to zwitterionic surfactants [2].

Biocides are inorganic or synthetic organic molecules used to disinfect, sanitize or sterilize objects and surfaces, and to preserve materials or processes from microbiological degradation [3]. Biocides are a large group of compounds that have been classified for the mechanism of biocidal action. The scheme of their division is presented in fig. 1.

Sulfobetaines are compounds interesting due to their biocidal activity. Experimental data shows that this activity is differentiated. To the most active compounds from the group of N-alkyl-N,N-dimethyl- 3-ammonio-1-propanesulfonates and N-alkyl-N,N-dimethyl-4-ammonio-1-butanedisulfonates are these with alkyl chain consisting of 14 and 16 carbon atoms in the molecule. Minimal Inhibition Concentration research indicates that antibacterial activity of sulfobetaines belonging to different homologues series is high but varied. Sulfobetaine type surfactants can act also as antifungal agent. They demonstrate activity against *Candida Albicans* also against drug-resistant strains of the fungi. They also show fungistatic activity against fungi from *Fusarium* strain. The experiments shows that sulfobetaines can increase the fungistatic activity of strobilurins and benzimidazoles fungicides [4].

Sulfobetaines present antimicrobial activity. It depends not only on the length of hydrophobic alkyl chain but also form the structure of hydrophilic head. It also is varied for microorganism tested.

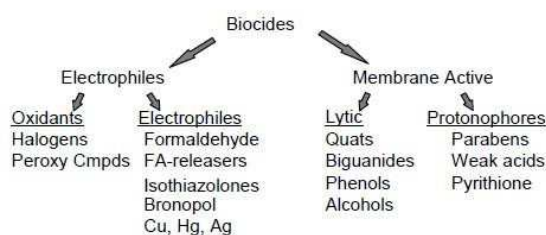


Figure 1. Mechanisms of action of biocides (Source: [Chapman 2003])

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Intracellular delivery of siRNA by polymer-grafted fluorescent nanodiamonds

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siRNAs are short protein-non-coding sequences of RNA, which are able to regulate gene expression *via* RNA interference (RNAi). This natural regulatory process by which siRNAs interact with mRNA leads to degradation of target mRNA in the cell cytoplasm. This approach allows downregulation of expression of pathological proteins resulting from genetic abnormalities. Nowadays, RNAi becomes a powerful tool for a regulation of many cell functions. Among all transfection systems used in gene delivery, polycationic polymers and lipids are considered as a “gold standard”. Herein, we report cationic polymer-grafted fluorescent nanodiamonds (FND@P) which can serve as traceable carriers for introducing of therapeutically active siRNAs into cells. Their specific properties as a high binding capacity, a possibility to attach targeting molecule, and an ability to protect siRNA against enzymatic cleavage together with unique optical features make them suitable for theranostic applications.

The main aim of this work is to design a new therapeutic construct based on the carrier FND@P delivering siRNA (FND@P@siRNA) in human cell line originating from Ewing Sarcoma tumor – a rare bone- cancer with genetic origin in the vast majority of cases (*EWS-Fli1* oncogene). In this study, we modified the FND surface with silica (hydrated SiO₂) and synthetic copolymers grafted directly from the surface. This “grafting from” coating approach leads to denser and better-protecting coatings than “grafting to” approach (polymer synthesized in solution and then attached to the surface). The positive charge of polymer layer allows siRNA molecules to bind to FNDs *via* electrostatic interaction. Moreover, due to electrosteric stabilization, this polymer coating protects FNDs against precipitating in biological solutions. We proved in cultured human Ewing Sarcoma cells, that FND@P@siRNA complexes inhibit the expression of the *EWS-Fli1* oncogene, with a similar efficacy as Lipofectamine transfection agent, but even in the presence of serum, a condition restricting the Lipofectamine function. These promising results show that newly designed polymeric complex with siRNA is a suitable candidate for *in vivo* testing.

Polyelectrolyte induced controlled aggregation of cells: metabolic coupling

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Using the layer-by-layer (LBL) approach charged polyelectrolytes can be deposited on surfaces [1]. This allows electrostatic modification of cellular surfaces [2], either by reversing or strengthening the cell's surface charge or by constructing a multilayer polyelectrolyte capsule around the cell [3]. Such nanocapsules complement the physiological characteristics of bacterial cells and allow to add new features through the incorporation of e.g. nanoparticles, enzymes or ligands.

Bacterial cells are usually negatively charged on the surface, which is mainly due to the negative moieties of bio-molecules incorporated into the cell membrane and/or cell wall. Using the LBL approach and polyelectrolytes, like polyethylenimine (PEI⁺), we electrostatically reversed the negative surface charge of bacteria to make it positive (Fig. 1). This way we could attach the modified positively charged cell to negatively charged surfaces including negatively charged cells. By using two or more different types of cells, we constructed artificial cellular aggregates in a controlled manner (Fig. 1).

We show how to produce bacterial aggregates in bulk to harbor in the center a single positively charged cell and around it multiple negatively charged cells that metabolically complement one another. By constructing an LBL capsule and by incorporating magnetic particles into the nanocapsule of the central cell, we further propose an approach for the enrichment of these artificially prepared aggregates.

The tight associations of the cells in the aggregates allow efficient transport of metabolites between the cells and thereby improves the efficiency of metabolic pathways. This offers the basis for the development of applications in industrial biotechnology, food production, biosensors, medicine and ecoremediation.

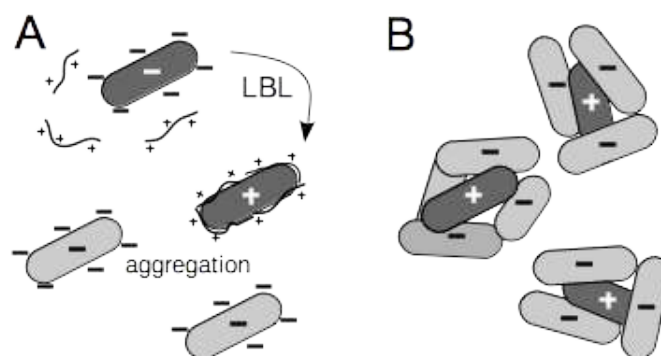


Figure 1: The preparation of the artificially constructed multicellular aggregates. (A) The surface charge of the first cell type is altered to be positive in order for it to be attached to negatively charged cells of the second type. (B) Aggregates of different combinations and number of cells can be constructed.

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Varied-core polyelectrolyte nanocarriers for sustained delivery of porphyrin photosensitizers to human ovarian cancer cells

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Since the uprising of nanobiotechnology in the past decades, the design and development of effective drug delivery carriers for anticancer therapy and diagnostics has become an important field of scientific research [1]. Much work is currently focused in the preparation of well-defined polyelectrolyte nanostructures in terms of their main components, template-type, size and surface charge which factors play a significantly role in the nanocarrier behavior *in vivo* [2]. Those functional nanocarriers can be fabricated by layer-by-layer (LbL) assembly of anionic and cationic polyelectrolytes on charged interface - emerged as one of the most versatile, convenient and, simple method of nanocontainers fabrication that may provide advantages of controlling the structure, composition and thickness of the formed layers and, thus, may allow the engineering of shells on the nano-level [3].

Thus, the present contribution deals with encapsulation of poorly water-soluble photosensitizing agents with high potential in photodynamic therapy (PDT) - porphyrin-origin dyes, i.e. Verteporfin (VP) and *meso*-tetraphenylporphyrin (TPP) in two types of disodium N-dodecyliminodiacetate, C₁₂(COONa)₂-stabilized multilayer nanocapsules (NCs) obtained by LbL coating of solid (nanoprecipitated), or liquid (nanoemulsion-templated) oil core via biocompatible, i.e. poly(L-glutamic acid)/poly(L-lysine) - PGA/PLL polyelectrolyte shells. Zeta potential measurements allowed to evaluate progress of the polyelectrolytes LbL deposition on both cores and the NCs' stability. Backscattering profiles (BS) confirmed the long-lasting stability of the optimized nanosystems, which size ($D_H < 200$ nm), polydispersity and morphology were examined by dynamic light scattering (DLS), atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques. The NCs photodynamic potential was evaluated via photobleaching rate, reactive oxygen species (ROS) generation and *in vitro* drug release under physiological conditions or in the presence of human serum albumin (HSA). The biological potential of the encapsulated VP and TPP for further *in vivo* NCs behavior was evaluated in cytotoxicity as well as photocytotoxicity studies upon well characterized human cancer cell line – ovarian carcinoma (A2780) – and normal human ovarian fibroblasts (HOF).

Our studies indicated that the encapsulation of VP and TPP in the varied-core multilayer NCs (primary with the solid one) increases their solubility in aqueous solution and protection from the surrounding medium by reducing the photobleaching rate and improving their photochemical properties during irradiation in regards to the free (non-encapsulated) PSs molecules. *In vitro* sustained release under physiological conditions or in the presence of human serum albumin (HSA) was achieved in favour of the solid core NCs for both VP and TPP. The biological response upon human ovarian cells provided the NCs biocompatibility upon normal ovarian HOF fibroblasts and improved photodynamic activity in the tumor A2780 cell line. To accomplish, the designed NCs - offering better chemical and physical stability, the high PS loading capacity, ability to release it in a controlled and continuous manner and biocompatibility - can be considered as effective nanocarriers for potential PDT of ovarian cancer.

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Modelling human stratum corneum with commercially available lipids

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Stratum corneum (SC) constitutes the main barrier for drugs diffusing through the skin, while also protecting the body from harmful chemicals and infection, and preventing trans-epidermal water loss. The skin barrier is commonly described by the “brick and mortar model” [1] with the corneocytes being the “bricks”, and the lipid matrix between the corneocytes forming the mortar. The lipid matrix is thought to be the main transportation pathway through the skin barrier. It is a complex mixture of mainly free fatty acids, ceramides and cholesterol, in a roughly equimolar ratio, assembling into two distinct phases; the long and short periodicity phases (LPP and SPP, respectively) [1]. The exact composition of lipids plays an important role in the proper formation of LPP and SPP, drug penetration over the skin, and skin barrier function. Lipid composition is often dysregulated in skin conditions such as atopic dermatitis and psoriasis [1]. There is a current need for reproducible, well-characterised models of human SC to test drug absorption through, as well as a better understanding of the significance of the individual lipid components in human SC matrix on SC barrier function.

The aim of this project is to develop physical models of the SC formed of commercially available lipids by spincoating lipid mixtures onto solid supports, in order to mimic the molecular structure of native SC lipid matrix. The structure and interactions of the supported lipid film with drug compounds will be characterised and compared to total extract of pig SC using neutron reflectometry, ATR-FTIR and QCM-D measurements.

ATR-FTIR: Attenuated total reflection (ATR) Fourier transformed infrared (FTIR) spectroscopy allows deposition of a lipid layer onto a prism, and the subsequent study of functional group environment as a function of temperature (phase transitions) or as a result of lipid multilayer interactions. Studying the SC lipid models with ATR-FTIR will allow us to compare their phase behaviour, lipid multilayer interactions with various drug compounds, and potential subsequent structural lateral changes to the lipid film.

Neutron reflectometry: Neutron reflectometry provides insight into the structure perpendicular to interfaces, making it possible to investigate the internal structure of the lipid multilayer at physiologically relevant conditions.

QCM-D: Quartz crystal microbalance with dissipation (QCM-D) quantitatively measures changes in film thickness and rigidity without the use of external probes. Changes in molecular structure of the lipid multilayers under different conditions are also possible to assess through changes in dissipation, which relates to rigidity of the supported lipid film. It is also possible to expose the lipid multilayers to various molecules of interest to study binding to the SC lipids.

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Evaluation of novel cationic pyridinium-based amphiphile C12-Man-Q as an efficient *in vitro* gene delivery agent

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Gene therapy has become the research focus for many laboratories in pharmacy, medicine, biochemistry and chemical engineering worldwide. Synthetic cationic lipids are widely used components of non-viral gene carriers and the factors regulating their transfection efficiency are subject of considerable interest.[1] The development of novel nontoxic cationic structures high gene transfection efficiencies is of great importance.[2]

A number of cationic 1,4-dihydropyridine (1,4-DHP) amphiphiles capable of transfecting plasmid DNA (pDNA) into different cell lines *in vitro* were developed by our research group. During these studies it was established that 1,1'-[(3,5-didodecyloxycarbonyl-4-phenyl-1,4-dihydropyridine-2,6-diyl)dimethylen]-bispyridinium dibromide (D-19) was the optimal structure among tested synthetic lipid-like compounds.[3-5]

The aim of the present study was to investigate the influence of remoted cationic moieties at the positions 2 and 6 of 1,4-DHP molecule on gene delivery activity. The results of transfection efficiency in various cell lines of synthesised amphiphile C12-Man-Q were compared with data obtained for cationic 1,4-DHP derivative D-19.

The target cationic 1,4-DHP derivative C12-Man-Q with remoted from 1,4-DHP cycle cationic moieties at the positions 2 and 6 was synthesised in the multistep procedure, including Mannich reaction with the subsequent amine quaternisation in 50% yield. Transfection efficiencies of compounds were evaluated in BHK-21, Cos7, Huh and HepG2 cell lines. The obtained data showed that compound D-19 possessed high activity when transfecting active proliferating cells. We propose that compound D-19 is cell type specific as the differences in the transfection efficacy were found for the tested cell lines. The most significant property of compound C12-Man-Q is its moderate ability to transfect many cell lines. Comparing with compound D-19, new derivative C12-Man-Q is less cell type specific.

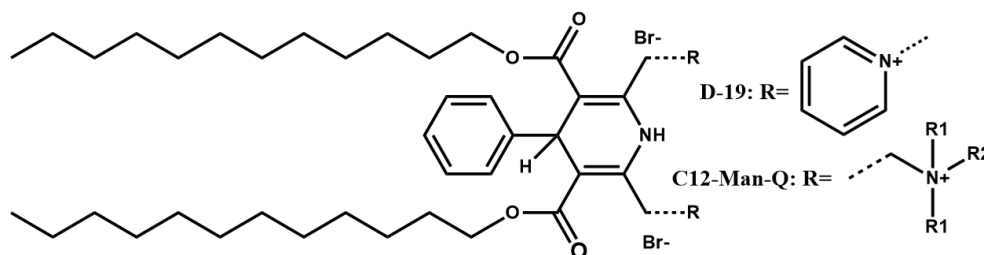


Figure 1. Structures of tested compounds: D-19 and C12-Man-Q.

Acknowledgements: The financial support of EuroNanoMed2 project INNOCENT.

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Controllable release of ketoprofen from chitosan nanoparticles deposited on graphene oxide platelets

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Biopolymers are of wide use in biomedicine and pharmacy owing to their versatile properties, including low rate of dissolution, hindering settling of suspensions, etc. Chitosan (CH) is a cationic polysaccharide, which can undergo biodegradation and, at the same time, it is biocompatible. Chitosan may be a feasible starting material for the replacement of synthetic polymers in many applications, because it is obtained from a renewable resource, chitin, in contrast to the polymers synthesized from other carbon resources such as crude oil. Graphene oxide (GO) is a layered particle prepared from graphite oxide by delamination. The rich surface chemistry and enormous surface area of GO makes it feasible as a platform for the immobilization of nanosized particles and drug molecules as well.

We have synthesized graphite oxide by the Hummers-Offeman method and obtained GO in aqueous suspensions. Chitosan nanoparticles (CH NPs) have been obtained from chitosan solutions using solutions containing hydrogenphosphate anions. Nanocomposites containing CH and GO particles have been prepared by heterocoagulation at different mass ratios.

These composites have been loaded with anti-inflammatory drug, ketoprofen. The effect of several parameters (most importantly, the mass ratio of the composite and the particle diameter of CH NPs) on the dissolution kinetics of the drug molecules have been investigated. It has been revealed that the release of the drug follows a first-order kinetics and the presence of GO platelets slows down the release of ibuprofen at constant CH NP particle sizes.

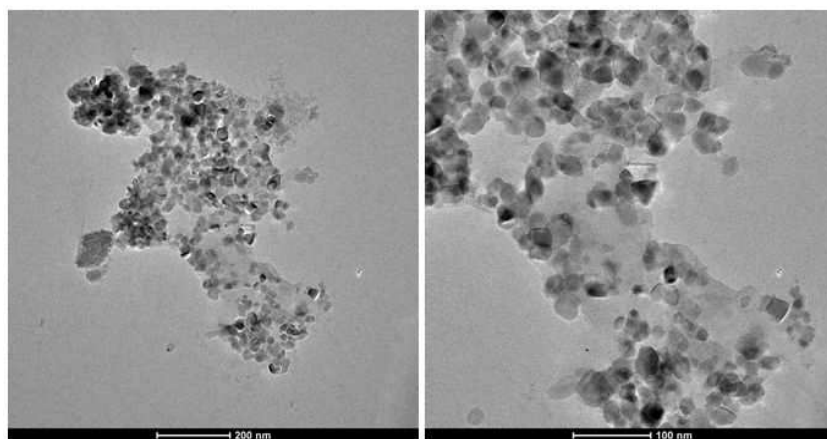


Figure 1. TEM image of a GO/CH NP composite at 50 to 1 mass ratios, at different magnifications (left: scale bar of 200 nm, right scale bar of 100 nm).

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Adsorption kinetics of heptadecafluoro-1-nanol: phase transition

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The adsorption kinetics of heptadecafluoro-1-nanol ($C_9H_2F_{17}OH$) onto a clean air-water interface at low surfactant concentrations studied. A video-enhanced pendant bubble tensiometer was used to measure the $\gamma(t)$ data of aqueous $C_9H_2F_{17}OH$ solutions. A new generalized Frumkin-Langmuir phase transition model was built up to simulate the $\gamma(C)$ and $\gamma(t)$ data (Fig. 1).

At higher surfactant concentrations, a constant- γ region at 64.8 mN/m was observed for one hundred to a few thousand seconds during the $\gamma(t)$ relaxation. This constant- γ region implies the existence of a phase transition of the adsorbed surfactant monolayer at air-water interface. The $\gamma(t)$ data of $C_9H_2F_{17}OH$ can be simulated perfectly using this mixed-controlled phase transition model with the adsorption rate constants $\beta_1=1.0\pm0.5$ and $\beta_2=13\pm4$ ($10^5 \text{ cm}^3/\text{mol.s}$). It is therefore concluded that the adsorption process of $C_9H_2F_{17}OH$ onto a clean air-water interface is of mixed-control.

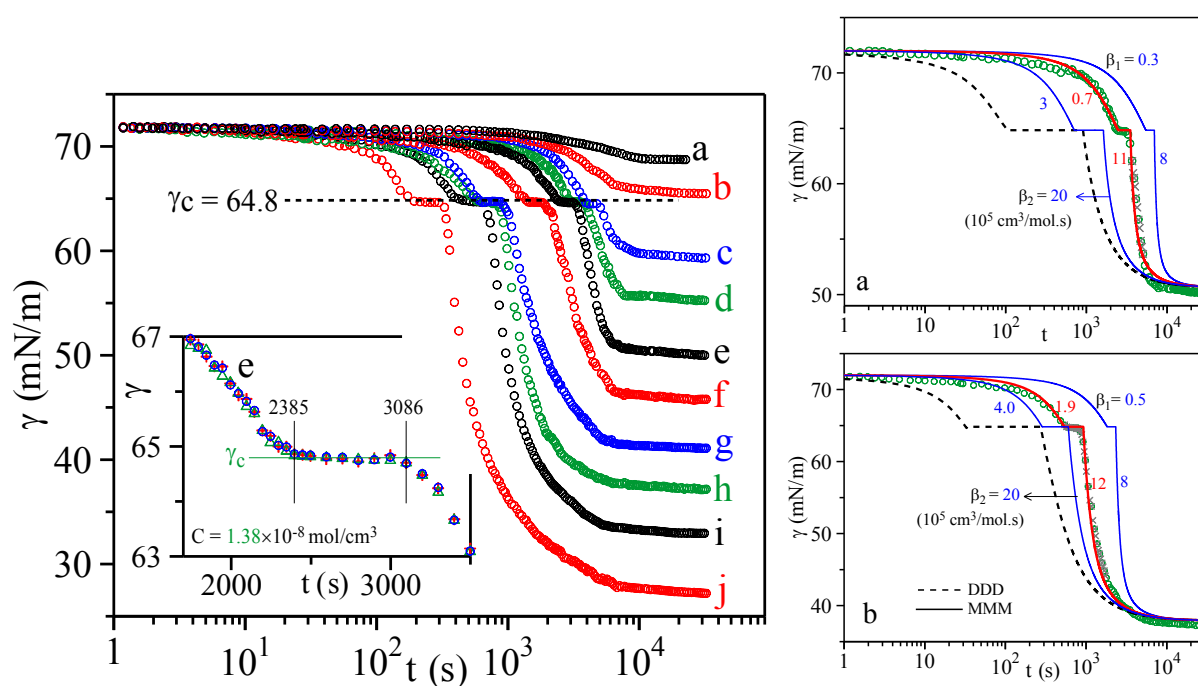


Figure 1. (left) Representative $\gamma(t)$ data for the adsorption of $C_9H_2F_{17}OH$ onto a fresh air-water interface for $C_0 = 0.4$ (a), (b) 0.6, (c) 0.99, (d) 1.21, (e) 1.38, (f) 1.62, (g) 1.89, (h) 2.15, (i) 2.48, and (j) 3.0 (10^{-8} mol/cm^3). (left inset) The reproducibility of the $\gamma(t)$ data near the plateau region at $C=1.38 \times 10^{-8} \text{ mol/cm}^3$. (right) Comparison between the experimental $\gamma(t)$ data and the simulated diffusion-controlled $\gamma(t)$ curves from the generalized Frumkin-Langmuir phase transition model: $C = 1.38$ (a) and 2.15 (b) (10^{-8} mol/cm^3).

Dynamic surface tension of ionic surfactant solutions during a rapid surface expansion

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The relaxation of surface tension (ST) is crucial in processes involving significant surface deformation, such as the impact of surfactant-laden liquid drop on solid substrates. The relaxations of ST and surface dilational rate of nonionic surfactant TX-100, ionic surfactant aerosol-OT (AOT) and sodium dodecyl sulfate (SDS) solutions during a rapid surface expansion were studied by monitoring a continuously expanding bubble using a pendant bubble tensiometer. The experimental data showed that during rapid bubble expansion, the STs of the AOT and TX-100 solutions increased with time, whereas the ST of the SDS solution remained nearly constant. A theoretical ST, $\gamma(t)$, curve of an isolated bubble surface was simulated, and this $\gamma(t)$ curve matched well with the experimental $\gamma(t)$ data for the AOT (Fig. 1) and TX-100 solutions. For TX-100, its mass transport was confirmed to be negligible at a surface dilational rate of $\lambda > 1.5 \text{ s}^{-1}$. For AOT, the rate of mass transfer of AOT molecules from the bulk phase to the bubble surface during bubble expansion (at $\lambda < 3 \text{ s}^{-1}$) is much slower than the depletion rate of surfactants at the surface. In contrast, the mass transport of SDS molecules from the bulk to the bubble surface is much faster than the depletion rate of surfactants at the surface.

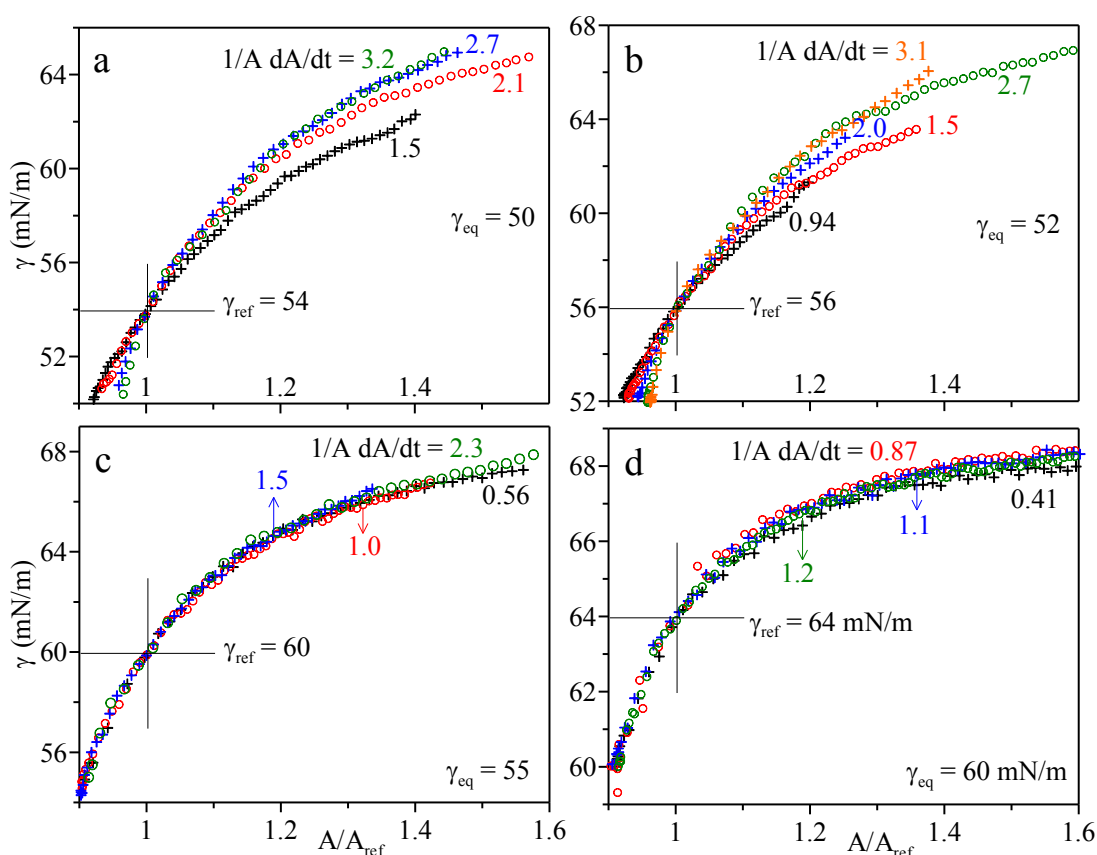


Figure 1. Dependence of ST (γ) on the relative surface area (A/A_{ref}) during the rapid expansion of the bubble in aqueous AOT+10 mM NaCl solutions with $C_{\text{AOT}} = 2.43$ (a), 1.50 (b), 0.88 (c), and 0.27 (d) (10^{-8} mol/cm^3).

A PEO-PPO-PEO block copolymer/sodium cholate system to host doxorubicin

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Nonionic triblock copolymers, known as Pluronics[®], have received a considerable attention as modern drug and gene delivery carriers [1]. They have the general formula EO_x-PO_y-EO_x, and are composed of a hydrophobic poly(propylene oxide) (PPO) block and two units of a hydrophilic poly(ethylene oxide) (PEO) block [2]. Their amphiphilic character results into surfactant properties, which include the ability to interact with hydrophobic surfaces and biological membranes. Above their critical micelle concentration (cmc), these copolymers self-assemble into micelles. Due to their core-shell structure, polymeric micelles such as F127 have the ability to solubilize hydrophobic drugs in the PPO core, thereby enhancing their solubility in water media. In addition, they are suitable for drug delivery in medicine [1] as they are non-toxic and stabilized to aggregation, protein adsorption and deactivation because of the presence of the PEO corona. The stability of the loaded pluronic micelles is however low due to their high cmc (~1 mM for F127) resulting in their disaggregation by dilution or interaction with the blood components. The mixture of pluronic micelles with other polymers/surfactants [3] enhances the stability of the resulting micelles thus increasing the bioavailability of the encapsulated drugs.

The loading efficiency of bile salt/pluronic coformulation [4] toward the fluorescent anticancer antibiotic doxorubicin (DX) has been studied. DX is administered as chlorohydrate to enhance its solubility in water. This limits its solubilization into F127 micelles to the corona region. To promote its solubility in the hydrophobic core of F127 micelles, a coformulation with the cationic bile salt sodium cholate (NaC) has been used. Indeed, in the presence of NaC the DX experience a more apolar environment, as indicated by its fluorescence spectra (Figure 1 – panel A) and its stability in water is sensibly enhanced. A slow evolution of the micellar aggregates dimensions at 40°C has been observed that matches the micropolarity changes deduced by the fluorescent properties of the guest molecule DX (Figure 1 – panel B).

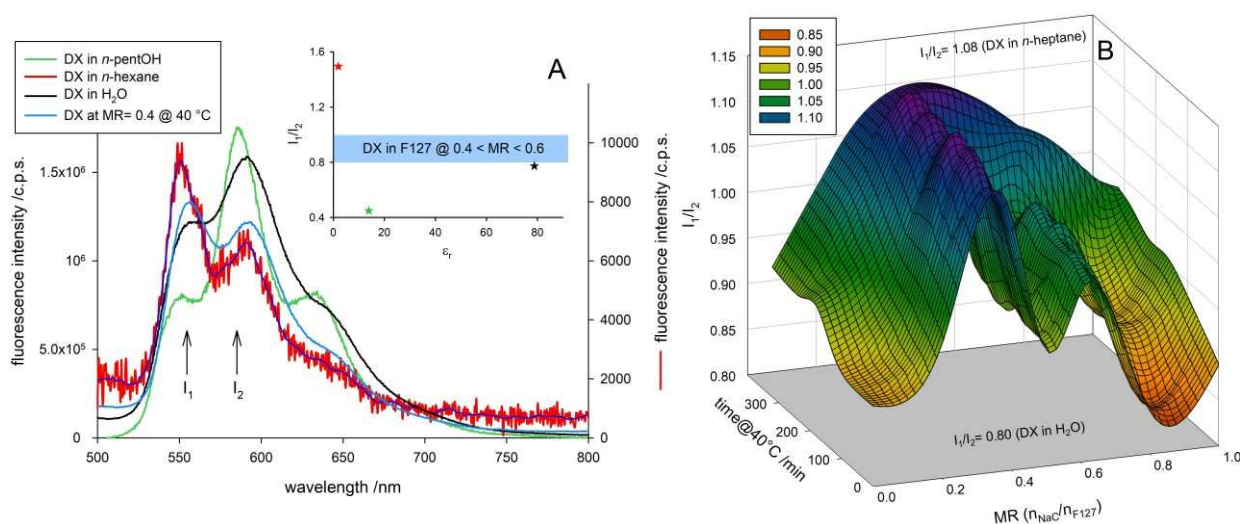


Figure 1. Panel A: Emission spectra of DX in different solvents ($\lambda_{exc} = 410\text{nm}$). The inset shows the value of the I_1/I_2 ratio as a function of ϵ_r (same colour as in the main graph) and in F127/NaC samples. Panel B: 3D plot showing the I_1/I_2 evolution with time at 40°C and as a function of MR.

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Fluorescent nanodiamonds coated in stimuli-responsive polymeric shells – platform for optical sensors

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Unique optical properties of fluorescent nanodiamonds (FNDs), especially the fluorescence stability and durability, concurrently with FNDs low toxicity attract attention in the field of bioimaging applications. Additionally, the possibility of various optical biosensors construction makes this material even more interesting. This was demonstrated for example as ratiometric change in FND fluorescence spectra with environmental charge changes [1]. However, FND-based optical biosensors are still in the beginning of their development making this field highly challenging.

Here we are showing a platform for construction of optical sensors based on FNDs coated in multi-stimuli responsive polymeric shell. The shell reacts reversibly on changes in its environment – namely pH and temperature, by swelling and collapsing. The complex shell composition contains four types of monomers: two are serving for pH (acrylic acid) and temperature (*N*-isopropyl acrylamide) response, one for further modification by click chemistry, and the last one works as a crosslinker. We have developed the optimum reaction conditions to synthesize shells with maximum response and confirmed their reversible behavior. The best working polymer composition shows the maximum pH response at elevated temperature which is very convenient for measurements in living systems requiring the temperature of 37 °C. Additionally, we measured the fluorescence response for both pH and temperature and observed monotonous ratiometric change for both. This indicates that our particles can be further used as a platform for optical construction of nanoscale pH sensors and nanothermometers.

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Mechanisms of fibrinogen/antibody interactions at silica substrates

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Revealing adsorption mechanisms of bioparticles at solid/liquid interfaces is of a major significance for a variety of fields. Especially significant are protein adsorption phenomena involved in blood coagulation, artificial organ failure, plaque formation, inflammatory response, fouling of contact lenses, ultrafiltration and membrane filtration units. On the other hand, controlled protein deposition on various surfaces is a prerequisite of their efficient separation and purification by chromatography, gel electrophoresis, filtration, for biosensing, bioreactors, and immunological assays.

Immunoassays are important application areas of proteins immobilized on solid substrates. Common adsorbed proteins are immunoglobulins G (IgG) or their active fragments, which specifically bind to its antigen with high affinity. Although immobilized antibodies play a critical role in immunoassays, the mechanisms of the immobilization processes are poorly understood. Little *in situ* research has been done on how IgG adsorb on immobilized proteins monolayers. There is lack of systematic investigations of the relationship between the immobilization conditions and resulting protein coverage, local distribution, and orientation of this adsorbed protein and their bioactivity. Therefore, the main goal was to elucidate mechanisms of fibrinogen/IgG molecule adsorption at silica substrates and to develop the protocol for a sensitive method for detection of trace amounts of antibodies based on physical attachment of the antibody to fibrinogen monolayers.

Experimental measurements have been performed using a variety of complementary methods adequate for study protein adsorption under wet, *in situ* conditions including streaming potential, OWLS, and QCM. The obtained results furnished vital information about the kinetics of the protein adsorption, maximum coverages and their interactions at silica substrates.

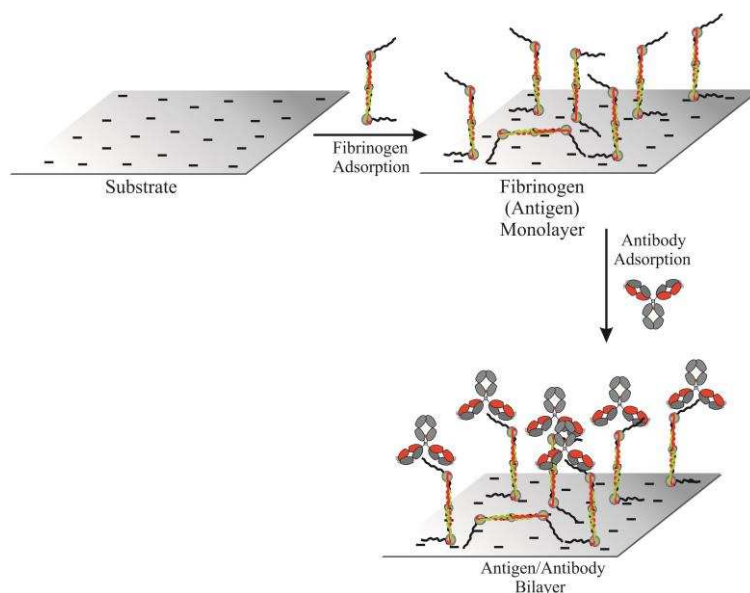


Figure 1. A scheme of HPF /IgG bilayer formation.

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Phase behaviour and structure properties of supported lipid monolayers and bilayers in interaction with GBV-C derived peptides of interest on HIV-1 inhibition

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Lipids in eukaryotic cell membranes have been shown to cluster in rafts with different compositions and molecular packing. It has also been demonstrated that these rafts play an important role in the assembly of enveloped viruses [1]. The human immunodeficiency virus (HIV-1) is one of them and its cellular infection takes place through a membrane fusion process which involves a lipid raft present at the host membrane. In turn, it has been demonstrated that HIV-1 virus shares their infection mechanism with GBV-C virus so its derived peptides have been studied in the context of HIV-1 inhibition

It explains that, new approaches have been developed to study the interaction by using models of biological membranes, mimicking their structure, but limited to only a few lipids in composition. Among these models, lipid monolayers on planar supports, usually built by Langmuir-Blodgett (LB) transfer [2], bilayers deposited by vesicle spreading and giant unilamellar vesicles (GUVs) made according to well described methodology [3] allow visualization of raft-like domains which provides tangible proof for the coexistence of liquid-ordered (L_o) and liquid-disordered (L_d) phases [4]. At last, these models are particularly well-adapted to surface-sensitive physical techniques, such as atomic force microscopy (AFM) and fluorescence microscopy (FM) [5]. On other hand, some HIV-1 inhibitors used in anti-AIDS therapy have shown certain affinity with these rigid domains of the membrane [6].

The aim of this work is focused on the formation of the membrane lipid domains, their structural properties and the changes caused by HIV-1 and GBV-C peptides when interacts with them. Figure 1 shows the L_o/L_d phase observed when GUVs of DOPC/DOPS/ sphingomyelin and cholesterol were obtained.

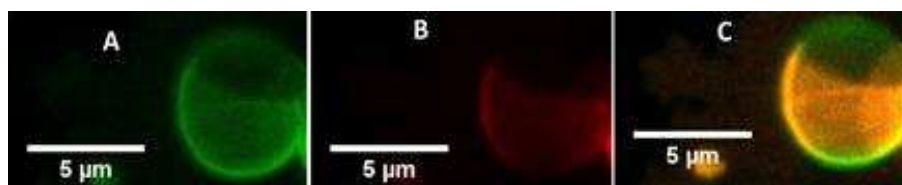


Figure 1. Confocal images of giant liposomes. Composition: LIP/Chol/SM (1:1:1) containing A: 1% NBD-PC, B: 1% DiI C20:0 and C: 1% NBD and 1% DiI C20:0. LIP: DOPC/DOPS (3:2), Chol: cholesterol, SM: sphingomyelin.

Acknowledgements: This work was supported by Grants CTQ2012-37589-C02-01/02 from the *Ministerio de Economía y Competitividad* and 2014 SGR 216 from the *Generalitat de Catalunya*.

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Drug encapsulation into polymeric nanoparticles

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Poly(lactic-co-glycolic acid), PLGA based drug loaded particles were prepared by nanoprecipitation method. Parabens were chosen as model drugs, because the polarity of the molecules with increasing length of alkyl chain changes gradually while the main part of the structure stays the same. Due to this property, the series of parabens can be used to examine the influence of the polarity of the drug molecule on the potential drug content of the carrier system. Our aim was to study the relation of the polarity of the methyl-, ethyl-, propyl-, butyl- and heptylparaben with the encapsulation efficiency into PLGA nanoparticles.

Size and size distribution of the prepared PLGA particles were characterized by dynamic light scattering. Drug content of the nanoparticles was determined by UV-VIS spectroscopy.

The molecular interaction between the parabens and the PLGA was studied in a Langmuir- balance. The thin layer of PLGA was prepared on the water surface by spreading its chloroformic solution. Penetration of the parabens was measured into the preformed PLGA monolayer. During the measurements the aqueous solution of the parabens was injected into the subphase. The change in the surface pressure was measured as a function of time [1] and used as the indicator of affinity to the PLGA. Surface pressure (π) – area (A) isotherms of PLGA and PLGA and paraben mixed films were also recorded at air/water interface. [2] The pressure of squeezing out of parabens was determined.

The results of the penetration and squeezing out measurements were compared to the series of parabens. The molecular interaction behaviour was evaluated taking into consideration the molecules' polarity and their surface activity determined by pendant drop method.

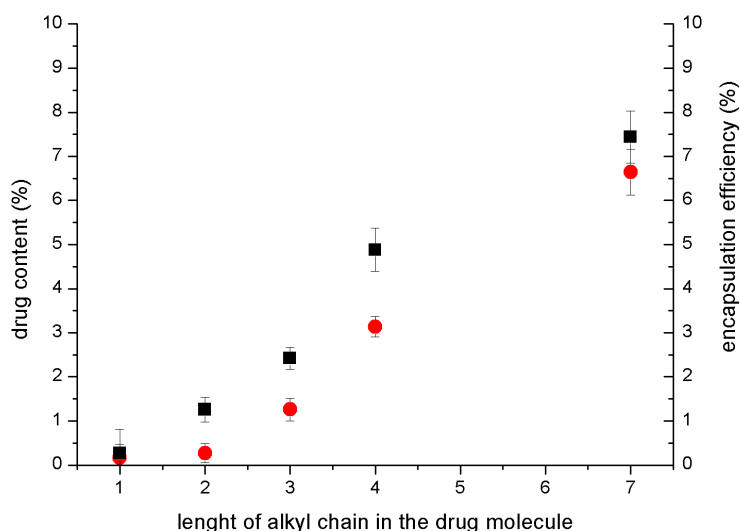


Figure 1. The drug content (red dots) of the PLGA NPs and the encapsulation efficiency (black squares) for the series of parabens

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Preparation of silver-lustrous organic crystals having a benzanilide skeleton

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There exist a number of silver-colored products around us. Most of the products are coated by metallic paints containing metal powders. Metal-colored films obtained metallic paints cut off radio wave, and therefore metallic paints cannot apply to communication devices. In addition, metallic paints may evoke metal allergy to people having sensitive skins [1]. In order to solve these problems, we have found that some organic compounds, azobenzene and stilbene derivatives, form gold- or silver-lustrous organic crystals [2-3]. Recently novel compounds having a benzanilide skeleton have been synthesized in our lab. They can form silver-lustrous organic crystals. In this paper, we will introduce the synthesis of the new compounds and the silver luster of their crystals.

Benzanilide derivatives (Figure 1) have been synthesized through two reaction steps. The derivative (1) forms silver-colored crystals by recrystallization using ethanol and the derivative (2) also gives silver-colored crystals by recrystallizing from acetonitrile and water (Figure 2(a) and (b)).

The luster of the silver-colored crystals was evaluated in terms of specular reflectance. The specular reflectance of the crystals of 1 or 2 was higher than that of gray *origami*. When the color of the lustrous crystals was estimated using CIELAB color space measurements, the color of the crystals of 1 or 2 was similar to that of silver-colored *origami*. The crystals of 2 were added to water, followed by vortex. The obtained dispersion was stable, which suggests that the crystals of 2 may be applied to water-soluble inkjet inks (Figure 2(c)).

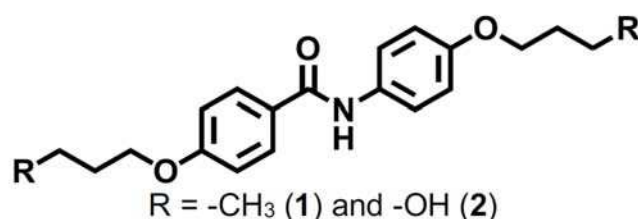


Figure1. Chemical structures of benzanilide derivatives



Figure 2. Silver-lustrous organic crystals of (a) 1 and (b) 2. (c) shows the stable dispersion of 2 in water.

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Surface-Active Stimuli-Responsive Polymersomes towards the Intracellular Delivery of Drugs, Genes and Proteins

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The extracellular and subcellular compartments are characterized by specific pH levels that can be modified by pathophysiological states. Accordingly, when pH-responsive nano-assemblies are exposed to such milieus, they can respond via changes in their structure and/or surface charge.[1-2] The structural changes of polymeric assemblies induced by environmental conditions can be exploited for the delivery of therapeutic drugs and genes into specific sites of action.[3] In this framework, we highlight the potential use of pH-responsive block copolymers for the intracellular delivery of hydrophilic therapeutics.

Several poly ([*N* - (2 - hydroxypropyl)] methacrylamide) - *b* - poly [2 - (diisopropylamino) ethyl methacrylate] diblock copolymers (PHPMA-*b*-PDPA) were synthesized by RAFT polymerization and characterized by NMR and SEC. Self-assembled vesicular structures (also known as polymersomes) with a desirable size for cellular uptake ($R_H \sim 50$ nm) and low polydispersity (PDI = 0.07) were produced from selected block copolymers using the microfluidic technique (MF). They were further characterized by static light scattering, zeta potential and TEM imaging (Fig.1). Cyanine 3 DBCO and Cyanine 5 DBCO were covalently bound to the block copolymers by copper free click chemistry reaction. The successful of this approach was evaluated by FRET measurements. In the steps further, the encapsulation and release of the chemotherapeutic drug doxorubicin and other therapeutic biomacromolecules will be investigated. Intracellular trafficking will be evaluated using fluorescent dyes attached by click chemistry as well as by the interaction of the produced polymersomes with biologically milieus.

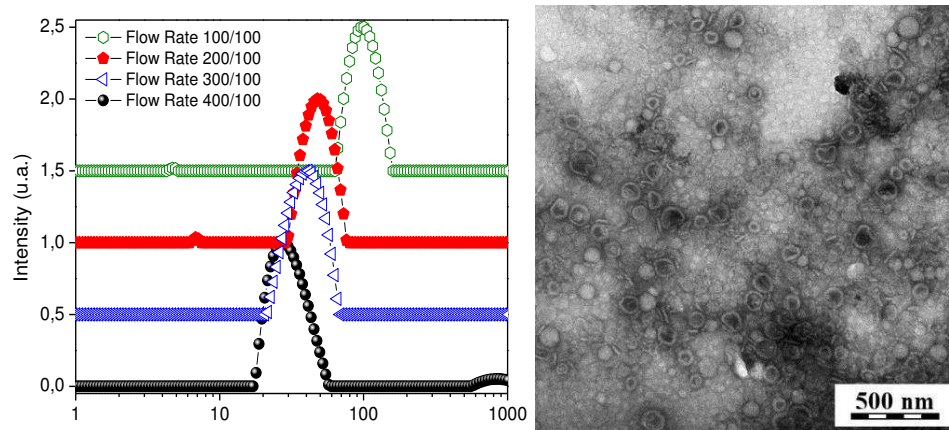


Figure 1. Size distribution for the produced Polymersomes by using MF in different flow rates (left) and TEM image of the polymersomes produced from the PHPMA₃₅-*b*-PDPA₆₁ diblock copolymer at flow rate = 200 L·min⁻¹ (PBS, pH 7.4) / 100 L·min⁻¹ (polymer solution at 5 mg·mL⁻¹).

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Strategies to monitor proteins adsorbed in mesoporous silica nanoparticles

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Protein functionalization of mesoporous silica nanoparticles (MSNs) represents a key factor in the design and engineering of new targeted and controlled drug-delivery systems. However, in order to visualize and determine the fine localization of proteins adsorbed in nanoparticles, we have employed specific transmission electron microscopy (TEM) analytical strategies based on the use of gold conjugates.

To date, we used gold-conjugated-bovine serum albumin to determine how different biopolymers affect the formation of a protein corona around functionalized MSNs through direct TEM observation of surface bound proteins [1], whereas in previous investigations we applied the Immune Gold Staining (IGS) method to prove the localization of lysozyme adsorbed inside SBA-15 pores [2]. IGS procedures have been extensively used to localize proteins in animal tissues and are mainly characterized by the gold conjugate antibody aptitude to recognize and bind specifically proteins allowing their visualization by conventional TEM. Additionally, in previous investigations [3] we visualized by means of the silver enhancement procedure antibody fragments F(ab')GAMlgG conjugated with ultra-small gold nanoparticles, GNPs (diameter 0.8 nm), immobilized into the mesopores of amino functionalized SBA-15 mesoporous silica. The silver enhancement technique permitted the amplification of the ultra-small size of GNPs that acted as nucleation sites for the deposition of metallic Ag atoms obtained by the reduction of Ag⁺ ions. The silver-enhanced GNPs are visible at conventional TEM thus allowing for an unequivocal imaging of the location of the antibody fragment-GNPs conjugates inside the channels of SBA-15. These nano-bioconjugates are being studied for either cancer therapies and imaging purposes.

The use of gold conjugates is gaining in popularity, representing a fundamental tool to design future applications of MSNs in biomedicine, pointing out that we are at the very beginning of a new age of the nanomaterial science: the “mesoporous golden age”.

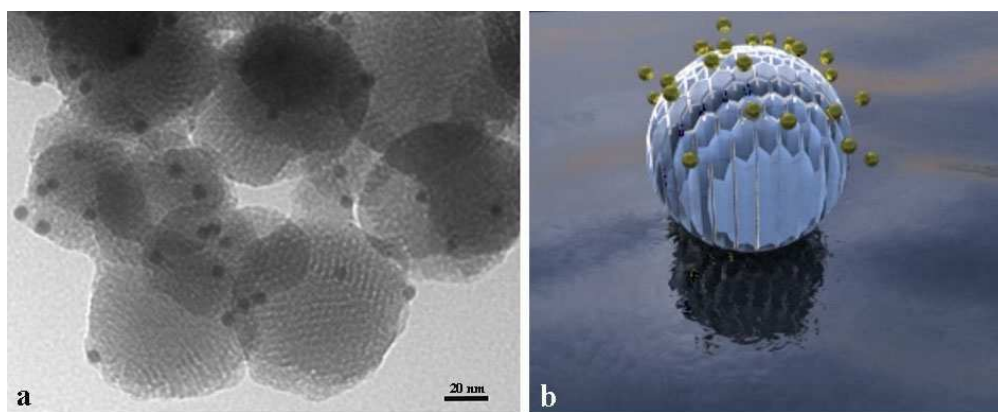


Figure 1. TEM micrograph of gold-conjugated bovine serum albumin adsorbed on MSN surfaces (a). Graphical representation of gold nanoparticle interaction with MSN (b).

Acknowledgements: This investigation was supported by RAS/FdS (CUP F72F16003070002, 2017).

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Immobilizing polymyxin B on self-assembled monolayers and probing their interaction with lipopolysaccharide

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Lipopolysaccharide (LPS), also known as endotoxin, is one of the major cause for sepsis [1]. Polymyxin B (PMB) is a molecule known to bind to the lipid A part of LPS with specificity [2]. However, because of its toxicity, PMB cannot be applied directly to human body as a free drug. Instead, the immobilized PMB was used in an extra-corporeal device, such as Toraymyxin®, to remove endotoxin in blood. Nevertheless, the adsorption behaviors of LPS on PMB immobilized surfaces are still not well understood. The aim of this research is to study the effect of surface density and immobilization conditions of PMB molecules on its adsorption behavior to lipopolysaccharide (LPS) molecules.

This work describes the immobilization of Polymyxin B (PMB) molecules to a mixed self- assembled monolayers (SAMs) of alkanethiolates on gold derived from the 1-Undecanethiol and the 16-Mercaptohexadecanoic acid ($R_{COOH, soln} = 0.0-1.0$), and studies of biospecific binding behaviors of lipopolysaccharide (LPS) to these SAMs with different PMB surface concentration. The method involves the generation of activated *N*-hydroxy- succinimidyl (NHS) esters from the carboxylic acid groups of 16-Mercaptohexadecanoic acid and the reaction of these active esters with amino groups of PMB molecules. The influences of $R_{COOH, soln}$ to the amount of PMB that was immobilized and the kinetics of adsorption and desorption of LPS to/from the PMB immobilized surfaces were investigated with Ellipsometry and surface plasmon resonance (SPR) spectroscopy. Langmuir (one to one binding) and Bivalent analyte interaction models are used to find out the best-fit solutions of the rates of adsorption/desorption rate constant.

Experimental results indicate that LPS bind with PMB in the ratio of $[LPS]:[PMB]=1:2$ when PMB molecules are immobilized in coupling buffer at pH 8.4, while for PMB immobilized at pH 9.4, Langmuir model of $[LPS]:[PMB]=1:1$ gives better results. The binding stoichiometry of LPS with PMB remains the same at 25°C and 37°C suggesting that LPS in gel phase (<30°C) or in liquid crystalline phase(>35°C) does not change its binding stoichiometry. Beside, $R_{COOH, soln}$ was adjusted to modify the surfaces with different surface concentration of PMB. The demonstration of the resistance of mixed SAMs to nonspecific adsorption of PMB and LPS showed the nonspecific adsorption of PMB and LPS on these surfaces both decreased with the increase of $R_{COOH, soln}$. Therefore, the adsorption of LPS molecules on a PMB immobilized SAMs derived from $R_{COOH, soln}$ close to 1.0 should be mainly specific binding between LPS and immobilized PMB in mixed SAMs.

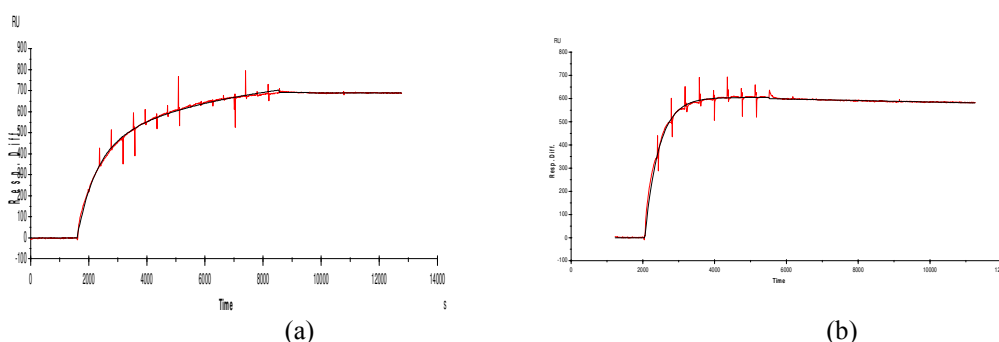


Figure 1. (a) Sensogram obtained by passing 200nM LPS over pure Au-S(CH₁₅)COOH SAM surface to which polymyxin B (2mgmL⁻¹ in 10mM hepes buffer at pH 8.4). Bivalent analyte interaction model are used to find the best-fit solutions to determine the kinetics of association and dissociation of LPS to the surface. (b) Sensogram obtained by passing 200nM LPS over pure Au-S(CH₁₅)COOH SAM surface to which polymyxin B (2mgmL⁻¹ in 25mM phosphate buffer at pH9.4). Langmuir model are used to find the best-fit solutions to determine the kinetics of association and dissociation of LPS to the surface.

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Novel water-in-oil (W/O) microemulsion as gallic acid carrier for pharmaceutical applications. A structural and efficacy study

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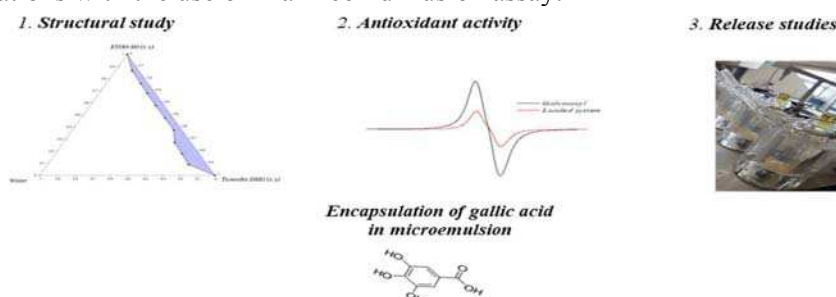
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Gallic acid (GA) is a natural phenolic compound known for its high antioxidant capacity. The last decade the interest for its wide spectrum of activities has been increased with emphasis to its antioxidant, antimicrobial, anti-inflammatory, anticancer, neuroprotectant and antidepressant activities [1, 2]. Prime concern regarding GA targeted delivery is the improvement of its therapeutic efficacy through different strategies for higher bioavailability and prolonged activity. Nanodispersions, due to their unique properties have attracted increasing attention as potential drug delivery systems either as vehicles for topical administration or as bioavailability enhancers for poorly soluble bioactive compounds. Particularly, microemulsions offer a protective and stable environment for the encapsulated molecules, higher solubilization capacity and faster permeation as a result of their small globule size [3].

In the present study, we propose a nonionic water-in-oil (W/O) microemulsion based on extra virgin olive oil (EVOO) combined with sunflower oil (SO) as an appropriate vehicle for the delivery of GA. The system was constructed with the addition of distilled monoglycerides and polysorbate 80, as the nonionic surfactants. Polysorbate 80 is known for its penetration enhancement activity in drug delivery systems and its non-toxic nature. Structural characterization of the system, in the absence and the presence of GA, has been conducted regarding particle size distribution using the Dynamic Light Scattering Technique (DLS). Swollen micelles with diameter of approximately 28 nm were detected. The interfacial properties of the multi-component system were studied by Electron Paramagnetic Resonance (EPR) applying the spin-probing technique. Spin probe's (5-DSA) mobility was relatively decreased due to the complexity of the system, while the addition of GA showed a strong interaction between the encapsulated molecule and the surfactant layer of the system. EPR was also applied for the quantification of the antioxidant activity of the system with the use of the stable free radical Galvinoxyl. The high antioxidant activity of the GA, towards Galvinoxyl, remained after its encapsulation in the W/O microemulsion and the stability of the antioxidant activity examined as a function of encapsulation time. In addition, the cytotoxicity effect of the proposed system was assessed towards the nasal cell line RPMI-2650 in order to examine the suitability of the nanodispersion for the nasal delivery of GA. Furthermore, a microemulsion-based organogel was composed with the addition of the proposed microemulsion in Hydroxypropyl cellulose (HPC) in order to compare the release profile of GA from both formulations with the use of Franz cell diffusion assay.



Acknowledgements: We thank Dr Fabio Sonvico for his kind offer of the cell line RPMI-2650.

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Laser foaming of medicine solutions

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Current approaches of foaming liquids are limited to mechanical methods, pressure and chemical reactions; laser foaming being used in a few cases only for solids. Another method of foam generation was reported by Lazare in [1,2], where thin films of collagen and similar biopolymers were exposed to pulsed laser radiation. Laser pulses have generated micro-foams at the surface of biopolymers thin films. Laser foaming is also used at the surface of plastics, gas bubbles formed in the melted plastic allowing to create patterns, letters, etc.

This paper proposes to study the generation of foams in medicine solutions by exposing them to laser radiation, which, according to the best of our knowledge, is a novel method of foaming liquids.

Results obtained when exposing antibiotic solutions (Vancomycin in water) to a pulsed Nd-YAG laser radiation are the starting point of this paper. During irradiation, Vancomycin molecules are modified and new photoproducts are formed. These modifications were recorded in real time measuring the dynamic interfacial tension at the surface of an air bubble generated in suspended position through a curved capillary in the Vancomycin solutions. Some of the generated photoproducts were hydrophobic and migrated to the air/solution interface leading to a decrease in the surface tension of the solution recorded during irradiation. Several photoproducts generated during exposure of Vancomycin solutions to laser radiation were identified by UV-Vis-NIR absorption spectroscopy, FTIR absorption spectroscopy and liquid chromatography and time-of-flight mass spectrometry measurements [3].

The foams were obtained for two kinds of samples; one is a bulky sample, with a total volume of, typically, 0.5mL in which case the foam is produced if the laser beam has 40mJ minimum average energy. Below this value the foam is not produced and at much higher beam energies, losses of material from the samples in the cuvette may shuffle the foam forming process. The total exposure time to produce a significant foam quantity is two hours, but the start of the foam forming is noticed much earlier, after tens of minutes of interaction with the laser beam.

The sample solution may be exposed to laser radiation as droplet in pendant position in air. The experiments of this kind were made on droplets of 5μL volume, i.e. of 2.12mm diameter and the laser beam average energy to generate foam out of the droplet material was 7 mJ.

In terms of time intervals to obtain foams out of VCM water solutions, the foam production proves to be much faster (one order of magnitude) in droplet form than in bulk. More, in droplet all the material is transformed in foam whereas in bulk only a significant, but not all, part of the solution is generating the foam. The formation of foams in VCM solutions during exposure to laser beams requires a bubble nucleation, most probably generated by the transient acoustic wave induced by the laser pulse, similar to the process described in [1, 2]. A contribution to the foam production may have also the production of Cl₂ after VCM hydrochloride interaction with the laser beam, since the Cl₂ may not migrate outside the liquid/droplet due to the fact that the surface tension of the solution at the interface with the surrounding air is opposed to it.

The foam generation during laser irradiation produces modifications of the VCM molecules, especially to the tyrosine radicals in the molecule.

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The use of ATR-FTIR to study the mechanism of initial bacterial attachment and biofilm development on surfaces coated with different polymers

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The presence of biofilm causes problems in many walks of life, including the food and medical industries, where they can lead to contamination or infection. The irreversible attachment of bacteria on to a surface is the first stage of biofilm development. In this study the interaction between *Pseudomonas fluorescens* biofilm, a model gram-negative biofilm, on a surface treated with three kinds of polymer have been examined via Attenuated Total Reflectance FTIR spectroscopy and fluorescent microscopy.

Using the ATR-FTIR technique, the first stage of bacterial attachment and kinetic of biofilm evolution on the three polymers was registered. Based on the obtained spectra the differences in the bacterial mechanism of attachment depend on polymeric structure and functional groups and their changes over time have been measured. Additionally, the surfaces were examined via fluorescent microscopy to visualize the percentage of surface area occupied by the bacteria after their initial attachment.

Data suggests that the functional groups of the polymers interact with bacterial cells to stimulate them to secrete proteins and polysaccharides which leads to irreversible attachment of bacteria to the surface, and furthermore impacts on the development of biofilm. The results show that for each of the surfaces, the time for irreversible bacterial attachment and mechanism of attachment is closely related to the surface chemistry and interaction between functional group, cells membrane and adhesive proteins.

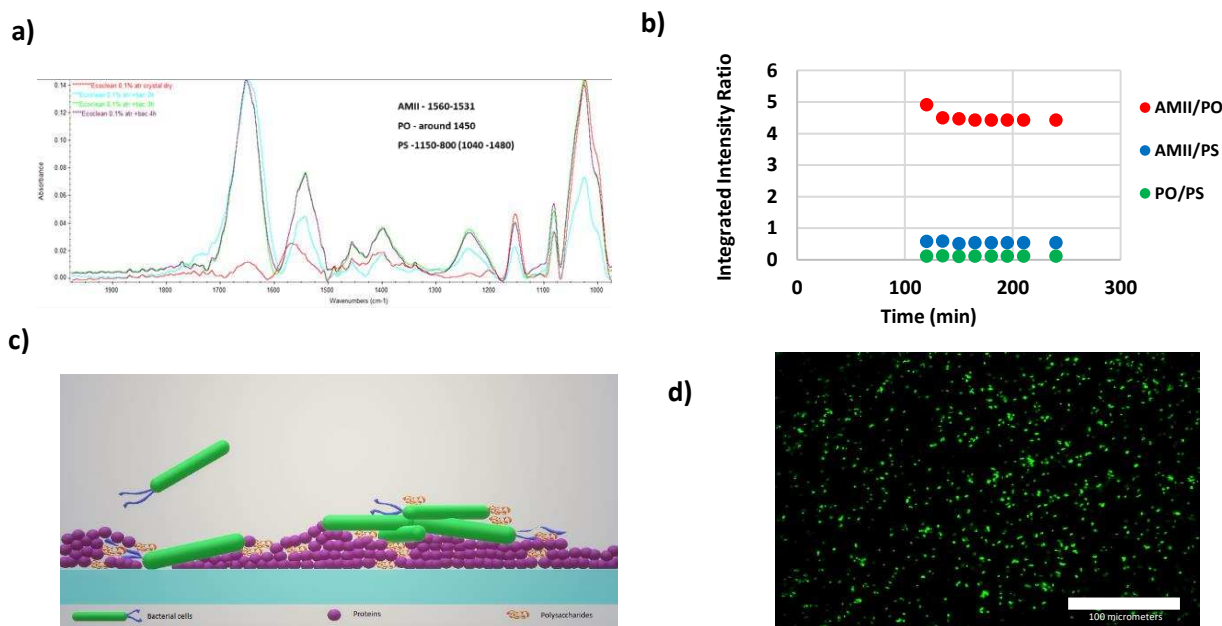


Figure 1. a) The ATR-FTIR spectra recorded shows biofilm evolution in time on Polymer n.1. b) Plot of integrated intensity ratio versus time under 3h growth of *P. fluorescens* biofilm on Polymer 1 layer. Key: AMII- amide II bond; PO- PO2- bond, the signal from phospholipids, phosphodiester; PS- C-O-, O-H coupled with C-O, the signal from polysaccharides. c) Visual interpretation of initial bacteria attachment during biofilm formation on the Polymer n.1. d) The Polymer n.1 surface with bacteria attachment after 3 hours from inoculation.

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Understanding the mode of action of different chemistry on the micro-structure of bacteria

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Due to the progressively increasing resistance of bacteria towards antibiotics, the search for different approaches and alternative therapies to suppress bacterial growth in different cases is a top priority [1]. Bacterial cells need to maintain their membrane architecture for regulating the trans-membrane potential, essential requisites for growth as well as metabolic activity [2]. The cell wall can be disrupted, for example, by cationic antimicrobial agents [2,3] and changes in bacteria size/shape or cell wall thickness, or even proteins and DNA/RNA 3D structure, can be accessed by small angle scattering techniques [4,5].

As a structure sensitive tool, SAXS provides a rapid feedback on drug induced ultrastructural alteration in bacteria which the most studied are *E. coli* cells [6]. At the ESRF we obtained useful SAXS information regarding changes in the bacteria size, cell wall thickness and cytoplasmic polymers radius of gyration when exposed at different pH (2, 7 and 12) as with different concentrations of hydrogen peroxide. As can be seen in figure 1, it was possible to observe multi-scale changes to the bacterial cell. This way, the effect of different actives is being assessed as well by applying mathematical models to quantify the changes in the microorganisms' morphology [7].

In support of the synchrotron SAXS information, dynamic/static light scattering and electrokinetic or zeta potential measurements have been used as bench top techniques [2, 8-10]. Moreover, we aim at obtaining information regarding reaction kinetics, mode of action and structure-function relationships between the active chemistry and the cellular response.

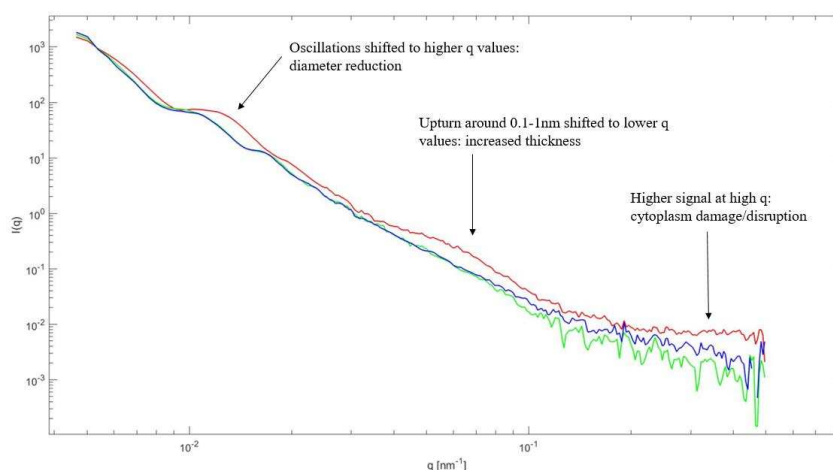


Figure 1. – SAXS signal of *E. Hirae* exposed to pH=2 and hydrogen peroxide (red), pH=7 (green) and pH=12 (blue).

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Molecular dynamics simulations of interactions between carbon nanotube coated with poly(ethylene oxide) and oligopeptides

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Presently, carbon nanotubes (CNTs) belong to the most important building blocks in nanotechnology because of their excellent electronic, thermal, and mechanical properties. Thus, CNTs are extensively studied from the viewpoint of their potential applications in composites, electronics, computers and hydrogen storage [1]. In nanomedicine the applications of CNTs include biosensors, biomolecular recognition devices, molecular transporters, and cancer therapy and diagnoses [2]. The interactions of CNTs with proteins attract attention of scientific community since it plays important role in biochemical processes in biological systems. In case of undesired protein adsorption, CNTs are coated with the protective layer of polymer chains. Thanks to its biocompatibility and nontoxicity poly(ethylene oxide) (PEO) is frequently employed for this purpose.

The molecular dynamics simulations have been performed to study the interactions between PEO-modified CNT and oligopeptides composed of 24 amino acids of different affinity for water. Specifically, oligoglycine and oligovaline represent small and large nonpolar protein moieties, respectively, while oligoserine represents small neutral polar moiety. Oligoaspartate and oligolysine serve, respectively, as representatives of negatively and positively charged polar protein moieties. In order to address the effect of PEO coverage on the interactions between CNT and different oligopeptides the interactions between oligopeptides and uncoated CNT are also investigated. In addition, the effect of water and NaCl at physiological concentration is scrutinized. The radial density distribution of grafted PEO chains and water molecules, the distance of oligopeptides from the coated and uncoated CNT as well as the effect of the CNT on the conformation of oligopeptides are evaluated.

This study is meant to contribute to understanding of the complex interactions between proteins and PEO coated CNTs in biological systems and to uncover the function of PEO, water, and salt in these interactions.

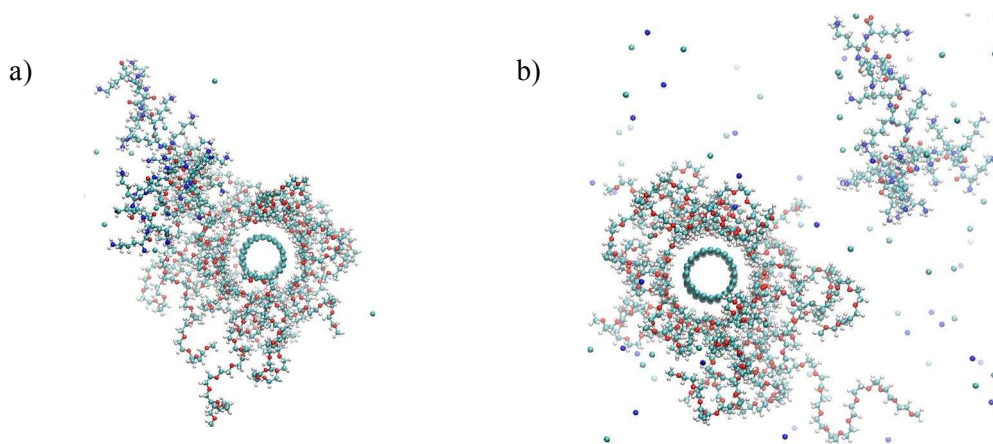


Figure 1. PEO-modified CNT interacting with oligolysine in water under salt free conditions (only the counterions Cl^- are considered) (a) and in water solution with physiological concentration of NaCl. Water molecules are omitted for the clarity.

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Tuning chitosan film properties by changing acidic dissolution conditions

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Food contamination due to the presence of microorganisms is a serious problem. New food preservation systems are being studied to kill or inhibit spoilage and pathogenic microorganisms that contaminate food and reduce shelf life of products. Chitosan films with potential application to food preservation have witnessed great developments during the last years. Chitosan is a cationic polysaccharide with the ability to form films and possessing antimicrobial properties. It is water insoluble but can be dissolved in acidic solutions. In the present work three different acids (acetic, lactic and citric), were used in Chitosan dissolution and both the resultant solutions and formed films were characterized. It was concluded that chitosan -water-acetic acid systems shows the highest antimicrobial activity due to the highest charge density, compared to the mixtures with lactic and citric acid. Viscous solutions are also detected. Chitosan – acetic acid films are also the best suitable since lactic and citric acids remain in the films, changing their properties, which does not happens with acetic acid. The incorporation of acetic acid leads to very resistant films while very fragile but elastic films are formed when lactic acid are incorporated. This was seen by the evaluation of elongation to break forces.

A good selection of the type of acid not only facilitates the dissolution of chitosan but also plays a key role in the properties of the formed solutions and films.

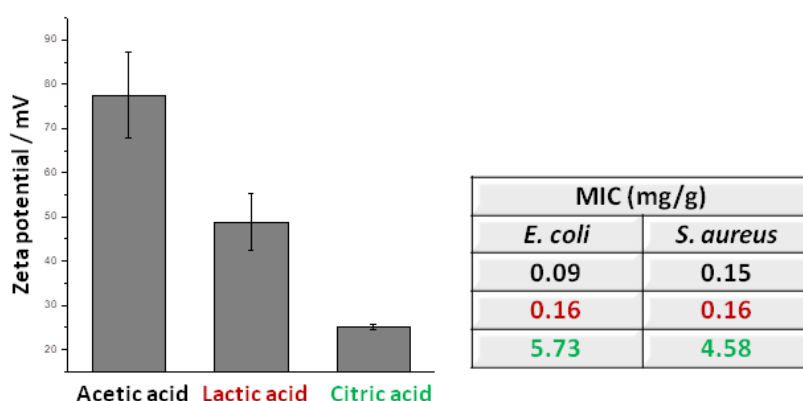


Figure 1. Zeta potential of chitosan solutions (0.5wt%) dissolved with different acids at pH=2 (left); minimum inhibitory concentration of chitosan dissolved in different acids (right).

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Laser Induced Colloidal Structures in Drugs Solutions

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This study presents the laser modifications of properties of two new hydantoin derivatives' colloidal solutions. The obtained results are useful to further investigate the specific interactions of these solutions with other materials, including biological targets.

The two chemical compounds under SZ2 and SZ7 general names are new developed hydantoin derivatives with promising antitumoral [1] and antimycobacterial [2] properties. They were prepared as solutions in ultrapure deionised water at different concentrations.

Using a dedicated experimental arrangement, the samples prepared as bulk or droplets were exposed to laser radiation emitted at 266 nm as the fourth harmonic of a Nd:YAG laser for different time intervals up to 1 h. The laser induced modifications on the colloidal solutions properties were investigated through FTIR and LIF (Laser Induced Fluorescence), as well as by using specific optofluidic measurements (surface tension dynamic and contact angle).

As general presentation, the colloidal solution samples precipitate after 1 h laser beam irradiation and SZ7 solutions change their colour. Furthermore, if SZ2 irradiated solution sample is centrifuged for a couple of seconds, a very stable foam is produced.

A general result of the experiments' analysis is that modifications are induced in molecular structures of hydantoin derivatives by exposure to laser radiation of microdroplets or bulk samples. This fact evidences that in both cases molecules are photoreactive. Changes produced in microdroplet presentation are faster than in bulk exposure. This could be due to higher ratio between the number of photons in the laser beam and the number of molecules in microdroplet comparatively with bulk samples [3].

The vibrational fluctuations observed in FTIR spectra upon 266 nm Nd:YAG pulsed laser beam could suggest the braking of SZ2 molecule and the separation of the radical attached to the thio-hydantoin ring accompanied by the rearrangement of the molecules and hydrogen bonds formation. Likewise, the interaction of SZ7 solution with laser radiation may conduct to the cleavage of the alkyl side-chain of the thio-hydantoin ring and could affect the thio-hydantoin structure itself [4].

The resonant interaction of laser beams with these hydantoin derivatives needs to be further studied, for example with respect to the photoproduct identification and their isolation. Performing microbiological assays for 'cocktail' photoproducts solutions is also of interest. The main conclusion at this stage is that our investigated materials are photoreactive, this opening many possibilities both in biomedical field, and in other industrial activities involving the use of hydantoins, as well.

Acknowledgements: The authors acknowledge the financial support of the UEFISCDI by project number PN-III-P2-2.1-PED-2016-0420 and the PN Nucleu project: 18.13/2018.

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Encapsulation of Mediterranean plants extracts obtained by means of non-conventional high voltage electrical discharges method

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Mediterranean plants are rich in biologically active compounds (BACs) such as essential oils, antioxidants and volatile compounds, which often have unique features, from nutritive to medicinal properties, as well as antioxidant and antimicrobial activities. These remarkable properties of BACs can be used in the production of functional foods.

From the economical point of the view, there are challenges to reduce the processing costs and to minimize the use of organic solvents. Thus, there is a need towards the implementation of innovative strategies and non-conventional methods, which are following the concept of Green Technology [1]. Extractions by means of high voltage electrical discharges (HVED) resulted to be very efficient in recovering BACs from plants. HVED can give highly valuable plant extracts with regards to an environmentally friendly way that follows the nowadays preferred „green concepts“. These procedures are rapid, convenient, economical, sustainable, and efficient, and with great potential for industrial upscaling [2,3].

Most of these biologically active compounds have low water solubility, strong flavors/odors and are generally unstable and degrade easily under conventional processing and storage conditions. Encapsulation of these compounds is an excellent choice to stabilize them and mask their strong flavors and odors, thus protect them and enable their delivery in food systems as well as the controlled and targeted release.

In our research, extracts and essential oils obtained by means of the non-conventional HVED method and with use of „green“ solvents, are to be implemented into different food matrices in order to obtain food products with high added values, e.g. functional foods. However, in order to successfully implement BACs into these food matrices, encapsulation technology was employed. Use of different biopolymeric carriers for the proper optimization and production of the microcapsules was investigated. Obtained HVED extracts with the highest share of sought BACs were encapsulated with Büchi Encapsulator B-390 via the simple ionic gelation method. Also, lyophilization was used as a method to compare the stability and longevity of encapsulated BACs vs non-encapsulated. Either hydrophilic BACs or lipophilic as well as the combination of both were encapsulated into different biopolymeric carriers with different number of layers.

Combination of the main carrier, sodium alginate, different co-biopolymers was more thoroughly investigated. Physicochemical analyses were performed for different combinations as well as the morphology of obtained microcapsules. Additional coatings were also applied to obtain microcapsules with optimal properties for desired retention and release of the encapsulated bioactive compounds. Release kinetics of BACs from microcapsules were also evaluated and statistical predictions for desired achievements were performed.

In the end, obtained optimal microcapsules will be implemented into desired food matrices with sought properties.

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Enhanced penetration in 3D extracellular tumoral matrices of Au nanocarriers through passive and stimuli-responsive delivery

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Nanoparticles offer a great potential as drug delivery systems [1]. However, in order to design efficient tumor-penetrating drug nanocarriers, the relationship between physicochemical properties (e.g. size, form, charge) of such nanocarriers and their therapeutic activities must be understood in detail. In this work we explored the influence of NP size in the delivery of mitomycin (MEMC), a DNA alkylating agent, to tumor cells using classic monolayer cell cultures and multilayer tumor spheroids models [2]. Both passive targeting and actively enhanced cellular internalization play significant roles in tumor-targeted therapy. Programmed specific responsive ligands on the nanoparticles expects that nanocarriers respond to external stimuli and transform into more cell-interactive forms upon arrival at the tumor tissue for enhanced cellular internalization. In this perspective, we have also recently described a supramolecular chemistry approach to control the cellular uptake of small AuNPs (2 nm) based on a host–guest interaction between pyranine and an oligocationic covalent cage. We proved that attaching enough pyranine molecules onto AuNPs hamper their cell internalization owing to the build-up of a high negative potential on their surface. Addition of cage switches the negative surface into positive, and induces the cellular uptake of AuNPs [3].

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Interfacial properties of compounds derived from hemicellulose

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Softwood is a natural source of one of the most abundant polysaccharides found in plant cell walls. Hemicellulose (galactoglucomannan, GGM) makes up to 25% of the wood in Sweden, however, most of it is treated as waste from agriculture and forest industries. Our goal is development of sustainable and efficient methodology based on biocatalytical processes to convert GGM into products with added value like surfactants for detergent formulations and coatings for wood and paper. This study is focused on interfacial behaviour of compounds derived from hemicellulose. This includes the surface tension and micelle formation of the novel hexyl mannoside surfactant synthesized within the project by means of enzymatic catalysis using β -mannanase and alcohol acceptor [1]. Furthermore, the influence of the extraction technique on the adsorption kinetics of unmodified GGM to spin coated cellulose surfaces will be presented. Using ellipsometry and neutron reflectometry measurements we will show how adsorption behaviour of GGM can be controlled by changing galactose substitution degree and molecular weight.

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Surface chemistry, morphology, friction and nanostructure of fibres and fabrics.

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Natural and man-made fibres possess desirable properties such as structural integrity, high mechanical performance and processability, making them functional components in a wide range of applications [1]. In many cases (e.g. personal care products or textiles), the sensation of touch facilitated by fibres is a key performance indicator. Although different empirical methods have been developed to introduce softness into synthetic fibres (e.g. crimping and surfactant additives) to mimic that of natural fibres, there is still a lack of understanding of how the sensation of touch on fibres could be tailored for different synthetic fibres in different applications. On a fundamental level, fibre softness can be related to frictional properties they mediate, which are in turn related to their surface topography, nanomechanical characteristics (e.g. stiffness and adhesion) and crystal structure. Optimisation of these properties via fibre processing is thus essential.

In this study, optical microscopy (OM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-Ray diffraction (XRD) have been used to characterise the surface topography, morphology and crystal structure, respectively, of fibres and fabrics [2, 3]. Seven commercially available synthetic fibres have been studied. These fibres are from three different suppliers and vary in composition and surface morphology. Two of the samples are nonwoven sheets with the rest of them being single fibres [4]. The fibre geometry, especially its crimping, was observed by OM (Fig.1 a). SEM (Fig.1 b) revealed differences in fibre surface topographies, with some of them exhibiting smooth surfaces whereas others the presence of irregular aberrations. High resolution AFM (Fig.1 c, d) provided detailed topography and mechanical properties across fibre surfaces such as rigidity, stiffness and adhesion. The results suggest that erucamide (a surfactant additive) in the fibre might have migrated to the fibre surface during processing, giving rise to the observed surface features. Preliminary XRD on fibre bundles (Fig1.d) show that the crystallinity of the fibres differed, which underpin all the above observed topographic and mechanical properties. We will discuss such detailed morphological and structural information in the context of the sensation of touch mediated by these fibres.

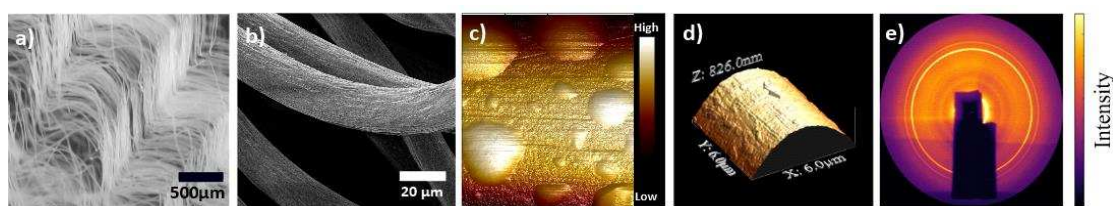


Figure 1. a) OM crimping in fibres; b) SEM image of the same fibres; c) QNM AFM image of surfactant additives on a single fibre surface; d) 3D AFM image of fibre with surfactant; and e) XRD of bundles of fibres.

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Colloidal stabilisation of permanently-magnetic nanoplatelets in aqueous suspensions for bio-medical applications

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The stabilisation of nanoparticles in physiological buffers is essential for their use in various biomedical applications. The colloidal stabilisation is especially challenging when the nanoparticles display platelet shape and permanent magnetic moments. Magnetic barium-hexaferrite nanoparticles (BFNPs) appear in the form of very thin platelet crystals – nanoplatelets and are permanent nanomagnets with the easy axis of magnetisation oriented perpendicular to the platelet. Therefore, in addition to van der Waals attractive forces, long-range magnetic dipole-dipole interactions have to be considered when preparing their stable suspensions. The platelet shape of BFNPs is also an important factor, as the inter-particles forces are larger for the plate-like particles than for spherical particles of the same volume.

In this work, we successfully stabilised the suspensions of BFNPs in physiological buffers used for *in-vitro* tests on cells. The BFNPs, ~50 nm wide and 3 nm thick, were synthesised hydrothermally. First, the BFNPs were stabilised in aqueous suspension with adsorption of citric acid, which provided high zeta potentials at high pH values. Subsequently, the nanoplatelets were coated with a thin (2-3 nm), uniform silica layer using a modified Stöber process. The silica layer maintained a high zeta potential and provided a non-magnetic layer that reduces magnetic dipole-dipole interactions. Both citric acid-adsorbed and silica-coated BFNPs were colloidally stable in deionised water but slowly aggregated in complex aqueous media, such as cell culture media (DMEM medium with 10% fetal bovine serum). The stability of the BFNPs in such complex media was only enabled by grafting with dextran. The dextran was pre-reacted with (3-glycidyloxypropyl)trimethoxy-silane and then reacted with silanol –Si-OH functional groups at the surfaces of the silica-coated nanoplatelets. The covalently-bonded dextran assured the colloidal stability of the BFNPs also in the physiological buffer by providing steric repulsive forces.

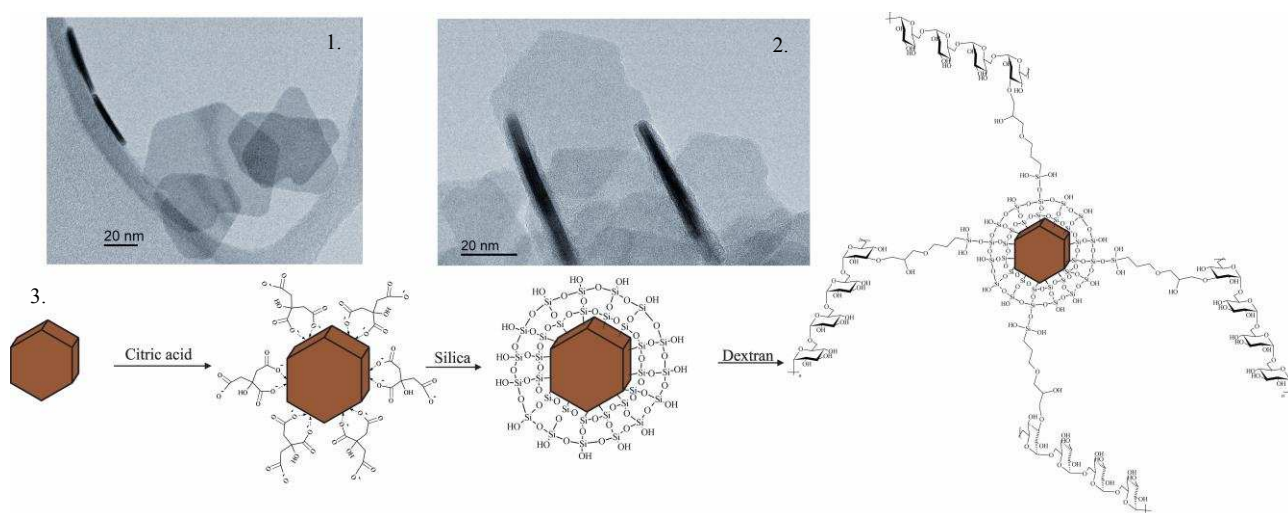


Figure 1. TEM image of as-synthesized BFNPs, 2. TEM image of silica-coated BFNPs, the thin amorphous silica layer can only be seen when platelets are oriented perpendicular to the surface, and 3. Schematic presentation of the coating of the BFNPs.

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Black foam film method in studies of pulmonary surfactant disorders

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Pulmonary surfactant (PS) is a multicomponent complex of lipids and proteins which covers the alveolar surface. The pulmonary surfactant system has proven to be of crucial importance to breathing process. The lack, deficiency or inactivation of PS is the cause of severe respiratory disorders, sometimes lethal, such as the Neonatal Respiratory Distress Syndrome, or the pulmonary dysfunction related with different processes as injury, inflammation or sepsis, due to action of a variety of inhibitory substances (e.g., plasma proteins, free fatty acids, lyso- and unsaturated phospholipids).

The gained knowledge on black foam films (BFF) from aqueous solutions of phospholipids, phospholipid-protein mixtures and PS (or its components) is successfully applied for the investigation of structure and stability of alveolar surface. The conditions for BFF formation are close to the physiological in order to “serve” the in vivo situation. Microscopic foam films studied by means of microinterferometric technique enable measuring the dependence of probability W of BFF formation on bulk concentration C , dependence of film thickness h on electrolyte concentration and isotherms of disjoining pressure Π vs. film thickness h . The very sensitive parameters related to BFF formation and stability are used as a diagnostic method for foetal lung maturity assessment and to analyze the PS properties.

In the present study, the obtained dependence of probability W for BFF formation versus bulk concentration for films from gastric aspirates (GA) from healthy neonates are compared with data for GA samples from prematurely born babes. The updated version of Exerowa black film method will be presented.

The inactivation effect on PS surface activity due to action of different type of inhibitors is also investigated by the BFF method. The results show that addition of inhibitors causes destabilization of the BFFs and formation of mixed adsorbed layers at the solution/air interfaces. The studies also outline the perspective for the potential application of the BFF method for investigating the effect of a variety of inhibitory substances and could help in better understanding of processes of pulmonary surfactant inactivation in pathological conditions.

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Electrostatically attached microbes affect processes of biofilm formation

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The deposition of charged polyelectrolytes to surfaces using the layer-by-layer (LBL) approach [1] allow the electrostatic modification of biotic and abiotic surfaces [2-3]. Using this approach, we electrostatically modified the surface of bacterial cells and the metal surface to construct a multilayered artificial biofilm structure on the the steel surface (**Fig. 1**). By applying such artificial biofilm, we aimed to (i) affect the early stages of microbial attachment to the raw material, (ii) alter the successive development of natural biofilms and (iii) change the final composition of the surface bacterial community. This way the MIC-promoting community is not established, because the succession process, which normally leads to the development of microbiologically influenced corrosion (MIC), is altered. This ecological and evolutionary (ECO-EVO) approach used here does not actively prevent the growth of unwanted target bacteria, but rather steers the development of a community towards the desired final composition (Fig. 1).

For the application of the LBL approach we used combinations of positively and negatively charged polyelectrolytes, PEI[+]-PAA[-] and chitosan[+]-lignosulphonate[-]. The use of oppositely charged polyelectrolytes allowed us to change the cell surface layer-by-layer as well as apply the encapsulated cells to the oppositely charged surface in the same manner (**Fig. 1**). The chosen antibiotic producing bacteria and the polyelectrolytes both acted anti-bacterially, forming the basis for alteration of the natural communities that were to develop on the exposed metal surface. The prepared artificial biofilm was tested in the sea environment and the results showed significantly changed the composition and diversity of natural biofilms. As demonstrated by DGGE analysis and 16S rRNA gene sequencing their diversity was the highest on the raw metal surface, while the applied artificial biofilm out-selected a subset of only a few bacterial taxa, the most importantly excluding those previously associated with MIC.

In summary, our approach allows a controlled delivery of bacterial cells to the surface using electrostatic interactions, resulting in the construction of an artificial biofilm that can alter the succession of natural surface bacterial communities.

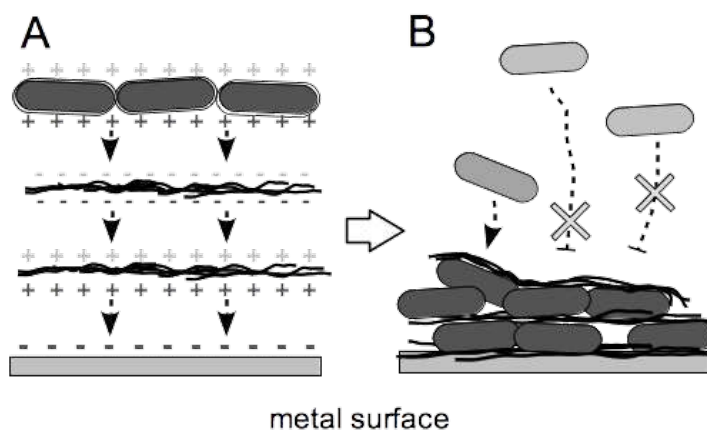


Figure 1: Artificial biofilms. (A) Electrostatic attachment of cells to the surface using charged polyelectrolytes to prepare multilayered artificial biofilms. (B) Artificial biofilms (dark gray) select the population of cells that attach to the surface and join the surface community.

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Active Pharmaceutical Ingredient (API) thin films studies by Grazing-Incidence X-ray Scattering and Diffraction

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Dissolution properties of drug molecules strongly depend on the surface morphology and the crystalline structure. Complex multicomponent systems (water-soluble inclusion complexes, self-emulsifying systems, nanosuspensions) are intensively studied for their potential of overcoming poor aqueous solubility and thus bioavailability. However, numerous interactions within such systems involve the risk of unpredictable changes during production or storage. In pharmaceutical production drug molecules are often crystallized in bulk solutions, which may fail in terms of inducing specific polymorphs. Altered molecular arrangements can be achieved by introducing environmental or geometrical constraints, i.e. by crystallization on a solid surface. Surfaces minimize the system's entropy and thus enable faster nucleation which makes polymorphic forms accessible via a solid substrate.

Pharmaceutical-relevant examples like phenytoin, clotrimazole and paracetamol reveal distinct morphologies or surface-induced polymorphism. Variation in the morphology, in particular the crystal size, as well as subsequently introduced API top-coatings allow adjusting the dissolution properties.

We investigate the film-forming properties of selected APIs and the influence of morphological variations on the dissolution behavior. Thin films are studied in dependence of different annealing/temperature-treatment processes. The surface and crystalline properties were investigated by atomic force microscopy and grazing-incidence X-ray scattering (GISAXS, GIXD).

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Unravelling the interfacial behaviour of polyelectrolyte–surfactant mixtures with technological interest

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The understanding of the physico-chemical bases underlying the behavior of polymer – surfactant mixtures in bulk and upon adsorption at interfaces presents high interest due to the importance of such systems in different technological and industrial fields, ranging from drug delivery systems to mineral processing, and from tertiary oil recovery to the development of cosmetic formulations for hair care [1].

In this communication, we present a comprehensive study of the behavior of mixtures of cosmetic interest formed by poly(diallyldimethylammonium chloride) and different rhamnolipids, which differs on their hydrophilic character. For this purpose, the complexation occurring in bulk has been correlated to the adsorption of these mixtures at interfaces (solid or fluids). This is interesting because conditioning performance is related to the adsorption of polyelectrolyte – surfactant complexes onto the intricate surface of hairs, whereas the cleansing and foaming properties of the mixtures are related primarily to the behavior of these systems at the water/vapor interface.

We have combined several bulk characterization techniques: dynamic light scattering, ζ -potential, turbidimetry and surface sensitive techniques such as tensiometry, quartz crystal microbalance, ellipsometry, neutron reflectometry and atomic force microscopy. This has allowed us to obtain a direct correlation between the bulk behavior and the adsorption properties. The study of the adsorption of the mixtures onto solid surfaces has shown an increase of the adsorbed amount as the composition is closer to the onset on the phase separation, which can be considered as an example of a precipitation enhanced adsorption [2]. It is worth mentioning that in the studied systems, phase separation is not associated with the formation of neutral complexes as in most of systems studied in the literature, as in this case it is associated with the formation of complexes involving several polymer chains which remain overcharged. The type of surfactant and its concentration allowed us to tune the adsorbed amount and the hydration properties of the adsorbed layers onto solid surfaces. When the adsorption at the water/vapor interface is considered, a direct correlation between the composition of the bulk complexes and the composition of the interface was found. This is an important difference with diluted systems [3,4]. This study provides important insights on the conditioning effect, lubrication (water content) and cleansing properties of polyelectrolyte – surfactant mixtures.

Acknowledgements: This work has been funded by MINECO and L'Oréal S.A.

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Bio-nano interactions: using iron oxides for downstream processing applications

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The so-called nanoera is leading to the diffusion of nanotechnology in all areas of research. Its benefit for medicinal applications is being fully exploited with continuously expanding application margins. Nanobiotechnology, however, is still generally limited to research studies, whereas the leap into the practical utilization of nanosystems in biotechnology is still lacking. This absence is surprising considering the real potential for enhanced results deriving from the colloidal dimension. Furthermore, the environmental changes in the world demand greater sustainability in all sectors, including industrial production. Here, biotechnology offers a true opportunity for more sustainable processing routes. Nevertheless, much more effort is needed with deeper and more targeted investigations. Downstream processing in particular, which is usually a time-consuming and expensive sequence of separation and purification steps, could benefit from nanosystems for bioseparation purposes far more than it currently does. The approach proposed here is to harness magnetic forces to develop a platform of separation strategies using iron oxide nanoparticles as adsorbents for biomolecules to meet downstream requirements.

Magnetic nanoparticles have been a research focus in the nanofield for several decades, generating an increasing number of publications and patents. Their synthesis, coating and functionalization is carried out employing multiple routes. We focus specifically on the use of the simplest and least expensive version, the bare iron oxide nanoparticles. Advantages for processing include their high specific surface area, the lack of degradation over time or due to environmental conditions, as well as the absence of mass transfer limitations. Large scale biomaterial recovery is carried out using high-gradient magnetic separation, a method which enables the reduction of processing steps due to the direct capture of the target material from the cell homogenate or fermentation broth [1]. Our work combines a thorough understanding of the nanoparticles' surface properties and the mechanisms at the interphase of the aqueous medium with interaction studies of different classes of materials, from amino acids [2] to peptides [3-4], proteins [5] and whole cell systems. We develop strategies to control biomolecule adsorption and desorption based on our understanding of the binding forces responsible for the bio-nano interaction and the impact of environmental conditions. Moreover, we demonstrate that the binding patterns reported in laboratory scale studies open exciting doors for sustainable and economic processing routes beyond the limits of conventional purification processes. By means of numerous examples of magnetic biomolecule recovery, e.g. of self-engineered tagged proteins or of microalgae cells, we illustrate the range of application for downstream processing goals.

From our work of the last few years, we know there are still many unanswered questions about working with colloidal systems. Issues such as how the agglomeration behaviour of nanoparticles influences their capacity for biomolecule adsorption, the symbiotic role of different types of biomolecules in enhancing nanoparticle surface utilisation, the role of the ions from the medium in affecting the probability of binding or unexpected adsorption results are all questions which cannot be answered at the moment, which go beyond our own understanding and are formulated to seek possible answers. For sustainable progress in downstream processing, further knowledge on the driving mechanisms at the bio-nano interface is essential.

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In Situ Study of the Growth and Ripening of Poorly Water-Soluble Organic Nanoparticles Prepared by Antisolvent Precipitation

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The antisolvent precipitation is an established bottom-up approach to produce nanoparticles (NPs) of poorly water-soluble active pharmaceutical ingredients (APIs) [1,2]. It is intended to enhance the bioavailability of an API by producing smaller particles, but little is known about the growth and the stabilization mechanism of organic NPs during the precipitation process. However, this knowledge is crucial for the production of smaller and long-term stable API NPs.

Studying the formation and growth of poorly water-soluble organic nanoparticles with in situ small-angle neutron scattering (SANS) enables us to characterize the growth and the stabilization of the particles during the precipitation process with a temporal resolution in the ms regime. The influence of two structurally different and commonly used stabilizers (sodium dodecyl sulfate (SDS) as an anionic and tetraethylene glycol monododecyl ether ($C_{12}E_4$) as a nonionic surfactant) on the growth and ripening of the model API fenofibrate has been studied (cf. figure 1). Fenofibrate has been solved in ethanol and mixed together with 25 wt% surfactant solved in D_2O with a ratio of 1 : 9 using the stopped-flow technique.

The analyses of first in situ SANS data reveal an early beginning of Ostwald ripening for all surfactant systems already after the first 250 ms. Since nonionic surfactants have low critical micelle concentrations, we additionally studied a micellar stabilization for $C_{12}E_4$ (cmc = 0.08 mM), which solubilizes the API, reducing the supersaturation and leading to an increased growth rate and an inhibited ripening (cf. right side of figure 1). The results for the used model API fenofibrate will be compared to small (below 20 nm) and long-term stable alkane NPs, also prepared by antisolvent precipitation and without the need of any additional surfactant.

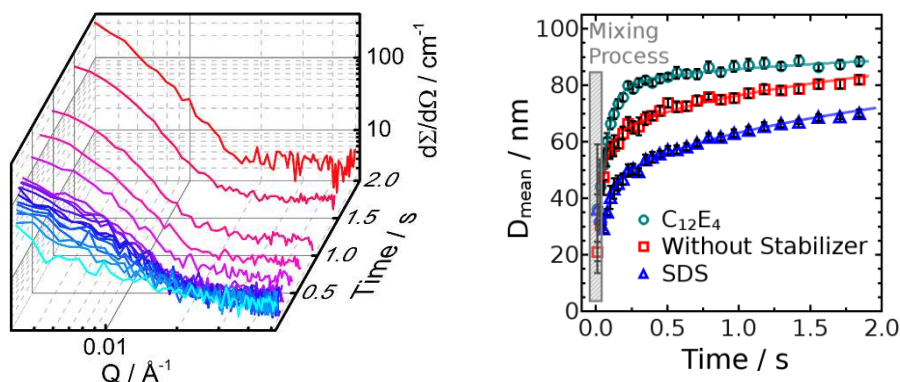


Figure 1. *left:* First in situ SANS data of the fast growth kinetics of nanoparticles of the model API fenofibrate during the antisolvent precipitation with SDS as anionic surfactant. *Right:* First analyses demonstrate the growth of fenofibrate nanoparticles during the first 2 seconds. The calculated mass-weighted mean diameter of the used log-normally distributed particles sizes is shown as a function of time. The model reveals an early beginning of ripening for all surfactant systems already after the first 250 ms.

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Interfacial Properties of Ophthalmic Surgery Silicone Oil in Blood Serum Solutions in Relation to Emulsification

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We report a study concerned with the interfacial properties and emulsification features of high viscosity Silicone Oils (SO) in the presence of blood proteins.

SO are commonly used in a variety of ophthalmologic surgeries to replace the vitreous body: the gellike substance that fills the vitreous cavity of the eye. Such procedure, called vitrectomy, is performed to treat several pathological or traumatic vitreoretinal conditions. The main drawback of using these SO is their tendency to emulsify in the aqueous phase produced in the ocular cavity. This results in various post-surgical complications in a significant number of patients. With the SO presently in use, emulsification invariably occurs, often in a period shorter than the time suitable to achieve the complete healing of retinal damages. Elucidating the role of endogenous surfactants in the above emulsification phenomena is an important step to support the development of new SO for ophthalmology more resistant to emulsification.

In the present study, therefore, we have investigated the adsorption kinetics of blood serum in an aqueous buffer solution at the interface with a 1000 cSt Silicon Oil, also obtaining the equilibrium interfacial tensions.

In addition, the viscoelasticity module of these adsorption layer has been measured as a function of the area perturbation frequency, in a range between 10⁻³ and 10⁻¹ Hz.

These measurements have been compared with those obtained using only some key blood proteins, such as albumin and globulin, in order to identify the components most involved in the emulsification process.

Overall, the results show significant effects on the interfacial tension and the dilational viscoelasticity compatible with a facilitation of the formation of stable emulsions.

These results have been also compared with preliminary emulsification tests.

Surface properties and foamability of Saponine and Chitosan solutions

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Natural surfactants at fluid interfaces are widely investigated as stabilizers of emulsions and foams for many applied fields where it is important to have bio-compatible and biodegradable products, such as body-care and bio-medical fields.

The present work focuses on the properties of solutions containing Saponine, which is a natural surfactant mainly extracted from some plant species and Chitosan, a bio-active bio-polymer with antibacterial and antifungal properties and for that used as natural preservative. We investigated the surface properties of these dispersions in comparison with the properties of formation and stabilization of the respective liquid foams.

To this aim, measurements of surface tension and dilational rheology were carried out by a Profile Analysis Tensiometer (PAT-1, Sinterface) varying the composition of the solutions, while the foamability and the behaviour of the obtained foams studied by different methodology based on membrane and syringe methods.

The results show that Saponine presents very important amphiphilic properties, characterized by, a strong decrease of surface tension and high values of the dilational viscoelasticity, already at very low concentration. These peculiarities are relevant for its utilization as foam stabilizer. On the other hand, the presence of Chitosan, seems to be very important because tends increase the viscoelastic modulus of the Saponin adsorption layer and to enhance the foamability of the system, under defined conditions.

Aim of the present study is to contribute to the development of new formulations of biodegradable and biocompatible foams for industrial application, able also to reduce the use of synthetic surfactants in commercial products.

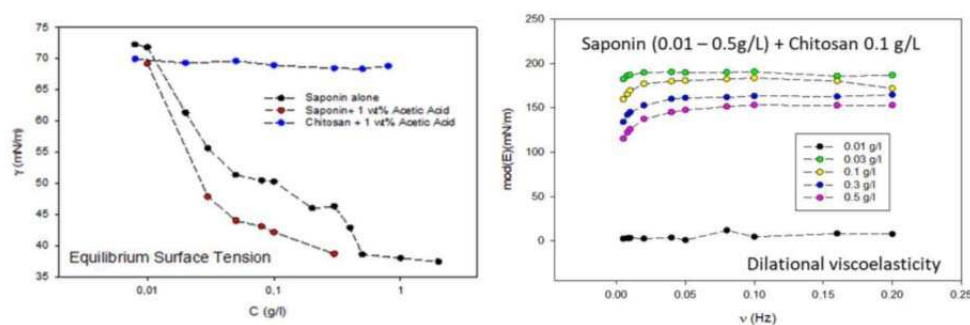


Figure 1. Surface tension and dilational viscoelasticity of Saponine and Chitosan solutions

Acknowledgements: The work has been financially supported within the project “Biocompatible particle stabilized foams and emulsions as carriers for healing agents”, PAN-CNR Bilateral Agreement 2017-2019

The re-assembly of phosphatidylethanolamine and phosphatidylcholine liposomes upon hydrolysis with phospholipase C

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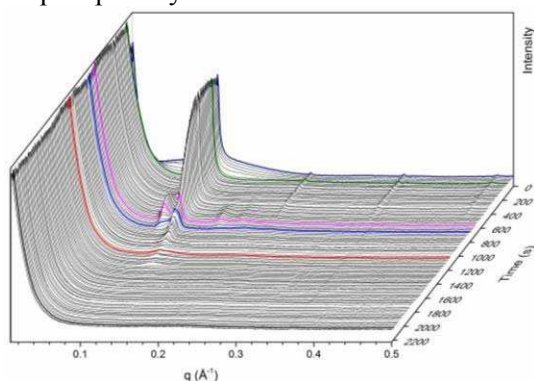
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In the search for better treatments, lipid based drug delivery systems are used to improve therapeutic outcomes. However, the *in vivo* fate of these materials is still unclear. There remains considerable uncertainty about basic processes like the nuances of enzyme function and consequently, the mechanism of lipolysis and the malfunction of lipases in diseases. Lipolysis can modify the self-assembly of a range of different lipid colloids, where the extent and direction of the reaction is contingent on the presence of bile salts and pH [1]. For instance, upon hydrolysis: medium chain triglyceride emulsions transition to vesicles [2]; monoolein cubosomes transition from inverse cubic through a variety of inverse nanostructures to dispersed oil droplets [3]; milk emulsions transition to a variety of differently ordered nanostructures [4]. The selective lipolysis of lipids from the interface of lipidic particles can also direct phase transitions [5, 6], where the products of hydrolysis align themselves within the lipid bilayer according to their physicochemical properties [7].

Towards the development of lipid based nanomaterials as drug delivery systems, this study seeks to understand nanostructural changes of phosphatidylcholine (PC) and phosphatidylethanolamine (PE) based particles during hydrolysis with phospholipase C; an interfacially active enzyme that was until recently viewed only as an instrument of lipidic degradation. Both PC and PE are extensively used in different ratios in the formulation of liposomal drug delivery products, however the molecular mechanisms of their respective roles in the final delivery to the site of action is not completely understood. Thus, in this study, lipolysis as mediator for triggered drug release and vesicle fusion is investigated using time-resolved SAXS (Fig. 1), NMR and cryoSEM. As the different phospholipids play different roles both in lipid homeostasis as well as drug delivery, it is important to study the dynamic behaviour of these formulations in order to understand both the contradictory events of unexpected drug release and the enhancement of drug release by this mechanism.

A. phosphatidylethanolamine



B. phosphatidylcholine

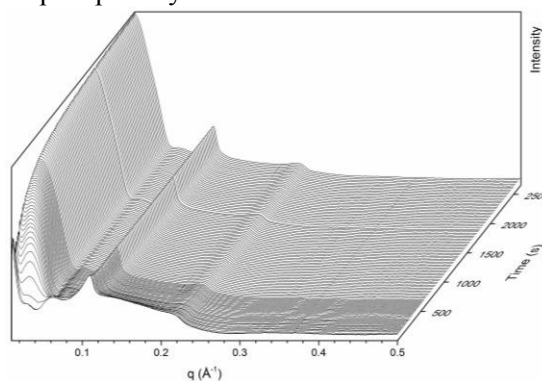


Figure 1. The hydrolysis of PE and PC particles by phospholipase C as observed via time-resolved SAXS. Both particle types undergo a series of phase transitions as lipolysis progresses.

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Enhanced release of the antioxidant flavonols induced by magnetic field of very low frequency

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Due to their specific porous structure and superparamagnetic property, mesoporous aggregates (MAs) could allow physical delivering of drugs to the desired target area through the influences of an external magnetic field [1]. Thus, the total drug concentration administered into an organism is reduced drastically and side effects are avoided. Intention was to use the flavonol loaded agglomerates of magnetite nanoparticles as vectors that can be directed by means of magnetic field gradient towards a certain location.

Loading of poorly soluble, hydrophobic flavonols (quercetin, myricetin and myricitrin) onto mesoporous aggregates comprised of uncoated magnetite nanoparticles and their release under the influence of permanent and/or alternating magnetic field was investigated [2]. Besides low toxicity due to the lack of nanoparticle coatings the investigated mesoporous structures are shown to possess an advantageous feature of high loading efficiency of flavonols [3]. In addition to electrostatic interaction between hydroxyl groups at the surface of the Fe₃O₄ MAs, governing the initial stages of drug loading, the interactions between flavonol molecules contribute to high loading efficiency. The stabilization is considered crucial especially in biological applications. However, if the idea is to bring unusually high quantity of flavonol into the intestinal tract the use of flavonol loaded agglomerates seems reasonable.

This study confirmed that the mesoporous Fe₃O₄ structures presents an universal, stable and excellent drug delivery material particularly able to load and release with high efficiency flavonols of different physico-chemical and/or structural properties. The fine-tuning of their drug release by means of weak external magnetic field oscillating with very low frequency was demonstrated indicating the high potential of mesoporous material as drug carriers.

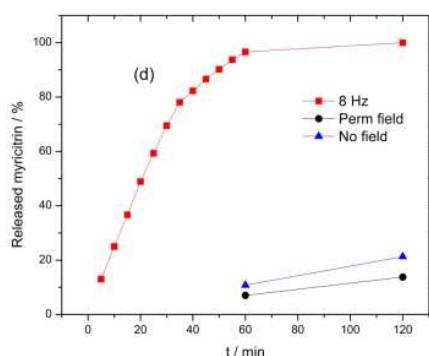


Figure 1. Comparison of cumulative release profile of myricitrin from MA with feeding ratio 1:6 in PBS/EtOH (50:50 v/v) without and with permanent and alternating magnetic field (8Hz).

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Helicene grafting on halloysite nanotubes for drug delivery: layer structure, surface selectivity and pH triggered drug release

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Halloysite nanotubes (HNTs) have recently emerged as promising candidates for targeted drug delivery [1]. HNTs are low-toxic and low-cost aluminosilicate clays with nanotubular structure, presenting a positively charged $\text{Al}(\text{OH})_3$ inner lumen and a negatively charged SiO_2 outer surface, which can support a selective functionalization of the two surfaces. In this work, we investigated the loading and release mechanisms of the tetrathia[7]helicene (7-TH) derivative linked via an imine bond to HNTs. The 7-TH scaffold displays promising intercalation properties for DNA, with a high degree of enantioselective recognition [2]. Moreover, a 7-TH derivative showed potent inhibitory activity against telomerase, demonstrating the great potential of 7-TH as therapeutic cytotoxic molecules [2,3]. We analyzed functionalized HNTs as well as Al_2O_3 and SiO_2 layers, as models of the inner and outer surfaces, by means of surface-sensitive synchrotron-based techniques (XPS, UPS and NEXAFS spectroscopies). The oxide surfaces were analyzed both before and after functionalization with helicene derivatives through a (3-aminopropyl)triethoxysilane (APTES) linker [4]. Furthermore, the effect of a treatment in acidic conditions was investigated to prove the release of the helicene moiety from the oxide carrier at the extracellular pH of tumor cells. The surface state and atomic ratios of key elements within the organic layer determined by XPS proved the successful coupling of the helicene aldehyde to the APTES-functionalized films, clarifying differences in the reactivity of the two oxides. The sulfur peak confirmed the results obtained on the model films, supporting the reliability of the two adopted model surfaces. Moreover, NEXAFS results provided indication of a preferential orientation of helicene moieties at the oxide surface, which is lacking in APTES-functionalized layers. A further confirmation of the complete release of helicene moieties upon treatment in mild acidic conditions was given by NEXAFS spectra, showing a random orientation of the C and N functional groups after the release treatment. Preliminary *in vitro* toxicity tests on cancer cell lines characterized by different extracellular pH values show data consistent with a pH-triggered release of the 7-TH moiety, as also supported by kinetics data about the release in various physiological conditions. Work is currently under way to achieve a selective functionalization of the inner and outer surfaces by orthogonal functionalization strategies.

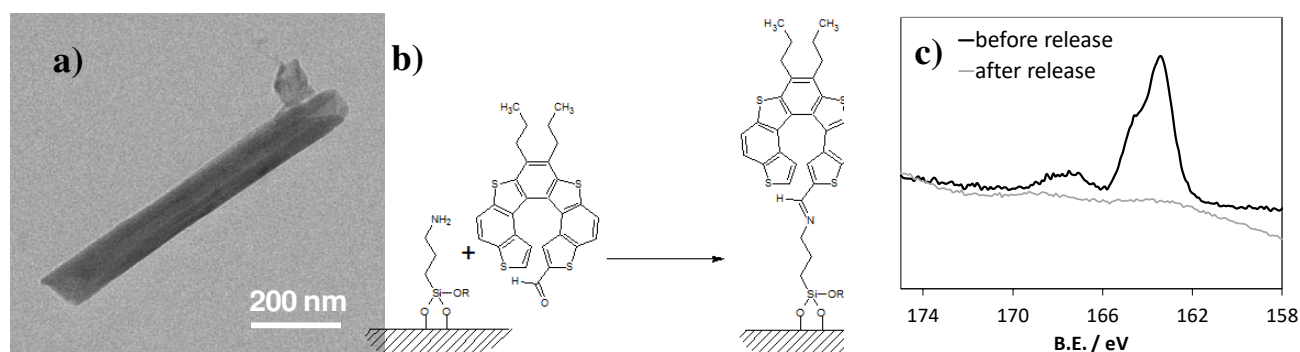


Figure 1. a) TEM image of a halloysite nanotube; b) Proposed reaction mechanism between the helicene derivative and the APTES-grafted surface; c) S 2p region of alumina films functionalized with helicene before and after release.

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Volatile surfactants: characterization and areas of applications

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The research aiming at the development of experimental and theoretical basis of the interfacial behaviour of volatile surfactant will be presented. As non-conventional volatile surfactants we study commercially available compounds such as synthetic perfumes, essential oils, terpenes. Typically such light amphiphilic compounds possess a distinct odour, and have low to negligible solubility in water. In contrast to basic physico-chemical properties, e.g. boiling temperature, solubility, partition coefficient, such properties of volatile amphiphiles as polarity, volatility and interfacial activity are not systematically studied and therefore are not available in handbooks and databases.

A distinctive feature of volatile amphiphiles is that they provide low dynamic values of the surface tension. Also they can act as plasticizers for fabrics, plastic and hair. On the other side, in contrast to conventional surfactants, volatile amphiphiles evaporate from air-water interface, so that the static surface tension increases with the surface age time on a time scale of seconds. Using facile and low cost measurements such as static and dynamic tensiometry, we systematically evaluate valuable information on the volatility of the volatile surfactants which is not straightforward to evaluate using even more complex analytical techniques. Several examples of experimental database of characterized volatile surfactants with established “structure-property-function” relationship will be presented. This methodological approach is further developed to disclose dynamic interactions of volatile surfactants with other components of detergent and cosmetic formulations.

Due to their high surface activity, volatile surfactants are envisaged to be useful in processes and technologies which involve newly creating interfaces at the time scales of milliseconds and below, such as spraying, coating technologies, laundry, stabilization of emulsions in cosmetic and food industry.

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Applications of Surface Chemistry in the Cosmetic Industry. Optimizing the use of surfactants and water with foams

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A great diversity of materials are used to protect or improve the structural and sensorial properties of Surfaces (hair, skin, nail...). From shampoos to lacquers or gels, materials are used commonly used to perform a particular function (mechanical, optical, etc.) upon adsorption and/or penetration in the fiber or either after a particular change in a external conditions that may trigger its activation (temperature, weathering, etc.).

Knowledge of the structure and nature of the substrate is essential if we want to clearly determine the degree of improvement of its physical properties. This description will be further illustrated with a few examples of our current research efforts deciphering the physical chemical properties of hair at the bulk and surface level and at the macro, micro and sub-microscopic scale.

The contact and spreading of complex fluids on real surfaces is essential for various physicochemical applications such as, in cosmetics the deposition of personal care products on hair and skin. As an example of common surface treatment (cleaning) of the cosmetic substrate, we will describe the nature and properties of polymers and surfactants commonly used in shampoos. One of the characteristics of these kind of products is the formation of foams, but little is known about their contribution for cleaning.

In this study, we developed a new protocol to precisely measure the cleaning efficiency of surfactant solutions and foams made with the same surfactant solutions based on a spectroscopic method. More precisely, we add a well-controlled amount of colored sebum, we clean the hair with our test foam or solution and we remove completely the unwashed sebum. The sebum remaining after washing is quantified by visible spectroscopy.

We tested either classical detergents such as SLES at different concentrations or white egg. The studies were performed on natural or bleached hair. In all the studied cases, we did not observe any difference in the cleaning efficiency between the bulk solutions and the foams made from the solutions. In addition we studied the entrainment mechanism of dry monodisperse foams when a solid plate is pulled out of a bath. This situation is found commonly during hair's or skin water rinsing situation that controls the efficient removal.

The results of this study could allow to develop new shampoos formulations or dispensers in order to replace washing solutions by foams that could have the same cleaning efficiency with a lower amount of surfactants; diminishing the water rinsing needs during application to the consumer's advantage.

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Fabrication and functionality of novel almond gum-shellac nanoparticles as an oral delivery system

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In recent years, biopolymer nanoparticles (NPs) have attracted great attention as a promising carrier system for targeted delivery of functional ingredients. New natural ingredients with functional applications is becoming a challenge. We therefore utilized a novel hydrocolloid known as almond gum (AG) to fabricate nanoparticles as a delivery system for bioactive compounds. We found that combination of AG and shellac biopolymers using co-precipitating technique could create a colloidal dispersion resistant to a proposed stomach pH (1.2) meaning that they can likely survive the stomach conditions reaching the intestines. The negative surface charges obtained from electrophoretic mobility data and particle size confirmed the electrosteric stabilization of the particles. The physical stability of this colloidal dispersion was greatly improved with incorporation of the surfactant polysorbate 80 (PS 80) resulting in a substantial decrease in particle size to 90nm, which remained stable in stress conditions (very low pH and thermal processing). Quercetin, as a bioactive compound model, was used for encapsulation within the nanoparticles. Our results suggested that the encapsulation efficiency was 78% with no surfactant while this increased to 99% in the presence of PS 80. SEM confirmed that nanoparticles were formed whereas FTIR proved the interaction of quercetin within the core material of biopolymer matrix. The solid-state studies performed using differential scanning calorimetry (DSC) confirmed the conversion of quercetin crystals to a solid amorphous form. The release study showed that more than 80% of the encapsulated quercetin released from the nanoparticles at simulated intestine pH (7.4). The antioxidant activity and UV-visible chemical stability studies indicated that incorporation of quercetin within the nanoparticles significantly decreased the chemical degradation of quercetin at alkaline pH conditions as compared to the bare quercetin.

This research has important consequences for fabrication of novel biopolymer nanoparticles applicable in bioactive delivery in the food industry or drug delivery.

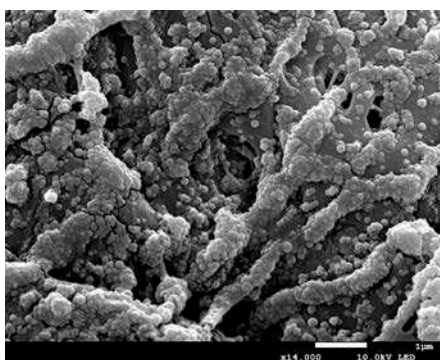


Figure 1. A Cryo-SEM photograph of the quercetin loaded nanoparticles.

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Prediction of biosurfactants solubilization capacity based on experimental and literature data

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Micellar solubilisation, next to wetting, emulsification and mobilization plays an important role in everyday hygiene, cleansing but also in environmental protection [1], drug delivery systems, and even in digestion of fats. For the industrial application of solubilization it is crucial to provide high efficiency and at the same time reduce human or environmental impact which are pronounced respectively by skin irritation and accumulation of hardly-biodegradable compounds in the environment. To reduce these effects, a promising and alternative for synthetic surfactants, namely biosurfactants (BSs) may be applied for solubilisation. Biosurfactants are most efficiently produced by microbial synthesis, with rhamnolipids (RLs) being the most widely examined group of these natural surfactants.

RLs are a promising and environmentally friendly alternative for synthetic surfactants as they are easily biodegradable [2], and mild to the skin [3]. Moreover, they form micelles at lower concentrations than synthetic surfactants [2] and solubilize hydrocarbons at concentrations even below the CMC [4].

Nowadays the industrial application of biosurfactant for cleansing or ground and water remediation processes has to be preceded by a multitude of experiments and analyses allowing to optimize the composition of the product. Myriads of successful laboratory experiments do however not guarantee the success on industrial scale. This altogether makes the process of fitting product to application very complicated and time-consuming. Therefore, we aimed at simplification of this procedure by creation of a mathematical model to predict efficiency of solubilisation in biosurfactant solutions.

Database for the model covered literature and experimental results. In our experimental part we assessed the influence of pH and the purity on solubilization efficiency of biosurfactants. We used purified rhamnolipids (RLs), their mixture with microbial polysaccharide and RL biocomplex with polysaccharide as solubilizing agents, and dodecane and canola oil as solubilizates of different hydrophobicity. We observed that pH of the process had larger impact on the solubilisation efficiency, expressed as molar solubilisation ratio (MSR), than the purity of solubilizing agent.

In the mathematical part of the research we used a series of chemical and phenomenological descriptors to predict the MSR of RLs aqueous solution. The model was created using an evolutionary algorithm with *i.e.* CMC, purity of BS, pH, and $\log K_{ow}$ of solubilizate as descriptors. The purity of BS was described using the arbitrary purity scale that we created before [5]. The most suitable equation with coefficient of determination $R^2 = 0.842$ was found. Based on the model we ranked the parameters upon their increasing influence on solubilization efficiency.

To our knowledge this was the first approach to predict solubilisation efficiency. The results of our research may be used for both, the design of scientific solubilisation experiments and for creation of optimal formulations for application of interest.

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Oxide and cobalt removal of foam decontaminating agent

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The decontamination performance was investigated according to the type and concentration of the foam decontaminating agent containing nanoparticles [1-2]. For this purpose, the weight loss of the simulated FeCr_2O_4 oxide specimen was measured by the decontamination time for four kinds of foam decontaminating agents, and the surface before and after decontamination were analysed using SEM & EDX. The decontamination behavior of these foam decontaminating agents were compared with those of the chemical solution decontaminating agents. The radioactive demonstration test of foam decontamination was performed on the SG plug drawn from the nuclear power plant site.

It can be concluded that the Ce (IV) concentration rather than the HNO_3 concentration has a large effect on the foam decontamination behavior, and that a Ce (IV) concentration of 0.5 M or more is required. Comparing the decontamination behavior of foam decontamination and solution decontamination using the same chemical decontaminating agent for 8 h decontamination based on the weight loss, the removal rate of the foam decontamination method (formulation of 2M HNO_3 / 0.5M Ce (IV) in 1%(v/v)TBS + 1wt.% M-5 silica) is about 75.6% of the solution decontaminating method, showing a relatively effective decontamination performance.

The radioactive decontamination demonstration test performed on the SG plug drawn from the nuclear power plant site revealed that the Co removal % of KAERI foam decontaminating agent showed 50.3% during the first 2 h and then 59.3% and 64.0% after 4 h and 6 h, respectively. It can be seen that the removal rate by the second decontamination shows only 14-15% of the removal rate by the first decontamination, and thus the effect of repeated decontamination is not large.

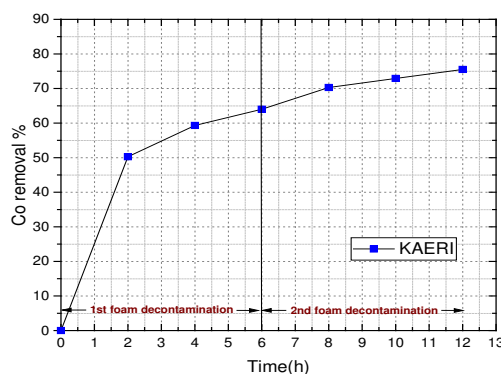


Figure 1. Cobalt removal % of KAERI foam decontaminating agent.

Acknowledgements: This work has been carried out under the Nuclear R&D Program (NRF-2017 M2A 8A 5015144) funded by Ministry of Science, ICT & Future planning.

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Langmuir monolayer properties of Gemini type perfluorinated surfactants with DPPC at the air-water interface

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Fluorinated surfactants are more efficient than hydrogenated surfactants because of the surface tension can be reduced by small amounts of fluorinated surfactants. Moreover, the feature of hydrophobicity and lipophobicity provides phase separation and self-assembly. These properties are useful for applications in various fields such as biomedical and industry fields [1]. The perfluorinated double long-chain salts with divalent counterions which have various hydrocarbon spacer lengths have been synthesized [2, 3]. Herein, in this study, the binary monolayer properties of the fluorinated compounds and dipalmitoylphosphatidylcholine (DPPC) were investigated to understand the spacer length effect and an aspect of biomembrane interaction on their interfacial behaviour.

The fluorinated compounds, 1,1'-(1, ω -alkanediyl)-bispyridinium perfluorotetradecane carboxylate (abbreviation: CnBP(FC14)₂; $n = 2, 6, 10$), were synthesized. DPPC was obtained from Avanti Polar Lipids (Alabaster, AL). Surface pressure (π)-molecular area (A) and surface potential (ΔV)- A isotherms were measured on 0.15 M NaCl at 298.2 K. Brewster angle microscopy (BAM), fluorescence microscopy (FM) and atomic force microscopy (AFM) were also employed.

We have investigated that the binary Langmuir monolayers of DPPC and CnBP(FC14)₂ behaviour. Two-dimensional phase diagrams were constructed on the basis of the disordered/ordered phase transition pressure and the monolayer collapse pressure versus the molar fraction of CnBP(FC14)₂ ($X_{\text{CnBP(FC14)}_2}$). The transition pressures and collapse pressures changed against $X_{\text{CnBP(FC14)}_2}$. In the morphology (BAM and FM), the dispersion degree of two regions (ordered and disordered) were depending on the spacer length of Gemini type perfluorinated surfactants. The miscibility is also confirmed by AFM at nanometer scales.

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Monolayers of a tetrazine-containing gemini amphiphile: Interaction with biomembrane lipids

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The property of a newly synthesized tetrazine derivative comprised of double C18-saturated hydrocarbon chain (C18-rTz-C18) has been studied in situ at the air–water interface. C18-rTz-C18 or a gemini amphiphile contributes to restriction of its tetrazine moiety on the interface, which is expected to be used for bioimaging and analytical reagents. Herein, to understand lateral interactions between Tz and biomembrane constituents, we investigated the interfacial behavior of Langmuir monolayers composed of C18-rTz-C18 and biomembrane lipids such as DPPC, DPPG, DPPE, PSM, and Cholesterol (Ch). The lateral interaction of the binary monolayers was analyzed with the surface pressure (π)–molecular area (A) and surface potential (ΔV)–A isotherms. These thermodynamic data indicate that all of the two-components are miscible with each other. In particular, as opposed to the others, the monolayer stability of DPPE, which is a major constituent of the inner surface of cell membranes, is attenuated by the small-amount addition of C18-rTz-C18. This specific interaction implies the membrane destruction from the inside. The phase behavior during monolayer compression was visualized with Brewster angle microscopy (BAM), fluorescence microscopy (FM), and atomic force microscopy (AFM). The obtained morphologies exhibit a coexistence state of two different liquid- condensed domains derived from extra phospholipids and phospholipids–C18-rTz-C18 monolayers.

Acknowledgements: This work was supported by a Grant-in-Aid for Scientific Research 16K08216 from the Japan Society for the Promotion of Science (JSPS).

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Enhanced antimicrobial effect of berberine and chlorhexidine in nanogel carriers with cationic surface functionality

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We report a strong enhancement in the antimicrobial action of berberine and chlorhexidine encapsulated into polyacrylic acid-based nanogels followed by further surface functionalisation [1]. Due to the highly developed surface area, the nanogel carrier amplifies the contact of berberine and chlorhexidine with microbial cells and increases its antimicrobial efficiency. We show that such cationic nanogel carriers of berberine can adhere directly to the cell membranes and maintain a very high concentration of berberine directly on the cell surface. We developed a novel surface functionalized nanocarrier for berberine by using polyacrylic acid based-nanogel particles (Carbopol Aqua SF1) coated with a cationic polyelectrolyte (PDAC) which shows a strong boost of the berberine antimicrobial action. We demonstrated that the antimicrobial action of the PDAC coated nanogel loaded with berberine and chlorhexidine on *E. coli*, yeast, and *C. reinhardtii* is much higher than that of the equivalent solution of both free berberine and free chlorhexidine due to the electrostatic adhesion between the positively charged nanogel particles and the cell membranes. Our results also showed a marked increase in their antimicrobial action at shorter incubation times compared to the non-coated nanogel particles loaded with the same antimicrobial agent under identical conditions. We attribute this boost in the antimicrobial effect of these cationic nanocarriers to their accumulation on the cell membranes which sustains a high concentration of released berberine or chlorhexidine causing cell death within much shorter incubation times. This study can provide a blueprint for boosting the action of other cationic antimicrobial agents by encapsulating them into nanogel carriers functionalised with a cationic surface layer. This nanotechnology-based approach could lead to the development of more effective wound dressings, disinfecting agents, antimicrobial surfaces, and antiseptic and antifouling formulations.

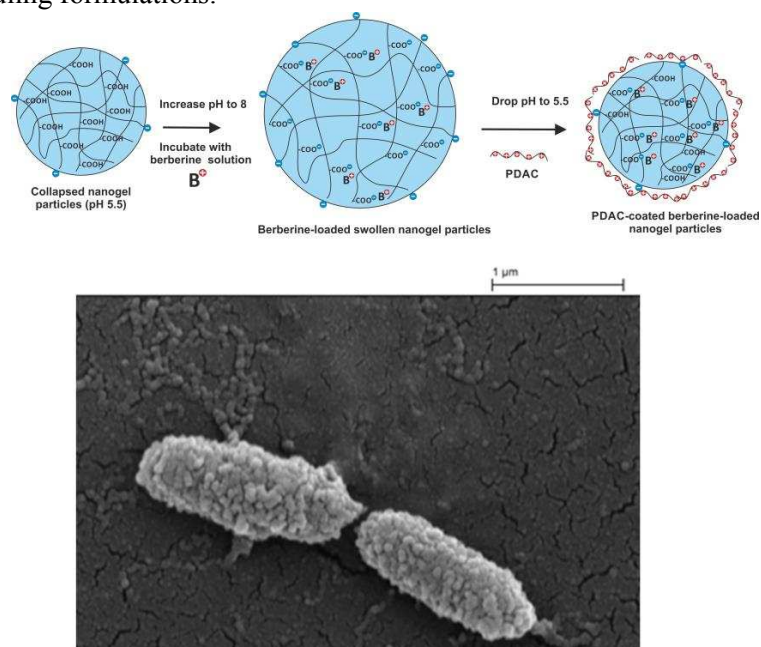


Figure 1. TOP: Fabrication of cationic surface functionalised nanogel particles loaded with berberine and their antibacterial effect; BOTTOM: *E.coli* cells after incubation with berberine-loaded carbomer nanogel surface functionalised with PDAC.

Acknowledgements. M.A. is grateful to the Higher Education Ministry of Iraq for financial support from his PhD studentship.

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Positive charge brought by CTAB to acrylic and styrene copolymers enables formation of antimicrobial films

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Despite the spectacular success of antibiotics over recent decades, the risk that the bacteria will eventually learn how to develop resistance to most known antibiotics is relatively high. The reason of increasing the number of antibiotic-resistant bacteria is that the survivors are capable of transmitting the resistance to other species. Therefore, alternative solutions are needed to fight bacteria using non-specific interactions which are more difficult to overcome, e.g. electrostatic ones. Basing on a concept of Anti-Microbial Peptides (AMP), that constitute the first line of defence of most higher organisms, and taking advantage of inherently negative surface charge of all bacteria, we aim to fabricate polymeric surfaces with permanent positive surface charge. They should be able to electrostatically attract and contact-kill bacteria in areas especially prone to bacterial colonization.

In this contribution we present the synthesis and characterization of methyl methacrylate – ethyl acrylate and styrene - ethyl acrylate copolymers obtained by emulsion polymerization initiated by a cationic or anionic initiator in presence of a cationic surfactant – cetyltrimethylammonium bromide (CTAB). The positive charge of CTAB introduced during the synthesis remains on the latex surface even after extensive dilution and dialysis, providing electrostatic barrier to coalescence of the particles (Fig.1). Also the films produced from the positively charged dispersion maintain positive zeta potential values and display pronounced electrostatic antimicrobial activity.

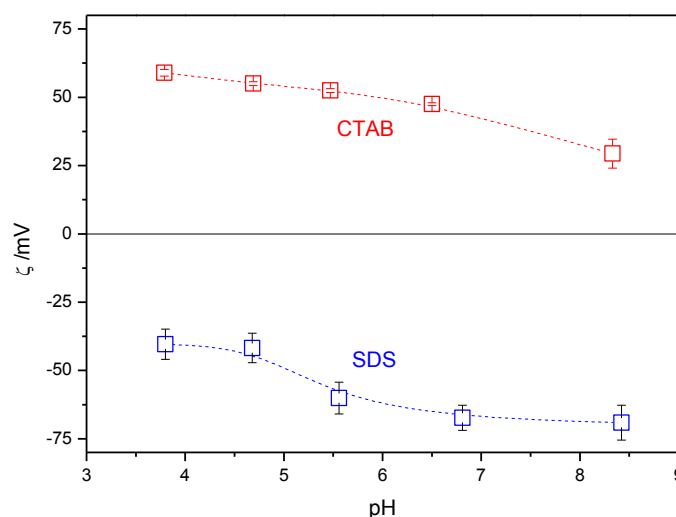


Figure 1. ζ -potential vs pH for acrylic latex obtained in presence of SDS and CTAB

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Surface activity of saponin-rich plant extracts

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Numerous living organisms produce biosurfactants, typically considered as secondary metabolites which are usually assigned to self-defence mechanisms. In plant kingdom, saponins are one of the most abundant biosurfactants. They share steroidal or triterpenoid hydrophobic backbone, which is substituted with 1-3 hydrophilic oligosugar groups. As a consequence, many saponins exhibit not only biological (e.g. membranolytic) activity, but may also be used as natural surfactants, emulsifiers, foaming agents, etc. In this respect, they offer an interesting alternative to synthetic surfactants, which provide often better sensorial properties, but are inferior in terms of biocompatibility and biodegradability.

Besides the currently most employed sources of saponins (*Yucca shidiggera* and *Quillaja saponaria* Molina), many other plants have been reported to be potential sustainable sources of saponins. They include e.g. soapwort, chestnut, quinoa, rupturewort, oat, soybeans, licorice, rosemary, horsetail, etc.

In this contribution we present the results of the study dedicated to screening the foaming and surface tension-reducing ability of saponin-rich plant extracts. To preserve the original composition of temperature-sensitive saponins the extracts were obtained by cold-maceration and subsequently spray-dried.



Figure 1. Soapwort (*Saponaria officinalis*, L.)

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Formulation Dependent Interfacial Activity of Monoclonal Antibodies and its Impact on the Physical Stability

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During their lifetime, monoclonal antibodies (mAbs) encounter multiple interfaces starting with the production process until their long-term storage. The amphiphilic nature of proteins accounts for their adsorption to interfaces. While still not fully understood, adsorption is generally considered an initial step towards mAb aggregation and particle formation [1-2]. The aim of the study was to characterize the adsorption tendency of mAbs towards the air interface and correlate it to formulation instability.

Drop Shape Analysis (PAT1M; Sinterface, Germany) was used to measure the mAb affinity towards the air interface. Three mAbs from the EU-PIPPI Project were formulated at 1 mg/ml in 10 mM Histidine buffer (pH = 5, 6, 7.5; \pm 140 mM NaCl). In solution molecular properties were investigated using intrinsic and extrinsic fluorescence for determining the monomeric folded state and surface hydrophobicity in the different formulations. Dynamic Light Scattering (DynaPro; Wyatt, USA) was used to determine the diffusion coefficients of the different mAb formulations and for calculation of the diffusion interaction parameter (Kd) as a predictive tool for colloidal stability. Mechanical stress studies were done at the same formulation conditions using a reciprocal shaker (HS260; IKA, Germany). Stressed samples were analysed for aggregate formation using flow microscopy (FlowCam; Fluid Imaging, USA).

In-solution mAb characteristics impacted the measured adsorption kinetics to the air interface. The extent of mAb adsorption determined by the loss in the measured surface tension reflected on the mechanical stability of the different formulations. Furthermore, the Kd measurements corresponded to the aggregation behaviour.

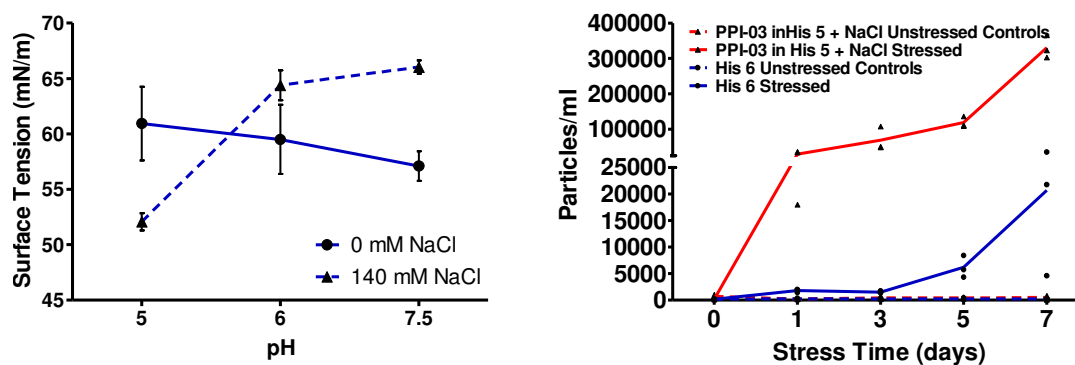


Figure 1. Exemplary results for one mAb **Left:** Equilibrium surface tension. **Right:** Subvisible Particle concentration upon mechanical stress.

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Visible light controlled absorption-desorption on goethite nanowires for drug delivery applications

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Visible light as an external stimulus for smart drug-delivery systems is advantageous for a number of reasons including its non-invasive nature, temporal control, convenience, ease of use and abundance during daily activity.

We found that colloidal system of goethite nanoparticles at specific pH range adsorbs cationic dyes such as methylene blue (MB) rapidly (in less than one minute) and desorbs in long term (5 h) under visible light (Figure 1). We are hypothesizing that visible light irradiation causes heating of goethite nanoparticles, thereby promoting desorption of the MB. Light is absorbed by goethite and photogenerated holes and electrons are recombining but energy is released as a heat thus promoting desorption.

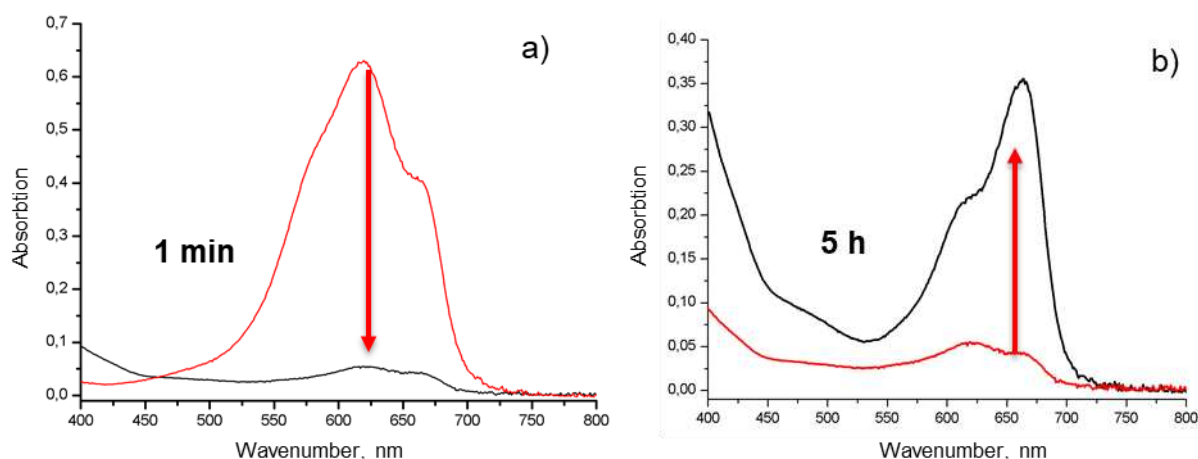


Figure 1. Absorption spectra of MB adsorption (a) and desorption (b) onto goethite nanoparticles

The observed results show a potential for practical application as a visible light driven drug release system, for example, in a natural sunlight, where, depending on the intensity of the sun, drug release is initiated.

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Nanocapillary bridging of particles to design ultra-flexible magnetic chains and colloidal networks

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The capillary forces on the macro- and nanoscale are emerging as a research theme of interest, because of the unusual characteristics of the attraction potential induced by liquid bridging as compared to the traditional surface interactions. Capillary attraction between particles can lead to their assembly into complex architectures at sub-micron length-scale. However, the presence of capillary forces at the nanoscale has not been used as a tool for nanoparticle binding in liquid media. Recently, we demonstrated that nanocapillary forces can be used for permanently assembling superparamagnetic nanoparticles covered by lipid shell into magnetically responsive ultraflexible chains and self-healing gels [1].

We show that maghemite nanoparticles wetted with lipids can be assembled into microfilaments upon the application of external magnetic field. Initial burst of magnetic field aligns the particles into bundles. After switching off the field the particles retain their linear arrangement by a soft attractive potential induced by the lipid junctions playing the role of nanocapillary bridges. The bridges formed between the particles enable their permanent binding and sustain the flexible microfilament structure (Figure 1). The role of surface wettability and formation of liquid menisci was related to the thermodynamic phase of the surface adsorbed lipid. The presence of nanocapillary bridges provides high flexibility to the resulting chains by allowing for particle rolling and sliding. We evaluate persistence length of the chains by finding the decay in bond correlations along the chain contour. We demonstrated that the persistence length is comparable to persistence length of bio-molecules proving the ultrahigh flexible nature of the assembled chains.

This lipid based capillary binding is an unconventional way of assembling structures at meso-, micro and nanoscale. This assembly mechanism opens new pathways for making multifunctional materials, which can be dynamically reconfigured and programmed, including reassembling microbots, and self-repairing gels with unusual magnetic and rheological responses [3-4].

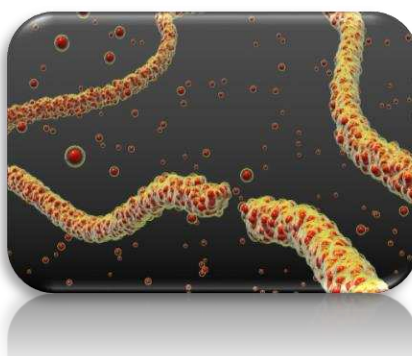


Figure 1: Illustration of nanocapillary bridged filaments assembled into 2D gel-like network.

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Evaporation of drops: The role of *long-range* colloidal interactions

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The drying of a colloidal droplet has attracted considerable attention because of its inherent complexity as well as its significance in applications such as coating, printing, and layering processes [1, 2]. There has been great interest in controlling the well-known 'coffee-ring' effect, in which the contact line of an evaporating drop is pinned to the substrate so that dispersed particles are deposited onto the three-phase contact line [1]. Large $\sim\mu\text{m}$ -scale convection-driven flows typically determine the structure of the deposited film. Interparticle forces which operate on nm-separations, at least in aqueous systems, are relatively unimportant. Our aim is to explore if much longer-range colloidal forces, comparable to hydrodynamic flows, could be used to control particle drying.

We generate controllable μm -range electrostatic interactions in a suspension by using a charge control additive (the surfactant, dioctyl sodium sulfosuccinate [AOT]), and an organic salt, tetradodecylammonium tetrakis (3,5-bis (trifluoromethyl)phenyl)borate (TDAT) in a nonpolar solvent. The drying of drops containing monodisperse, fluorescent poly-(methyl methacrylate) (PMMA) particles was studied by confocal light scanning microscopy (CLSM). Image analysis was used to quantify the spatial deposition of the particles onto a hydrophobically-coated glass substrate. The existence and extent of a 'coffee-ring' deposit was characterized.

We find that the drying patterns are controlled by a competition between the evaporation rate of the solvent and the strength and range of the electrostatic interactions. In highly-volatile solvents, such as hexane, hydrodynamic flows dominate particle deposition. With weak electrostatic interactions a well-defined coffee- ring is produced. Increasing the strength of repulsions, the intensity of the 'ring' is observed to first reduce and then in highly-charged systems to be totally suppressed. In less volatile solvents, such as dodecane where evaporation is diffusion-controlled, the role of colloidal forces is more complex with evidence for modification of both particle-particle and particle-substrate interactions. Finally, high salt concentrations induce particles attraction and the formation of clusters in bulk solution which inhibit the formation of a ring-like deposit.

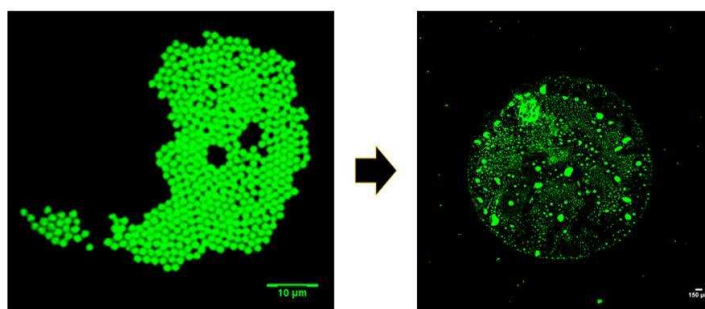


Figure 1. The formation of particle cluster in the bulk solution (left) inhibits the formation of 'ring-like' deposition pattern (right).

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How do responsive microgels respond to crowding?

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Microgels are macromolecular networks swollen by the solvent they are dissolved in. They are unique systems that are distinctly different from common colloids, such as, e.g., rigid nanoparticles, flexible macromolecules, micelles or vesicles. [1] When swollen, they are soft and have a fuzzy surface with dangling chains and the presence of cross-links provides structural integrity - in contrast to linear and (hyper-) branched polymers. Finally, microgels reveal interface activity without being amphiphilic.

The combination of being soft and porous while still having a stable structure through the cross-linked network as well as the possibility to introduce chemical functionality at different positions will allow to tune the microgels behaving as hard or soft objects. At high packing density, or in other words in crowded environments, microgels might deswell, interpenetrate or deform and one can imagine that not only the degree of crosslinking but also the morphology of the microgels are important.

We will discuss the interaction of microgels of different chemical functionality and architecture as, e.g., core-shell, hollow [2-4] and multi-shell hollow microgels [5,6] in bulk solution as well as at fluid interfaces.

The structure is probed by means of neutron scattering employing contrast variations as well as by (super- resolved) fluorescence microscopy. [7] Properties of microgels at interfaces are determined by means of scanning force and electron microscopy as well as by compression isotherms and interfacial rheology. The experimental results will be compared to computer simulations.

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Evolution of nematic phase in a colloid of magnetic nanoplatelets

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Suspensions of magnetic nanoplatelets in isotropic solvents are very interesting examples of ferrofluids. It has been shown that above a certain concentration Φ_{NI} such suspensions form ferromagnetic nematic phase [1], which makes this system a unique example of a dipolar fluid. The formation of nematic phase is driven by anisotropic electrostatic and long-range dipolar magnetic interactions.

We studied the evolution of short range positional and orientational magnetic order in the suspensions with volume fractions below and above Φ_{NI} , using small angle neutron scattering (SANS). The results show that in the absence of an external magnetic field, short range positional and orientational order already exist at relatively low volume fractions. The scattering patterns have distinctive peaks located along the platelets axis, and smaller peaks at lower scattering vectors in the perpendicular direction (Fig. 1a). Polarized SANS (Fig 1b) revealed that the average magnetic orientation in two types of peaks points in opposite directions, as schematically shown in Fig. 1c. In the nematic phase the peaks along the platelets axis, which correspond to ferromagnetic ordering, are stronger indicating that the contribution of magnetic interactions to the formation of the nematic phase is significant. The observations can be qualitatively explained by a simple model, which takes into account screened electrostatic and dipolar magnetic interactions.

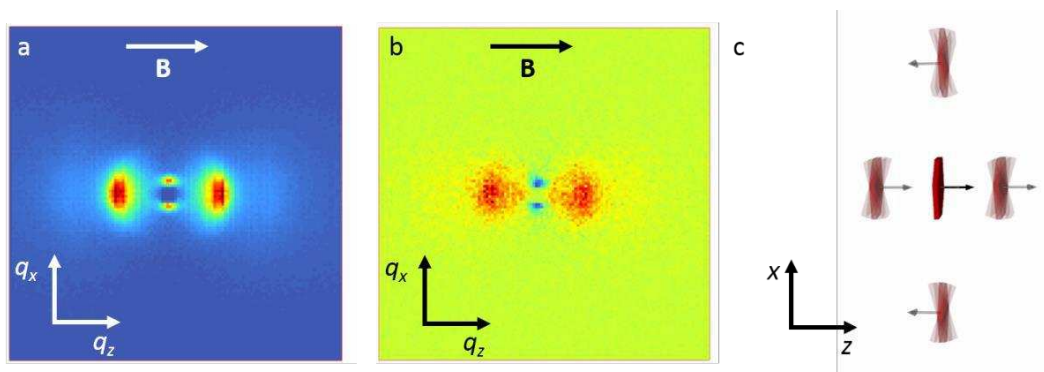


Figure 1. a) SANS intensities showing positional correlations. The peaks in the horizontal direction correspond to ~ 30 nm, while the ones in the vertical direction to ~ 90 nm. b) SANS POL intensity difference showing magnetic correlations. The blue regions corresponds to antiferromagnetic and the red to ferromagnetic correlations. c) Scheme of positional and magnetic correlations of the neighboring platelets. $\Phi = 0.07$, $B = 0.19$ mT.

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Dynamics, structure and stresses in repulsive glasses and attractive gels of colloidal rods

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Anisotropic rod like colloidal particles have a much richer phase diagram, compared to their spherical counterparts including a variety of liquid-crystalline (LC) phases. Such phases are controlled by particle concentration, external stimuli (thermal, electric, magnetic or flow) or by tuning the inherent inter-particle potential [1]. Predicting microstructural changes in rod like colloidal suspensions undergoing shear flow is challenging due to the interplay of particle's orientational and positional distribution with the imposed field. These lead to shifting phase boundaries in the isotropic-nematic region and are influenced by particle size, aspect ratio, surface properties, polydispersity, flexibility, shear rate, etc. Experimentally, the combination of probing techniques such as scattering and microscopy in conjunction with rheometry is valuable for an in-depth understanding of rodlike colloidal behavior under flow.

Micron-size charged stabilized silica rods are a model system to study ideal colloidal rods of low aspect ratio (~ 5 -10) with interactions that are tunable from long range repulsive to strongly attractive [2]. Here we present a comprehensive study of shear induced microstructural changes of suspensions of repulsive and attractive silica rod particles at different particle volume fractions and their effect on the linear and nonlinear viscoelastic properties. Micron sized fluorescent silica rods ($L = 4 \mu\text{m}$, $L/D = 10$) (Figure 1 (a)) were tuned from repulsive in glycerol/water solvent mixture to attractive in glycerol/NaCl or water/CsCl mixtures. A combination of rheology and confocal microscopy (Rheo-confocal) captures the microstructural changes under shear (Figure 1 (b & c)), tracking single particle dynamics (via confocal microscopy) or large length scale structures (at lower magnifications). The linear and nonlinear rheological response is monitored in dilute and concentrated regimes to build a “phase diagram” with shear equilibrium and out-of-equilibrium shear-induced microstructures. In repulsive glasses, we visually confirm that the peak stress associated with start up shear experiments are due to the alignment of rods in the flow direction. Rods aligned in the flow direction form the new “shear equilibrium” state which is irreversible upon shear cessation. In attractive colloidal gels “log-rolling” structures are created at concentration around 1 to 2.5 c^* at rates $Pe_r = 0.5 - 32$ as an interplay between shear and confinement, with implications in the rheology. We discuss these findings linking structure dynamics and rheometry.

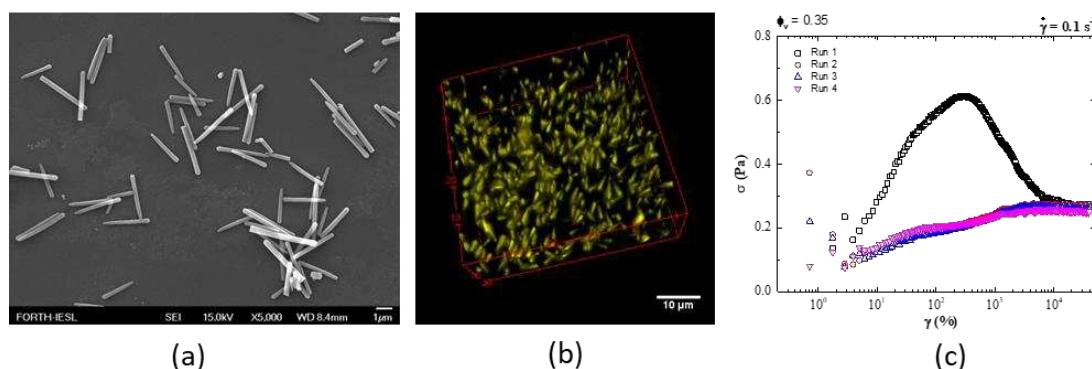


Figure 1. (a) SEM images of silica rods, (b) 3D confocal microscopy image of the repulsive silica rod suspension and (c) start-up shear experiment on a repulsive silica rod suspension.

Acknowledgements: We acknowledge financial support from EU Marie-Curie ITN project “DiStruc”

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Tuning the properties of colloidal dispersions by playing on the nanoparticles' interface and on the solvent

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We evidence here how the tuning of the interface between the nanoparticles and the solvent as well as the solvent itself can modify the properties of a colloidal dispersion [1,2]. We are here mainly interested in the interparticle interaction, the nanostructure, and the thermodiffusion properties, *i.e.* the behaviour of the nanoparticles in a temperature gradient. Indeed, depending on the tuning of the interface, they may move either towards cold or hot regions, which is quantified by the Soret coefficient [1]. Knowing the thermodiffusion properties is mandatory for all applications that necessitate a thermal gradient, such as thermoelectric or heat transfer ones [3].

The system presented is constituted of iron oxide nanoparticles (NPs) of γ -Fe₂O₃ (diameter \sim 8 nm) dispersed in polar solvents, ionic liquids or mixtures of solvents.

In water, changing the nature of the counterions of negatively charged identical NPs (counterions Li, Na tetramethylammonium, tetrabutylammonium) modifies the interparticle interaction and the sign of the Soret coefficient [1]. The same effects are obtained by keeping the same particles (then positively charged with perchlorate counterions) however dispersing them either in water or in dimethylsulfoxide (DMSO) [2]. Stable dispersions can be obtained in the whole range of compositions from water to DMSO however modulating the properties in an unexpected way.

The nature of the counterions of the nanoparticles (Li, Na, Rb, Sr) also controls the nanostructure and interactions of the particles dispersed in a pure ionic liquid (here ethylammonium nitrate, EAN). Mixing molecular solvents like water or DMSO and an ionic liquid (EAN) allows tuning the properties, which depend now both on the nature of the counterions and on the nature of the ionic liquid; this latter behaving as an electrolyte at low contents. Depending on the system, colloidal dispersions stable on the whole range of compositions from pure solvent to pure ionic liquids can be obtained, despite the high electrolyte concentrations in the intermediate range.

Acknowledgements: We acknowledge funding from the French Agence Nationale de la Recherche (ANR-TE-FLIC Grant no ANR-12-PRGE-0011-01), and from the Horizon 2020 FET-PROACTIVE project (MAGENTA, associated with the Grant n° 731976).

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Viscoelastic Surfactants: Boost Applications in Harsh Environment

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The viscoelasticity of surfactant solutions is resulted from the three-dimensional network from the entanglement of wormlike micelles (WLMs) that are elongated, flexible aggregates formed by the spontaneous self-organization of surfactant molecules in aqueous solution. Such nano-structured threads can entangle each other above a threshold concentration, imparting remarkable viscoelastic behaviors, reminiscent of polymer solutions. Thus such type of surfactants are also called as “viscoelastic surfactants” (VES) [1]. However, the continuous rupture and reformation of transient network differ them from the classical polymer solutions [2].

While the formulation and relevant basic properties have been well explored and understood, the applications of such soft colloidal materials were constrained in drag reduction, cosmetics, personal, particularly in upstream oil industry under relative mild conditions [3]. Recently, a great attempt has been made in our laboratory to maximize the potentials of WLMs to be uses in high-pressure, high-temperature, highly-acidic or extreme-low-temperature environments.

The first example is the use in water-alternate-CO₂ (CO₂-WAG) flooding to boost oil production. Despite successful stories have been evidenced for over 40 years, inadequacy is still evidenced during CO₂-WAG flooding because both of the low-viscosity water and gas tend to follow highly-permeable paths or open “thief” channels under high pressure, finally resulting in a loss of the chasing fluid and by-passing of oil-bearing zones. We demonstrated that the water slug containing a CO₂-sensitive surfactant can be thickened at 60 °C and 5 MPa when contacting with the pre- and post-CO₂ slug, thus blocking the channels and to recover incremental 5.1% oil relative to pure CO₂-WAG.

A further illustration comes from use of customer-tailed made WLMs in matric acidizing at high temperature. To slow down the reaction between acid and rocks, viscosifiers, see, wormlike micelles, are always introduced into strong acid such as 20% HCl to dissolve the rock near the wellbore and increase the porosity, thereby increasing the flow of hydrocarbons from the reservoir into the well. Nevertheless, the currently-used surfactants cannot stand temperature higher than 120 °C. We developed alternative surfactants by introducing stronger bonds into the molecular architecture, and found even at 150 °C, nearly 40 mPa·s of viscosity can be generated with 3% surfactant in 20% HCl solution, which can well satisfy the high-temperature oil reservoir stimulation.

The last case is the use of WLMs as anti-icing fluids under frozen environment. Undesired ice accretion on the surfaces of aircrafts at subzero temperatures is known to cause severe problems in terms of safety and efficiency in the fields of transportations. Specially-designed water-soluble polymers were generally dissolved in alcohols to remove the accumulated ice. However, the residual polymer may form into hydrogels when it adsorbs moistures in the air, thus leading even more dangerous accidents when such gels are stuck in the elevator. We formulated novel anti-icing fluids by replacing polymer with WLMs, and found they show similar behaviors as polymer solutions do, but can be much easier to be removed during the takeoff of airplane because of its small-molecule characteristics, thus avoiding the possible disaster.

Acknowledgements: The authors would like to thank the financial support from the National Natural Science Foundation of China (21773161) and National Science and Technology Major Project of the Ministry of Science and Technology of China (2016ZX05048-004-007).

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Surface modification of magnetic nanoparticles through spontaneous segregation of binary polymer mixtures aiming at Janus character

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Nanoparticles-based research has advanced quickly becoming leading tools for a broad range of applications. Specifically, iron oxide nanoparticles presenting superparamagnetic behaviour (SPIONS) are interesting materials promising for applications in many areas specially in nanomedicine field [1]. The surface chemistry plays a critical role in the behaviour of NPs and can be modulated to include multiple functionalities within a single material [2]. Our group has reported the functionalization of gold nanoparticles based on the spontaneous segregation of a mixture of immiscible polymers at the particles surface resulting in Janus NPs [3]. Janus nanoparticles displaying amphiphilic properties can self-assemble or form hierarchical structures at different length scales imparting distinct and multiple properties [4].

The present work reports the same functionalization approach extended to SPIONS aiming to obtain magnetic Janus nanoparticles, combining the tunable assembly properties of Janus NPs in a magnetic material. SPIONS were synthesized by the coprecipitation technique and different binary mixtures of chemically distinct polymers (among them PEO, PMMA and PNIPAM) were attached to the iron oxide nanoparticles via phosphonic acid end-groups.

The obtained NPs were characterized by X-ray powder diffraction (XRD), vibrating sample magnetometry (VSM) and electron microscopy. It was observed the characteristics Bragg peaks of the spinel structure of iron oxide nanoparticles, a typical superparamagnetic behavior and particles with a semispherical shape with a size distribution around 10 nm. Spectroscopy techniques (FTIR, XPS) were used to confirm the polymers functionalization at the NPs surface and the size and assembly properties were also characterized using scattering techniques (DLS, SAXS). The assembly of the particles could be modulated depending on the solvent quality for the polymers as well as varying the ratio between the polymers pair. As the PMMA content is increased related to the PEO amount it was observed the emergence of a interference effect indicating the assembly of the particles. For PMMA/PEO-SPIONS in water/ethanol mixtures, chemical analyses confirm functionalization of SPIONS with both polymers, which render a temperature sensitive behavior, characteristic of an UCST behavior. This, however, was not enough to cause NP aggregation upon temperature changes. Evidences for co-nonsolvency effect were observed with colloidal instability at intermediate proportions of these solvents, as seen in Figure 1. This provides an interesting alternative for controlling nanoparticle aggregation upon changes in compositions of the solvent.

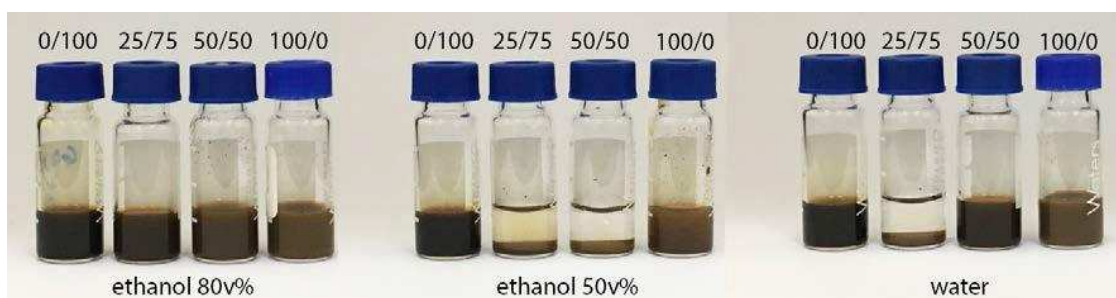


Figure 1. Picture of SPIONS functionalized with different PMMA/PEO ratios dispersed in ethanol 80v%, ethanol 50v% and water.

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Designing nano-colloidal dispersion of *thymol* as a potential natural antioxidant

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Food consumers are currently more concerned over food products containing synthetic ingredients and therefore it is crucial for the food manufacturers to substitute synthetic ingredients by natural ones. However, these alternative compounds should not only affect the consumer perception, but also in terms of functionality should be comparable to the original composition. Thymol (2-isopropyl-5-methylphenol) as a major constituent of some EOs, is a phenolic (monoterpene) compound found mainly in *Thymus vulgaris* L. and *Origanum vulgare*. Thymol has been used widely in different products owing to its antibacterial, antifungal, antioxidant, as well as anticancer properties. The hydrophobicity and crystal powder form of this compound have limited its utilization. Therefore, it has to be encapsulated within a delivery system. In this study, we used Quillaja Saponin (QS) as a natural and food grade surfactant to stabilize thymol nano-emulsions. Sunflower oil (SO), medium chain triglycerides (MCT), and cinnamaldehyde (CA) were utilized to dissolve thymol. Interestingly, incorporation of a low amount of solvents (SO, MCT, CA) (0.8%w/v) inhibited the instability phenomenon while droplet size analyses of the nano-emulsions during long-term (30 days) storage at 20°C showed no significant droplet size change (z-average = 145nm, PDI =0.2). DPPH radical scavenging and FRAP antioxidant tests revealed that nano-encapsulation of thymol significantly improved its antioxidant activity as compared to pure thymol. Moreover, our results suggested that thymol nano-emulsions could be a potential replacement for synthetic antioxidant agents.

The results of this study provide crucial information about formulation of a novel natural antioxidant with long-term stability.

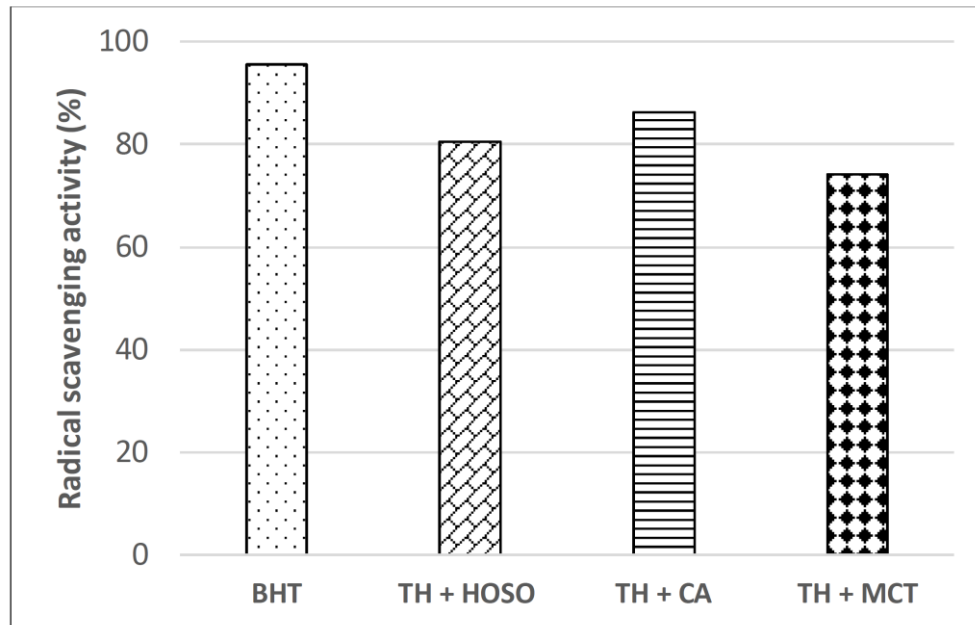


Figure 1. DPPH scavenging ability of thymol in different nano-colloidal systems.

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Long-range electrostatic *attraction* between like-charge colloids

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At school we are told that like-charge spheres repel, and opposite charges attract. Indeed ever since Coulomb's classic experiments in 1785 we have known that, at least for dielectric spheres in a vacuum, this statement is true. What happens, however, if the vacuum is replaced by an electrolyte solution. How do charged colloids immersed in a monovalent salt solution interact? The conventional answer to this question, outlined first in the 1940s in the seminal work of Derjaguin, Landau, Verwey and Overbeek (DLVO), is a prediction of a screened repulsion between like-charge colloids. Indeed subsequently it has been proved rigorously that the interaction between identical colloidal particles, within a mean-field framework, can never be attractive. Yet, despite these apparently robust predictions, several experimental groups have reported observations of an *attraction* between like-charge colloids, normally in low-salt concentrations environments.

To probe the origin of this like-charge attraction we determine the interactions between charged colloids in the extremely low salt environment present in a non-aqueous solvent. We measure directly the forces between a pair of uniformly-charged colloids dispersed in dodecane using holographic optical tweezers. The forces between particles are determined as a function of the mean particle charge $\langle Z \rangle$ and the concentration of added electrolyte. For high particle charges, we find repulsive forces consistent with the expected DLVO predictions. However, in situations where either (a) the mean particle charge $\langle Z \rangle$ is reduced towards zero or (b) where electrostatic repulsions are heavily screened by the addition of a high concentration of a monovalent electrolyte we find evidence for a long-range electrostatic attraction between particles. We discuss this evidence and propose plausible explanations for the apparent counter-intuitive observation of like-charge attraction in the context of current theories of colloidal interactions.

Controlling flocculation with carbamate-based surfactant

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Research studying systems based on hydrophobic particles that can switch between dispersed (“on”) and flocculated (“off”) state has recently gained momentum [1]. One simple way to practically achieve that is to use switchable amphiphiles that, once adsorb at the particle surface, respond to external triggers. Among others, a very popular trigger is the combination of CO₂/inert gas as a pH-regulator to switch the state of pH responsive amphiphiles, e.g. tertiary and guanine amine surfactants [2]. In this work, we suggest another way to utilize CO₂ to switch stability of hydrophobic particles, that is, by forming anionic carbamate surfactant.

We have previously shown that anionic carbamate surfactant can form by reacting CO₂ with a Y-shaped alkyl amine with two terminal primary amino groups (Y12-amine) at pH above pK_a and be reverted to its original form by exposure to N₂ and heating [3], and that the two species had different surface activities, see Figure 1, left. We could therefore hypothesized that the surfactant state could be exploited to disperse hydrophobic particles and to control their flocculation state and stability by switching/cleaving the surfactant, thus enabling an “on” and “off” control of the state.

In this work, two model hydrophobic particles were investigated, nanoparticles of organic pigment and hydrophobized silica particles (5 μm). We show that the surface charge of hydrophobized silica particles dispersed by Y12-amine in aqueous solution at pH 12, increased with time of CO₂ exposure as a result of the carbamate formation while adsorbed at the particle surface. Furthermore, we demonstrate that the organic pigment nanoparticles could be electrostatically stabilized by the adsorbed anionic Y12-carbamate surfactant. The pigment was then flocculated when the carbamate group was cleaved by exposure to N₂ and heating and was re-dispersed by subsequent exposure to CO₂. This cycle of re-dispersion and flocculation was repeated two times without affecting the particle size, as shown figure 1, right. However, further cycles increased particle size, indicating that all particles could not be completely dispersed again.

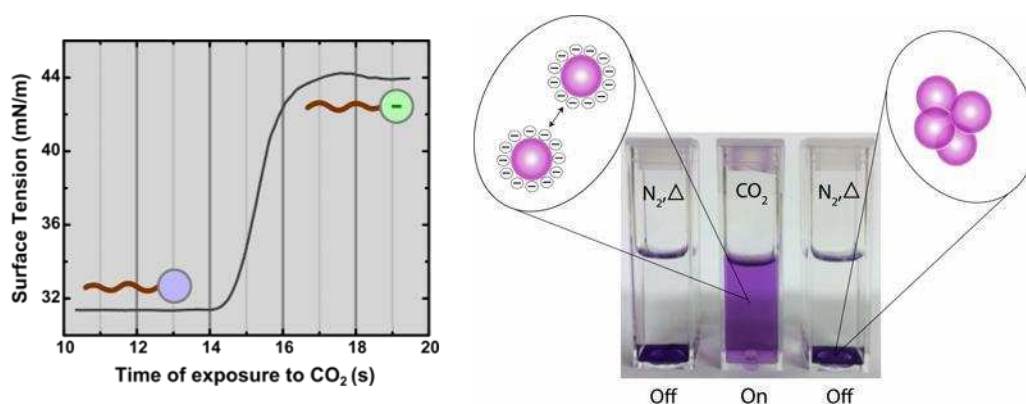


Figure 1. Left: change in surface tension due to carbamate formation. Right: On/Off cycles of dispersed hydrophobic nanoparticles.

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Kinetics of Depletion Flocculation in Concentrated Emulsions

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Emulsions are widely used in food or cosmetic industry. In order to influence their rheological and textural properties macromolecules like xanthan can be added. While a high xanthan concentration can stabilize the emulsion due to an increase in viscosity of the continuous phase, at lower concentrations these macromolecules can induce an emulsion destabilization due to depletion flocculation [1,2].

Depletion induced aggregates are fragile and can disintegrate easily by minor forces. Thus, the investigation of the kinetics of depletion aggregation poses challenges if e.g. sampling and dilution of concentrated emulsions would change the level of aggregation.

Photon Density Wave (PDW) spectroscopy is a light scattering technique that is based on multiple light scattering. It allows for the absolute, calibration-free and independent determination of the absorption and reduced scattering coefficient of highly concentrated, turbid liquid dispersions. With its time resolution in the sub-minute regime it allows for the dilution-free continuous monitoring of chemical, physical, and/or biological changes within emulsions [3,4].

PDW spectroscopy was applied to study the kinetics of the depletion flocculation in emulsions containing 10 wt% of oil with polysorbate 80 as stabilizer as function of time, concentration of xanthan, and temperature. It is found that depletion flocculation is a highly reversible, fast process. The rate of floc size increase can be influenced significantly by temperature changes. Beside the size distribution of the non-aggregated emulsion droplets also an effective diameter of the flocs can be derived from the reduced scattering coefficient obtained by PDW spectroscopy.

The findings indicate that two processes on different time scales lead to an increase in floc size. A fast increase in size in the sub-minute regime by an initial formation of small aggregates containing only few droplets and a growth of these initial aggregates on a time scale of days, causing macroscopic destabilization of the emulsion. The initial aggregation could be slowed down by lowering the temperature and thereby could be followed by PDW measurements.

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Characterization of turbid colloidal suspensions using differential dynamic microscopy (DDM)

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The characterization and dynamics of particles suspended in a solvent are of importance across a wide range of fields, from simple colloidal particles, to the characterization of micro-organism motility. Dynamic Light Scattering (DLS) and Microscopic Tracking are the most widely used techniques for studying such systems. DLS is an established technique which provides excellent ensemble averages, but is typically limited to scattering angles greater than $\sim 15^\circ$ (length scales less than $\sim 3 \mu\text{m}$), which limits the motions that can be probed; Microscopic tracking on the other hand is limited to objects of size \sim micrometres or greater, and as only a finite number of objects can be tracked, ensemble averaged measurements are time consuming and difficult.

A technique with great potential in this area is Differential Dynamic Microscopy (DDM) [1-2], in which a time-evolving sample is imaged at fast frame rates, and the intensity fluctuations in each pixel are correlated. Dynamics can be extracted by Fast Fourier transformation (FFT) of the difference between images, providing information much like DLS. However, DDM accesses larger length scales, allowing for studies of motile bacteria [3-4], and has been shown to work under a variety of sample conditions and imaging techniques [5].

This paper will focus on the application of DDM for characterization of colloidal suspensions - in particular we investigate the effects of multiple scattering, and show how this technique can provide reliable data at turbidities where traditional DLS fails.

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Outsized and very long-ranged electric and entropic forces in colloidal dispersions at finite concentration

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In polymer latex dispersions experiments it has been reported a coexistence of an ordered and disordered distribution of the macroions [1-4]. Because of the macroions' size this coexistence imply the existence of very long-ranged attractive and repulsive forces. However, molecular interaction potentials are relatively short ranged [5]. Even for charged fluids, at low colloidal concentration, the particles' correlation is at most a few hundreds of angstroms. Thus, the origin and attributes of these forces have been discussed in the literature [6]. Semi-phenomenological potentials have been proposed to explain the experimental results. In the past we applied an integral equations formalism to a Colloidal Primitive Model, to study the structure charged colloidal particles, *at finite volume fraction* [7]. Here, we extend our calculations to investigate now the force between macroions. We find a very long-ranged oscillatory force. We specifically explore the nature of this like- charged particles' repulsive-attractive interaction, i.e., we calculate its electrical and entropic components, and discuss their contribution to the total force, in terms of an energy-entropy balance.

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Fragility of soft IPN microgels

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Scientific interest in responsive microgels has hugely increased in the last years. They indeed succeeded as good model systems for investigating the unconventional phase behaviour of soft colloids, emerging as a result of the particle softness [1]. Their effective volume fraction and their elastic properties can be tuned through their response to the environmental conditions. This allows to modulate the interparticle potential and their reversible Volume-Phase Transition (VPT) (swelling/shrinking behaviour), leading to novel phase diagrams, drastically different from those of conventional hard-spheres-like colloidal systems.

Changing some control parameters, like temperature, packing fraction or ageing time, particles can approach the glass transition with their dynamics rapidly slowing down. In particular, in colloidal suspensions the glass transition is approached by increasing concentration, in analogy to decreasing temperature in molecular glass-formers, and many efforts have been devoted in understanding the role of the softness on the fragility. For deformable soft microgels fragility can be directly controlled through the elastic properties of the single microgel particle, allowing to encompass from a fragile to a strong behaviour as particles become softer and more deformable [1, 2].

The dynamics approaching the glass transition of soft interpenetrated polymer networks (IPN) microgels of PNIPAM and PAAc has been investigated through X-ray Photon Correlation Spectroscopy and Dynamic Light Scattering. The slowing down of the dynamics with increasing particle concentration shows an exponential increase of the relaxation time followed by a power law in the glassy state, which appears to be a general common feature of many different glass-formers [3]. Interestingly softness of IPN microgel particles can be tuned through the mutual PNIPAM-PAAc network composition [4,5], allowing to modulate the system fragility and to observe a strong-to-fragile transition.

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Stimulus Responsive Capillary Suspensions

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Stimulus-responsive capillary-structured materials can be formed from hydrophobized calcium carbonate particles suspended in a non-polar phase (silicone oil) and bridged by very small amounts of a hydrogel as the secondary aqueous phase [1]. Inclusion of thermally responsive polymers into the aqueous phase yielded a capillary-structured suspension whose rheology is controlled by a change in temperature and can increase its complex modulus by several orders of magnitude because of the gelation of the capillary bridges between the solid particles. The rheology of the capillary suspension and its response upon temperature changes can be controlled by the gelling properties as little as 0.1 w/w% of the secondary aqueous phase containing 2 wt% of the gelling carbohydrate. Doping the secondary phase with methyl cellulose, which gels at elevated temperatures, gave capillary-structured materials whose viscosity and structural strength can increase by several orders of magnitude as the temperature is increased past the gelling temperature of the methyl cellulose solution. Increasing the methyl cellulose concentration from 0 to 2 w/w% in the secondary phase increases the complex modulus and the yield stress of the capillary suspension of 10 w/w % hydrophobized calcium carbonate in silicone oil by 2 orders of magnitude at a fixed temperature [1]. By using an aqueous solution of a low melting point agarose as a secondary liquid phase, which melts as the temperature is raised, we produced capillary-structured materials whose viscosity and structural strength can decrease by several orders of magnitude as the temperature is increased past the melting temperature of the agarose solution.

We also demonstrate that capillary structured suspensions can be formed from hydrophilic calcium carbonate particles suspended in a polar continuous media and connected by capillary bridges formed of minute amounts of an immiscible secondary (oil) phase [2]. This was achieved in two different polar continuous phases, water and glycerol, and three different oils, oleic acid, isopropyl myristate and peppermint oil as a secondary liquid phase. The capillary structuring of the suspension was made possible through local in-situ hydrophobization of the calcium carbonate particles dispersed in the polar media by adding very small amounts of oleic acid to the secondary liquid phase. We observed a strong increase in the viscosity of the calcium carbonate suspension by several orders of magnitude upon addition of such secondary oil phase compared with the same suspension without secondary phase or without oleic acid [2].

The development of stimulus-responsive capillary suspensions can find potential applications in structuring of smart home and personal care products as well as in temperature-triggered change in rheology and release of flavours in foods and actives in pharmaceutical formulations.

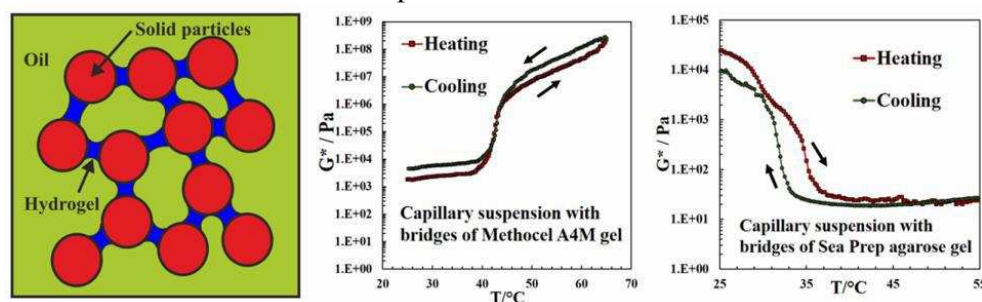


Figure 1. LHS: Schematics for oil-based capillary suspension where solid particles are bridged with an aqueous phase containing a gelling polymer. Gelling properties of gelling agent can determine the response of the capillary suspension towards temperature change with its complex modulus increasing in case of methylcellulose (CENTER) and decreasing in case of agarose (RHS).

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Effect of softness and architecture on the compression and interpenetration of microgels in overcrowded environments

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A polymer network can be compressed [1], deformed [2] or interpenetrated [3] in an overcrowded environment (Fig. 1). The prevalence of one of these mechanisms depends on both the softness and the architecture of the polymer network. By probing regular, ultra-low crosslinked [4], and hollow-poly(*N*-isopropylacrylamide) based microgels [5] we show that for the same architecture, a decrease in the amount of crosslinker during the synthesis produces a more pronounced deswelling. Nevertheless, for ultra-low crosslinked microgels, where no crosslinker agents are added, interpenetration between microgels is more dominant than compression. Surprisingly, if the crosslinker amount is kept constant, i.e. for comparable softness of the polymeric networks, the internal architecture has a significant effect on the deswelling once the particles are squeezed together: The presence of a cavity allows to rearrange the polymer chains in the empty volume leading to a larger compression [6]. For the studied concentrations, there is no evidence of significant deformation of microgels. Small-angle neutron scattering with contrast variation is used to directly access to the form factors of the different microgels embedded within a matrix of regular crosslinked ones. This work clarifies that to obtain compressible microgels that adapt their size in overcrowded environment, the presence of a cavity produces higher deswelling than decreasing the amount of crosslinker during the precipitation polymerization. The latter option can also lead to the opposite effect: For microgels that are too soft, i.e. with a weakly crosslinked network, interpenetration is the prominent mechanism once the microgels are squeezed together.

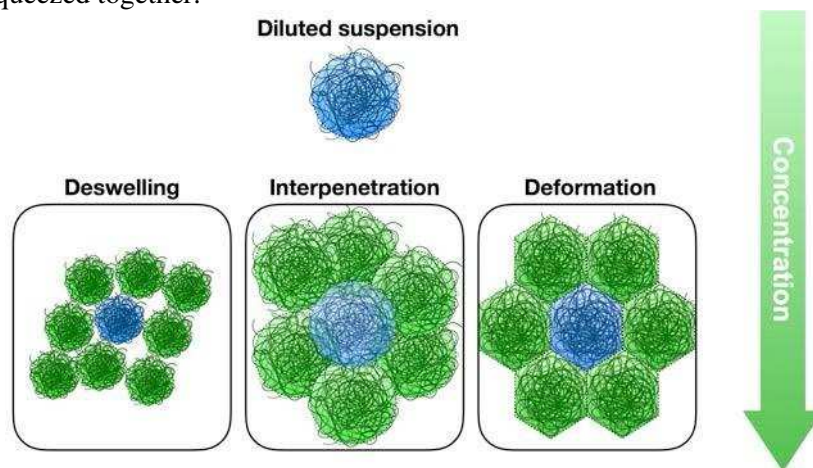


Figure 1. Possible responses of a microgel (blue) to the increase of concentrations: isotropic deswelling (bottom left); interpenetration (bottom central); and deformation with faceting (bottom right).

Acknowledgements: Alexander von Humboldt Foundation and SFB 985 “Functional Microgels and Microgel Systems” of Deutsche Forschungsgemeinschaft within Project A3 for the financial support

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Microstructure formation in freezing nanosuspensions

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The structural evolution of suspensions upon freezing is studied with optical microscopy in a suspended droplet configuration. Droplets have millimeter size and consist in an aqueous mixture of silica particles. Freeze-thaw cycles are applied and a two-step freezing mechanism evidenced. A fast adiabatic growth of dendrites that invade the full droplets is first observed, occurs within a few milliseconds. Then a slow process that lasts for several seconds and corresponds to the release of solidification latent heat into the hexane phase. Solidification front velocity is measured and shown to depend upon the nanoparticle concentration.

After the first freeze-thaw cycle flocculated microstructures are generated. When a second cycle is performed, microstructures further flocculate and generate, for dense silica suspensions, stable foam-like spheres. The SEM images (Figure 1) illustrate the obtained structures after drying. Porous system with clearly identifiable walls can be identified.

To explain this flocculation mechanism, the interplay between surface charge of solidification fronts in the liquid/solid coexisting system and interparticle repulsive forces is addressed. It is generated by particle confinement in a dendrite network.

This work demonstrates that suspensions strongly evolve under freezing and can produce solid foam-like flocculated structures. Methods are now being developed to produce large amounts of such materials.

We believe that the protocol used here could be an interesting and original route for the synthesis of new porous materials.

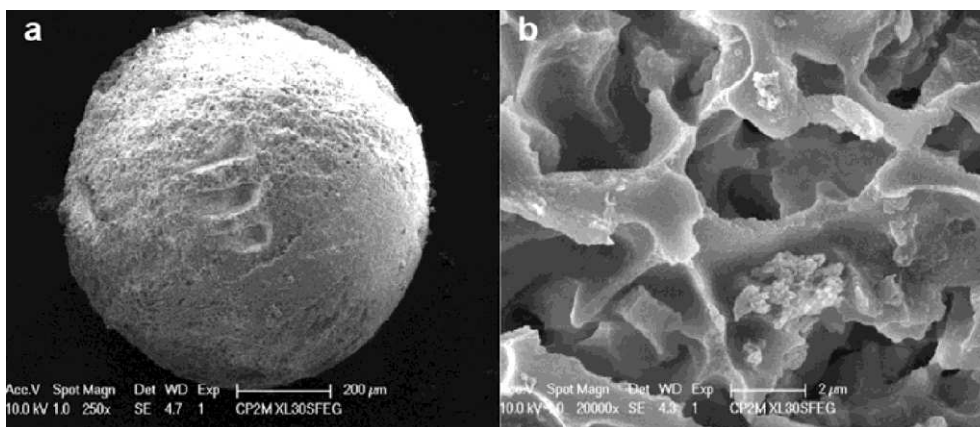


Figure 1. a) Scanning electron microscopy pictures of a freeze-dried droplet ($[\text{SiO}_2] = 300 \text{ g/L}$). Scale bar is $200 \mu\text{m}$. b) Zoom-in of (a) showing the foam-like structure of the medium.

The effect of the relative permittivity and the temperature response on the structural properties and swelling of Na⁺-, and Ca²⁺-montmorillonite

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The thermodynamical and structural properties of charged colloids are strongly affected by the valency of the counterions, the solvent, as well as the temperature. With monovalent counterions, the electrostatic interaction between the particles is repulsive, whereas for multivalent counterions, the interaction can be attractive due to electrostatic ion-ion correlation effects.

Here we will present results regarding the structural properties, and the intracrystalline swelling of the natural clay minerals Na⁺-, and Ca²⁺-montmorillonite (Na-, and Ca-mmt) as an effect of decreasing the relative permittivity of the solvent [1], and for the temperature response by mixing counterions [2]. For this purpose we have used the experimental techniques; small angle X-ray scattering, and osmotic pressure measurements, in combination with the continuum model utilizing coarse-grained molecular dynamics simulations, and Monte Carlo simulations of two parallel surfaces corresponding to two clay platelets.

It was found that it is possible to tune the electrostatic interactions to obtain a transition from a repulsive to an attractive system for Na-mmt by decreasing the relative permittivity of the solvent, i.e. from water to ethanol. This because when increasing the ethanol concentration, the Bjerrum length increases, and hence, the attractive ion-ion correlation forces are enhanced. For the Ca-mmt system, a non-monotonic behavior of the intracrystalline swelling as function of ethanol concentration was captured experimentally, where an increase in the osmotic pressure, and hence, an increase in *d*-spacing was found at low concentrations, indicating that short-ranged interactions dominate the system. Theoretically, the non-monotonic behavior could not be captured with the continuum model, probably due to the limitation that the electrostatic interactions solely enters the Hamiltonian via the Bjerrum length.

Moreover, it was found that the electrostatic interactions alone can give a positive, negative, or constant osmotic pressure response with temperature, depending on the monovalent/divalent counterion ratio. The increase in osmotic pressure with temperature, which occurs at a low fraction of divalent counterions, can be understood from the DLVO-theory. The origin of the opposite behavior can be explained by the enhanced attractive electrostatic ion-ion correlation interactions with temperature. Our theoretical predictions of the temperature response are in qualitative agreement with the experimental data, giving a further indication that our models can explain the underlying physics. The theory presented here is general and predicts that the temperature response for all types of charged colloids can be controlled by mixing counterions of different valence, if the interactions in the system are dominated by electrostatics.

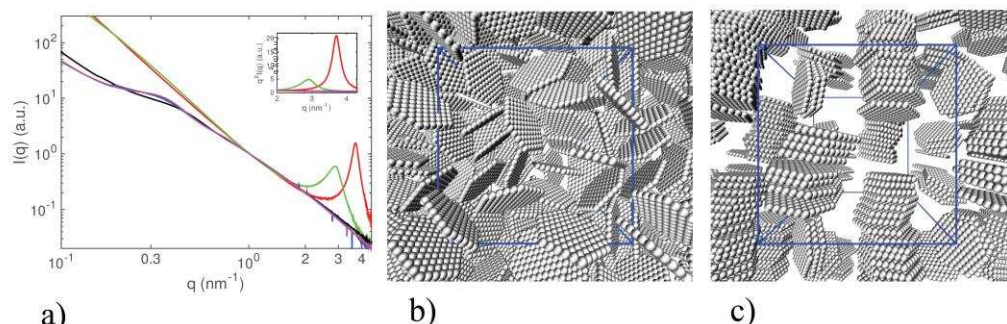


Figure 1. a) SAXS spectra for Na-mmt at 0 (magenta), 40 (black), 60 (green), and 95 (red) wt% ethanol, where the Bragg peaks represent tactoid formation in the system. Illustrative configurations obtained from the molecular dynamics simulations of Na-mmt with b) 0, and c) 100 wt% ethanol.

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Formation and characterization of multiple Water-in-Water-in-Water (W/W/W) emulsions

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Water-in-water (W/W) emulsions are liquid/liquid dispersions of two immiscible aqueous phases, which can be prepared in mixtures of edible components, such as water-soluble proteins and polysaccharides [1-4]. These emulsions can be formed because of thermodynamic incompatibility between two hydrophilic macromolecules, in absence of oil and without surfactant. These fat-free dispersions can be highly interesting for food and drug delivery applications.

The present work focuses on the formation and study of multiple Water-in-Water-in-Water (W/W/W) emulsions, which are prepared in a ternary system composed of H₂O, a protein and a polysaccharide. These multiple emulsions are prepared by using a two-step emulsification method, in which a primary water-in-water emulsion with small droplet size is prepared first, and later this primary W/W emulsion is dispersed in an aqueous solution that has a composition similar to that of primary droplets, by applying a gentle agitation. An Example of a multiple W/W/W emulsion is shown in Fig. 1.

Our results, in absence of stabilizer, have shown that W/W/W multiple emulsions are unstable, and tend to phase separation. We have prevented this adding a crosslinker in the intermediate phase, and thus, obtaining structured microgels with the same size and morphology that W/W/W multiple emulsions. These structured microgels are being studied for the encapsulation and controlled release of active components. The results demonstrate that W/W/W systems can be highly promising for the incorporation and delivery of hydrophilic molecules.

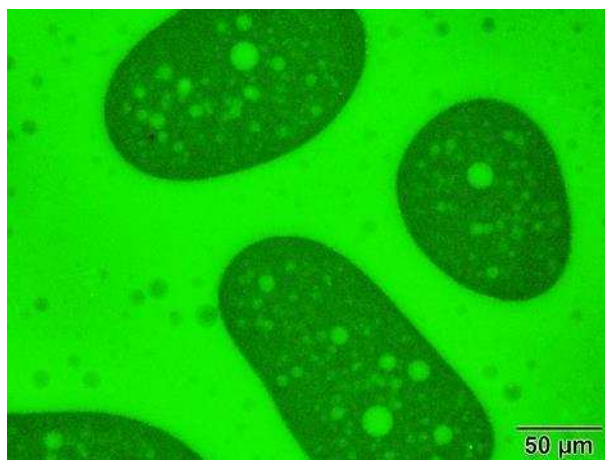


Figure 1. Image acquired by fluorescence optical microscopy, showing an example of a W/W/W emulsion. The inner and the external phase contain a polysaccharide, and the intermediate phase contains a protein. The polysaccharide has been labelled with fluorescein isothiocyanate.

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Dynamic properties of capillary suspensions: A molecular dynamics study using ESPResSo

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Capillary suspensions are a ternary liquid – liquid – solid system arising from the addition of a small amount of a second, immiscible liquid to a suspension. A sample spanning network is formed, which drastically alters the rheological properties of the suspension [1]. These properties can be tuned by adjusting the individual processing route as well as through the choice of the three components. Many in-vitro experiments have shown a strong influence of processing conditions on the rheological properties, implying a change in the micro- and network structure, however, a deterministic connection remains unknown [2-3]. Such a connection will open pathways for the rational design of materials with tunable properties.

We have developed a computational model for capillary suspensions in order to study the network formation process as well as the dynamic, rheological properties. Our model allows us to precisely tune microstructural parameters such as the liquid bridge volume and the ability of capillary bridges to rotate over the surface, as shown in Figure 1. We study the influence of these parameters on the resulting structure and shear moduli of the bulk material.

For our research, we use a model based on the open-source, coarse-grained, MD code ESPResSo [4], which includes rigid spheres and capillary interactions [5-6] as well as hydrodynamics. These hydrodynamic interactions are modelled via the lattice Boltzmann technique. A collision detection feature is used to construct the capillary bonds that connect individual spheres to form a network. Shear is introduced via Lees-Edwards (LE) boundary conditions [7-8]. The network analysis relies on both traditional techniques, e.g. the radial distribution function or the coordination number, and on new approaches derived from graph theory. We use the Python package networkx [9] for this purpose. We show that graph theory offers a new useful tool to quantify the interconnectivity of network sites via the clustering coefficient or the important sites for momentum flux by taking the minimum spanning tree into account.

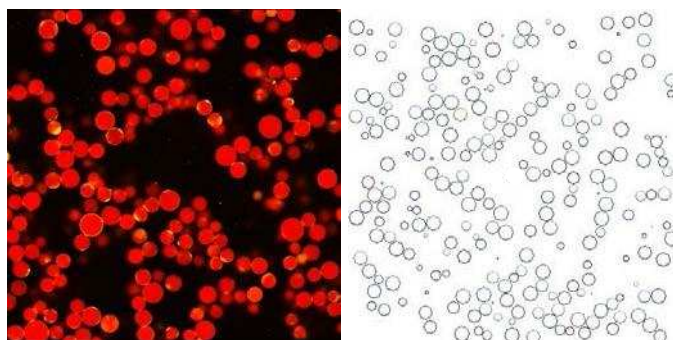


Figure 1. Comparison between (left) experimental confocal image and (right) simulation results.

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Interfaces of colloidal particles in liquid dispersions observed by combined SAXS and SANS studies

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The combination of small angle X-ray and neutron scattering (SAXS, SANS) allows a detailed analysis of the mesoscopic structure of colloidal dispersions such as organic or noble metal nanoparticles dispersed in aqueous solutions or inorganic semiconducting quantum dots dispersed in organic solvents. It is, however, the atomic and molecular structure of the interface between the nanoparticles and the dispersion medium that governs in many cases the formation, stabilization, and function of the nanoparticles.

In this contribution, novel insights into the molecular structure of interfaces in colloidal dispersions which are highly relevant for industrial applications will be presented. It will be demonstrated that it is possible to detect the details of the stabilizing acetate layer of ZnO quantum dots in ethanolic solution [1,2] (cf. Fig. 1 left), to discover and tailor the stabilizing mechanism of gold nanoparticles in aqueous solution crowded by CTAB micelles [3] (cf. Fig. 1 right), and to observe the ligand (oleic acid – porphyrins) exchange and their molecular orientation at the interface of TiO₂ nanoparticles by combined evaluation of SAXS and contrast variation SANS experiments.

Nevertheless, worldwide there is no instrument for simultaneous SAXS and SANS measurements available so far. This limits the applicability of the combined analysis of SAXS and SANS data significantly especially for metastable systems. However, we will briefly introduce the first combined SAXS/SANS instrument which is currently under construction and will be installed soon at the D22 instrument of the ILL (Grenoble, France).

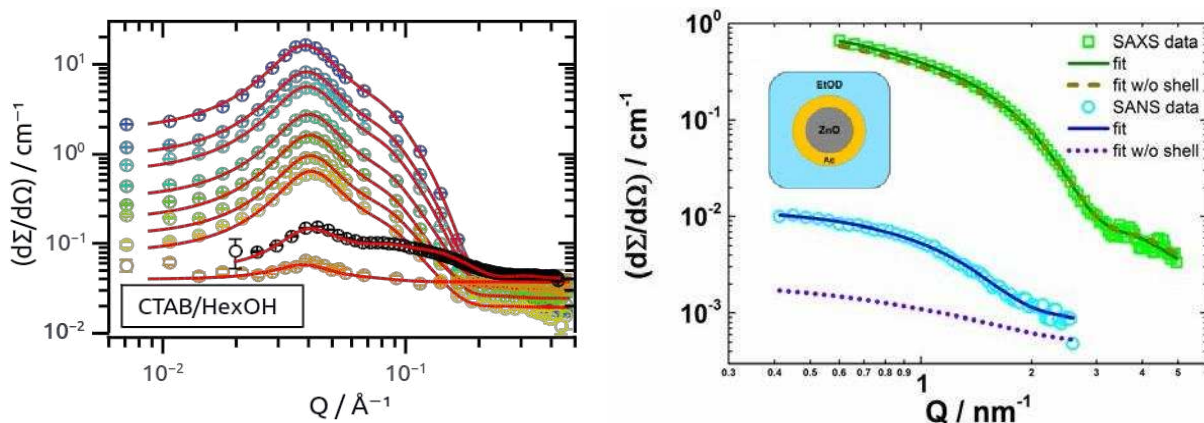


Figure 1: (left) SAXS (black circles) and contrast variation SANS curves of hexanol loaded CTAB micelles and fit of a self-consistent structural model for CTAB micelles loaded with short aliphatic saturated alcohols **(right)** SAXS (green) and SANS (blue) curves of acetate stabilized ZnO nanoparticles in ethanolic solution with best fits of a solid sphere (dashed and dotted lines) and a core shell (solid lines) model to the data.

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Colloidal Stabilization of Surfactant-free Water-in-Oil Emulsions with the Addition of Electrolyte in Water

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We have investigated the colloidal stability of oil-in-water (O/W) and water-in-oil (W/O) emulsions in the absence of any emulsifiers such as surfactants and amphiphilic polymers (named as surfactant-free (SF-) O/W and W/O emulsions, respectively) to evaluate the essential feature of colloidal stability of emulsions [1-3]. In particular, the connection between the physical properties of oil and the colloidal stability of SF-O/W and W/O emulsions has been investigated to elucidate the role of oil for colloidal stabilization of O/W and W/O emulsions. We found that the colloidal stability of SF-O/W and W/O emulsions was enhanced by mixing different kinds of hydrocarbon oils [3, 4]. In this work, we examined the effect of electrolyte in water on the colloidal stability of SF-O/W and W/O emulsions. We revealed that the SF-O/W emulsions were demulsified with the addition of electrolyte in water while the colloidal stability of SF-W/O emulsions was enhanced with the addition of small amount of electrolyte in water. For example, the colloidal stability of SF-W/linoleic acid emulsions was enhanced with the addition of NaCl at the concentration of 0.10 mol L^{-1} in water (see **Figure 1**). The colloidal stabilization of SF-W/O emulsions with the addition of electrolyte in water was also observed in the case of the addition of KCl, MgCl_2 , AlCl_3 , NaBr and NaI in water. We consider that the colloidal stabilization of SF-W/O emulsions with the addition of electrolyte in water is achieved by the reversible molecular diffusion among water droplets in SF-W/O emulsions. Water molecules diffuse from smaller droplets to larger droplets due to the different chemical potentials (solubilities) between smaller and larger water droplets as described by Kelvin's law. As a result, the smaller water droplets become smaller while the larger water droplets become larger. Since the electrolyte dissolved in water droplets remains in the water droplets during Ostwald ripening, the electrolyte is condensed in the smaller water droplets while the electrolytes are diluted in the larger water droplets. The different concentrations of electrolyte between smaller and larger water droplets lead to the diffusion of water molecules from larger water droplets to smaller water droplets to decrease the concentration of electrolyte in the smaller water droplets as described by Raoult's law.

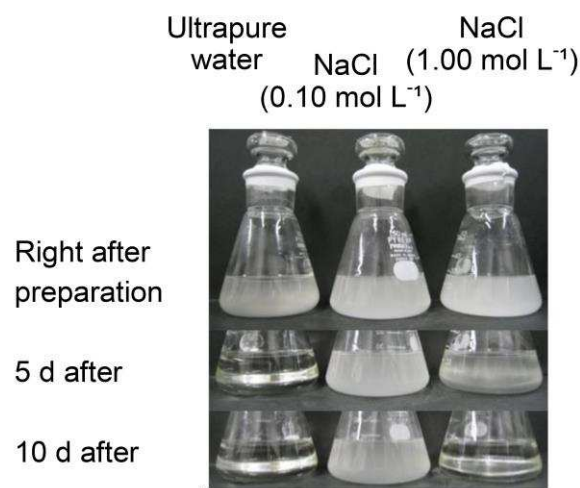


Figure 1. Colloidal stability of SF-W/linoleic acid emulsions. (Left-hand-side images) no NaCl (ultrapure water), (Center images) 0.10 mol L^{-1} NaCl in water and (Right-hand-side images) 1.00 mol L^{-1} NaCl in water.

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Microliter viscometry using a bright-field microscope: η -DDM

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Passive microrheology provides information on rheological properties based on the mean squared displacement (MSD) of tracer particles. The MSD is determined either by tracking the particles in a microscope or performing a scattering experiment. Here we combine the strengths of both approaches by using differential dynamic microscopy (DDM) which is based on a series of microscopy images but provides information usually obtained in scattering experiments, namely the intermediate scattering function $f(\mathbf{Q}, t)$ as a function of delay time t and scattering vector \mathbf{Q} . In the analysis of (\mathbf{Q}, t) we focus on the small-frequency limit and extract the steady-shear viscosity $|\langle\omega\rangle|_{\omega\rightarrow 0}$. DDM is particularly suited to provide information at small \mathbf{Q} values and hence large length scales which implies long time scales and hence small frequencies. We show that, therefore, DDM is particularly powerful to reliably measure $|\langle\omega\rangle|_{\omega\rightarrow 0}$. Furthermore, only an optical microscope and a small sample volume (about a few microliters) are required. This renders η -DDM particularly useful for groups without light scattering equipment but an interest in scarce soft matter and biological samples.

Development of a preparation method for model lipid membrane designed for the examination of skin barrier

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The stratum corneum (SC), the outermost layer of human skin, is well known to play a crucial role in the physicochemical barrier of skin. The SC consists of multilayers of nonviable corneocytes, embedded in a matrix of highly ordered intercellular lipids, which are mainly composed of several kinds of ceramides (Cer), free fatty acids (FFA), and cholesterol (Chol), and arranged in a lamellar structure. Recent studies have reported that the barrier properties are achieved by unique organization of the intercellular lipids. To understand the skin barrier mechanism and improve a percutaneous drug delivery, we need to clarify the effect of the molecular properties of each intercellular lipid on the barrier function. For this purpose, artificial lipid membranes mimicking the lipid composition and organization in SC are more favorable than the SC samples, whose lipid composition is uncontrollable.

In this study, we developed a simple preparation method for model lipid membranes containing a large ratio of non-hydroxy phytosphingosine (NP) as the Cer component [2]. It has been thought to be difficult to disperse the NP homogeneously in a model membrane due to its low miscibility [3]. In order to find an optimal conditions, we examined the effects of lipid composition, removal process of organic solvent, annealing process, and hydration on the structure of artificial lipid membranes containing NP, non-hydroxy sphingosine (NS), Chol, and FFA by X-ray diffraction (SPring-8 40B2). We collected their diffraction patterns between 25°C and 85°C in heating and cooling scan at the rate of 1 K/min.

Our results revealed that membranes with the lamellar structure and lipid organization similar to those in SC can be obtained only when they are prepared by the spray method and annealed below 65 °C. Annealing at temperatures higher than the phase transition temperature led to the phase separation of Cer crystals instead of making the membrane homogeneous. Thus, we demonstrated that NP can be dispersed homogeneously in a model membrane under proper preparation conditions.

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Amphiphile-assisted exfoliation of carbon nanotubes in water as probed by NMR diffusometry: adsorption mode, dynamics and competitive binding

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Non-covalent dispersion methods are one of the most common procedures to exfoliate carbon nanotubes (CNTs) in water. In this process, amphiphilic molecules (such as surfactants and polymers) adsorb on CNT surface through hydrophobic interactions while their polar headgroups provide colloidal stabilization of CNTs *via* electrostatic and/or steric repulsions.[1,2] Understanding the equilibrium and dynamics features of the interaction between the nanotubes and the dispersant molecules (e.g. fraction of dispersant adsorbed, residence time, binding strength, surface coverage) are important aspects to design ever more efficient dispersion and functionalization of CNTs. Moreover, these parameters may also play an important role in sorting carbon nanotubes with different chiralities through selective binding.

Herein we present a ¹H NMR diffusion study, where the adsorption, kinetics and role of block polydispersity of a polymer-assisted CNT exfoliation process was assessed. We were able to quantify the fraction of block copolymer (Pluronic F127) adsorbed, the residence time and the polymer lateral diffusion on the CNT surface.[3] Additionally, the competitive binding between Bovine Serum Albumin (BSA) and F127 was also evaluated. We could detect a displacement of BSA from the SWNT surface by adding F127 to the system. However, the opposite was not observed, which indicates that F127 binds more strongly to the SWNT surface than BSA.[4] Similar studies of competitive binding between several ionic surfactants (SDBS, SDS, Sodium Cholate, DTAB, CTAB) and F127 were performed.

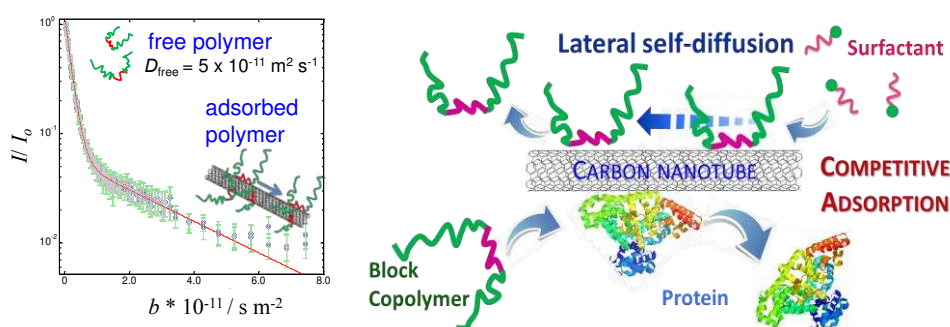


Figure 1. Biexponential signal decay observed for F127 by ¹H NMR diffusometry (left); dynamic processes studied on CNT surfaces from NMR data (right).

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Temporal stability of droplets distributed on an interface

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The Cahn-Hilliard equation was proposed to model the phase-separation of immiscible fluids [1]. More recently, it has been used to represent phenomena that involves interfacial dynamics such as wetting and tumor growth [2]. The multicomponent version of the Cahn-Hilliard model considers more than two phases and the corresponding interfaces between them. This study considers a system with three immiscible phases, specifically the stability of droplets that lie at the interface between two immiscible fluids. We are interested in spatial distributions of droplets that are stable in finite-time scales. Using a parametric study, we show the effects of the interfacial and bulk energy over the dynamics and stability of the droplets. Figure 1 shows the steady state solutions when the interaction energies between phases 1 and 2, and 2 and 3 remain constant and equal in magnitude, and the interactions between phases 1 and 3 are varied. We evaluate the average lifespan of droplets in a periodic pattern, based on the steady-state shape of isolated droplets, and the relation between the period of the pattern and the lifespan. Figure 2 present results of an initial condition that evolves into an unstable film that separates into small structures. Then, the coalescence process merge them into larger structures with longer lifespans. We identify the values of the interfacial and bulk parameters that trigger these instabilities and quantify their effect on the lifespan of the structures. Additionally, we examine the differences between results for straight and curved interfaces with different curvatures.

The Cahn-Hilliard model is a fourth-order partial differential equation and therefore requires a high-order continuous discretization [2]. Accordingly, we use an isogeometric analysis method that provides spaces with arbitrary polynomial order and continuity to discretize the model in space [3].

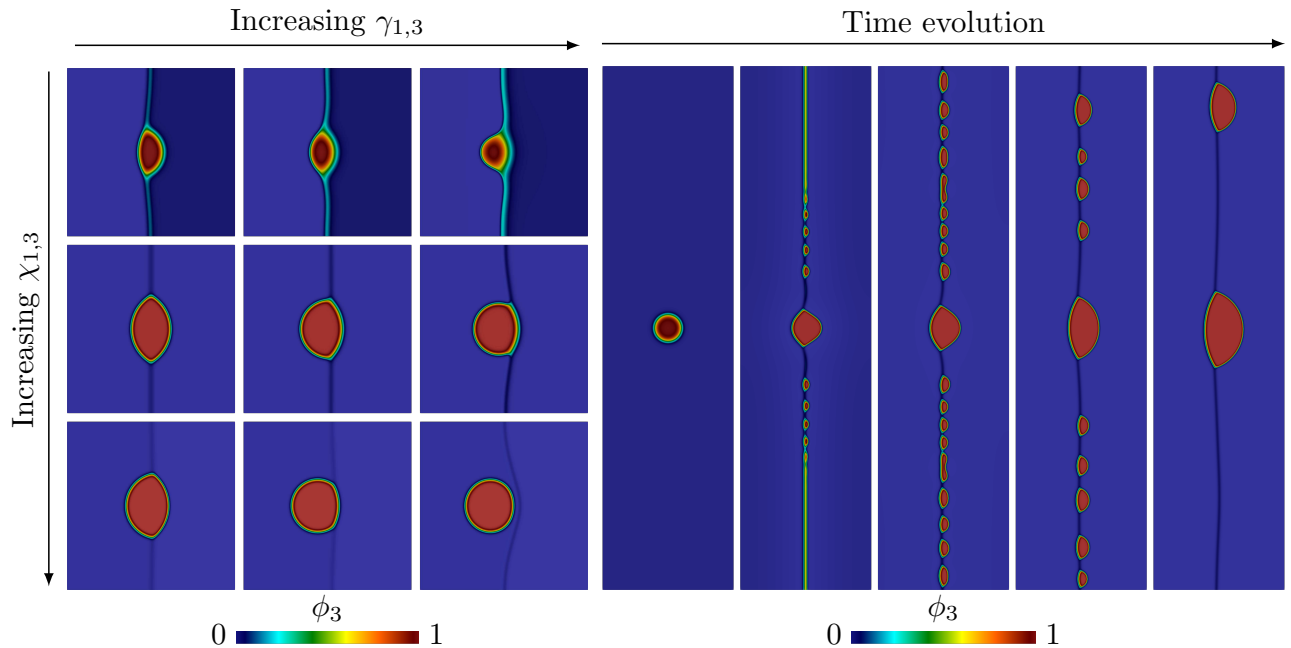


Figure 1. Steady state solutions for different values of bulk and interfacial energies.

Figure 2. Time evolution of an unstable film with breakup and coalescence.

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Experimental and theoretical study on lysozyme adsorption on colloidal silica

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Adsorption of proteins onto colloidal particles is one of the crucial processes in environments and industries such as pharmaceutical, cosmetic, and coating. Toward the understanding of the adsorption mechanisms of proteins onto colloidal particles, the comparison between experimental data and theoretical models is effective. However, it is difficult to measure the adsorbed amount for a wide range of proteins and particle concentrations, because of the limitations from the experiment methods. Also, theoretical models sometimes include a number of adjustable parameters, and it makes difficult to understand the exact adsorption mechanisms. In the present work, the adsorption mechanisms of lysozymes onto colloidal silica particles are investigated for a wide range of lysozyme and silica particle concentrations by combining the experimental and theoretical methods without or with small number of the adjustable parameters.

We used the well characterized lysozymes and colloidal silica particles [1,2]. The adsorbed amount and the zeta potential of lysozymes coated silica particles were measured as a function of silica concentration, mass ratio of lysozyme to silica, pH, and KCl concentration. The theoretical zeta potentials of lysozymes coated silica particles were calculated from the zeta potentials of lysozymes and silica particles through the combination of the equilibrium adsorption model and the electrokinetic model [3]. From the comparison between experimental and calculated zeta potentials for a wide range of silica particles concentration with fixed mass ratio of lysozyme to silica, the equilibrium adsorption mechanism was denied and, on the contrary, the irreversible adsorption mechanism was supposed. This method has possibility to be used for analysing and predicting the adsorbed amount in the samples with a wide range of protein and particle concentrations, especially for the low concentration regime.

The theoretical maximum adsorbed amount was calculated from electric properties of lysozyme and silica by the three-body random sequential adsorption (RSA) model [4]. The three-body RSA model could predict the qualitative trend of the dependence of the maximum adsorbed amount on KCl concentration at low pH condition. Besides, the theoretical values did not show the quantitative agreement with the experimental data. These results show that lysozymes are adsorbed onto silica particles almost irreversible state, and the surface heterogeneity of lysozyme and/or the ordered distribution affect the adsorbed amount.

Acknowledgements: This study was performed with financially support from the JSPS KAKENHI (17J00332, 16H0638, and 15H04563)

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Surface conductivity and polarizability of goethite particles in *KCl* aqueous electrolytes

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Surface conductivity is an important property of the electric double layer. According to the theory the particle polarizability and its anisotropy can be represented as a function of their surface conductivity, size, shape factor and conductivity of medium [1]. If particle polarizability is known the particle surface conductivity can be calculated.

Here we present the results of measurements of goethite particle polarizability anisotropy and its surface conductivity in aqueous univalent electrolytes of *KCl* in varying field frequency, which is then compared to the theoretically computed particle polarizability dispersion curve for thin electric double layer. In the conducted research goethite particles were approximated with prolate spheroids with long axis of 200 – 2000 nm, short axis of 20 – 120 nm and axis ratio of 5 – 25 as obtained from goethite particles TEM images. Electro-optical technique was used to particle size and anisotropy polarizability distributions in the colloids under study. Particle anisotropy polarizability was experimentally determined by studying electro-optical effects in aqueous goethite colloids. The intensity of transmitted through suspension light depends on particle orientation ordering along electric field applied to the disperse system. It also depends on transmitted light polarization. Electric field induced extinction for polarized incident light along and across the applied electric field was different and had different sign, which allowed us to measure conservative dichroism in the suspensions with high accuracy. The *KCl* electrolyte concentration dependence of goethite particle polarizability anisotropy γ was experimentally determined at frequency ν range 0.1 kHz - 4 MHz of applied electric field (See Figure 1). The measured dependences of γ on ν are in a good agreement with the ones calculated in frames of theory [1]. The values of particle surface conductivity at different concentrations of electrolyte were computed. It was observed that at low electrolyte concentrations it is proportional to electrolyte concentration, which is in line with the Henry law.

The theory of particle polarizability [1] used throughout these studies is applicable for the study of electric properties of goethite particles. The obtained particle surface conductivity values are close to ones of diamond particles in aqueous *KCl* obtained earlier [2].

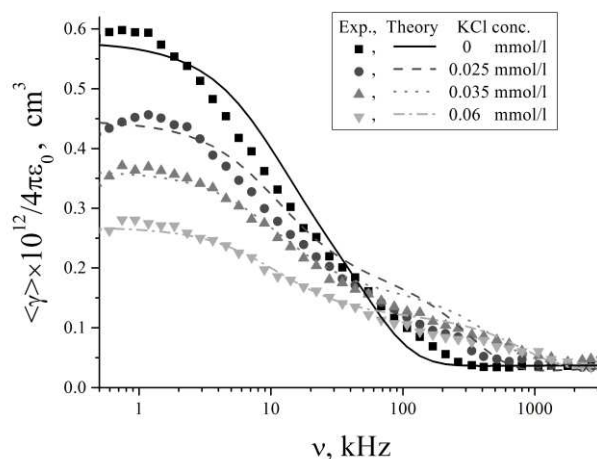


Figure 1. Goethite particle polarizability anisotropy dispersion for several concentrations of *KCl*.

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Choline-based solvents for the dispersion of maghemite nanoparticles

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Dispersions of nanoparticles (NPs) in ionic liquids (ILs) have numerous applications in various domains such as electrochemical devices, thermoelectricity, heat transfer ... [1]. In previous studies we showed the possibility of colloidal stability of such particles in a protic ionic liquid, ethylammonium nitrate [2]. However, ILs present some drawbacks that can hinder their development: first, their so-called “green” aspect is only based on their low vapour pressure and not on their biocompatibility or biodegradability. Second, their usually quite high viscosity can reduce their performances in particular when their conductivity is the relevant desired parameter brought by the carrier fluid of the colloidal dispersion.

To address this question, we studied solvents based on the cholinium cation (figure 1). Since the precursor choline chloride is a cheap biodegradable solid, they are particularly interesting due to their outstanding biodegradability and low toxicity. Two different approaches will be presented: “true” ILs formed by the association of the cholinium cation with an amino acid as the anion and mixtures of choline chloride with a hydrogen bond donor (HBD) such as ethyleneglycol or urea, leading to a liquid solvent at room temperature (often called Deep Eutectic Solvent).

We studied the viscosity characterization of these solvents, pure or mixed with water. These solvents were then used to disperse initially aqueous maghemite nanoparticles. A special attention was paid to the nature of the NPs surfaces that permit a good transfer of the particles. The amount of water present in the samples was correlated to the stability of the dispersion. This stability was examined by visual observation (figure 2), dynamic light scattering and small angle X-ray scattering.

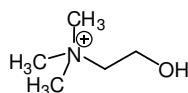


Figure 1. the cholinium cation



Figure 2 : (left) stable dispersion (right) unstable dispersion

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Turbulent hetero-aggregation rates of unequal-sized colloidal particles: Effect of size ratios

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The co-existence of different types of colloidal particles causes the aggregation between different particles called hetero-aggregation. Moreover, colloidal particles are usually subjected to flow fields in natural environments and industrial processes. In the present study, therefore, we have analyzed the experimental data of the turbulent hetero-aggregation with the theoretical calculation for a simple shear and an axisymmetric extensional flows. The hetero-aggregation experiments for unequal-sized latex particles with three different size ratios were carried out. The hetero-aggregation rates were evaluated from the reduction of the number of free smaller particles due to the hetero-aggregation with microscopic observation.

We show capture efficiencies of hetero-aggregation rates for unequal-sized particles as a function of size ratio in Figure 1, where the size ratio is defined as the smaller particle radius divided by the larger one. Symbols are experiments. The red and black lines are calculations by solving the convective-diffusion equation in an extensional flow [1] without and with Brownian diffusion, respectively. The blue line is the ones calculated with the correlation equation based on a hydrodynamic trajectory analysis in a simple shear flow [2]. The experimental capture efficiencies do not significantly depend on their size ratio, while the calculated one in a shear flow substantially slows down with decreasing size ratio. In contrast, the capture efficiency in the extensional flow is less sensitive to the size ratio. Comparing the experiments with these theories, we found that the turbulent hetero-aggregation rates of unequal-sized particles can be more comparable with the calculation in the extensional flow than that in the shear flow. This implies that the flow in the microscale of turbulence is approximated as an extensional flow rather than a simple shear flow.

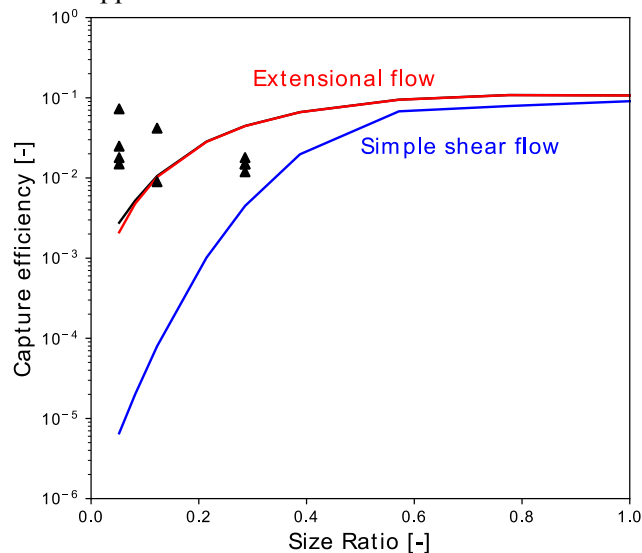


Figure 1. Turbulent capture efficiency vs. size ratio for unequal-sized particles, where the size ratio is defined as the smaller particle radius divided by the larger one: Symbols are experiments. The red and black lines are the calculated values by solving the convective-diffusion equation in an extensional flow [1] without and with Brownian diffusion, respectively. The blue line is the ones calculated with the correlation equation based on the hydrodynamic trajectory analysis in a simple shear flow by Han and Lawler [2].

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High Performance Laser Transmission Spectroscopy: a powerful technique to investigate colloidal suspensions

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Tuneable laser sources, in the spectral range from visible to infrared, allowed the development of Laser Transmission Spectroscopy (LTS) technique able to determine the density distribution of colloidal suspensions [1]. The LTS technique measures the transmittance of a laser beam through a suspension of particles as a function of the wavelength. The particle density distribution, as a function of their size, can be calculated through the Beer-Lambert law. Compared with traditional diffusion techniques (static and dynamic light scattering), LTS allows not only to study the size and shape of the particles in suspension but also to determine their absolute concentration. This is very powerful for both soft matter physics and biophysics. In particular, the high sensitivity of the LTS technique permits to study lipid nanovesicles at very low concentrations (e.g., exosomes) opening new scenarios in therapeutic and diagnostic applications [2]. To this aim, we have built an LTS apparatus combined with a high-sensitivity high-resolution conditioning optoelectronic system [3] capable to measure very small changes of the light power transmitted through the sample under analysis. Measurements on reference polystyrene nanoparticle suspensions differing in size and concentration have provided interesting results in terms of size resolution and concentration detection limit.

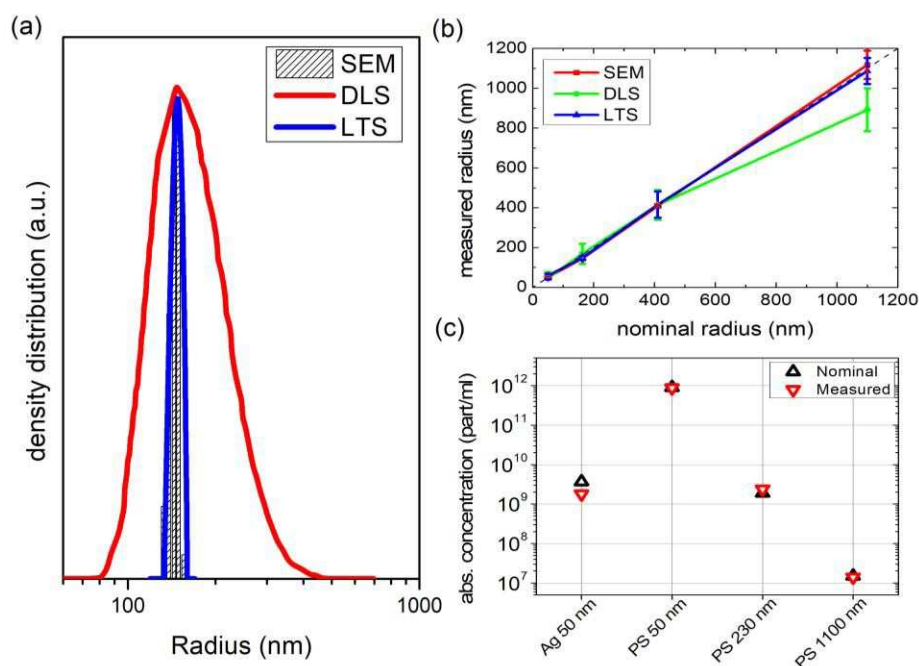


Figure 1: (a) Density distribution of polystyrene particles ($r=163$ nm) aqueous suspension measured by LTS, DLS and SEM; Comparison between measured and nominal radius (b) and absolute concentration measured and nominal (c) for different polystyrene and silver particles suspensions.

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Preparation of magnetorheological fluids and effect of additives on their stability

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Magnetorheological (MR) fluids are suspensions containing iron particles with magnetic properties, additives and non-magnetic carrier fluid. MR fluids are used for automotive like dampers, valves, brakes etc. Magnetic field generated by electromagnet has crucial effect on flow properties of magneto-rheological fluids especially on yield stress. The suitable features of MR fluids depend on a stability of these fluids, which is given by stability of iron magnetic particles in carrier fluid. Generally, iron particles are non-stable because of differences in density of particles and carrier fluid. Above mentioned are the most limiting factors in global utilization of MR fluids.

Stability of MR fluids in gravitational field can be affected by various additives, which are able to slow down the sedimentation process of iron particles. Suitable additives could be used, e.g. surfactants, fatty acids, polymers, etc. Moreover, it is very important be carefully by combination of additives, because the carrier fluid must have suitable viscosity and mostly the additives are increasing the viscosity of fluids.

The experiments were based on usage of surfactants like a stabilisation agent. Span 80 is emulsified in water and Tween 80 is used for chemisorption of iron particles, which it was used Park et al. [1]. Treated iron particles showed higher sedimentation stability in comparison with native (non-modified) iron particles. (Figure 1).

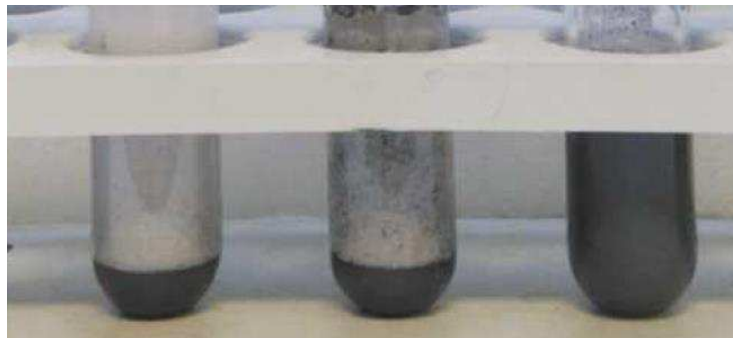


Figure 1. Sedimentation stability of prepared MR fluids.

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Sedimentation analysis of magnetorheological fluids stabilized by amphiphilic compounds studied by analytical centrifuge

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The analytical centrifuge (LUMiSizer) has been utilized for the sedimentation analysis of magnetorheological (MR) fluids. MR fluids have been prepared by dispersion of iron particles (5 – 44 μm) in carrier fluid (mineral oil). Non-stabilized MR fluids showed strong destabilization in both centrifugal and gravitational field.

Therefore the possibility of MR fluids stabilization by addition of amphiphilic compounds (surface active agents) has been tested. Span 80 (non-ionic tenside) has been used as a suitable agent for MR fluids stabilization. Iron particles have been treated by chemisorption of Span 80 (3 – 10 wt. %) and positive chemical treatment of iron particles has been tested by scanning electron microscopy. The sedimentation analysis under centrifugal field (17 hours, 200 RPM, 25 °C) has been performed for both stabilized and non-stabilized iron particles in carrier fluid.

The suppression of iron particles sedimentation has been compared by changes in transmission spectra as a time function and non-stability indexes obtained by measurement on analytical centrifuge (LUMiSizer, LUM GmbH).

Iron particles chemically treated by non-ionic tenside (10 wt. %) showed higher stability over the time in comparison with non-treated iron particles. The lower concentration (3 wt. %) of Span 80 had minor effect on the stability of MR fluids. The analytical centrifuge seems to be useful technique in the study on stability of MR fluids at different conditions.

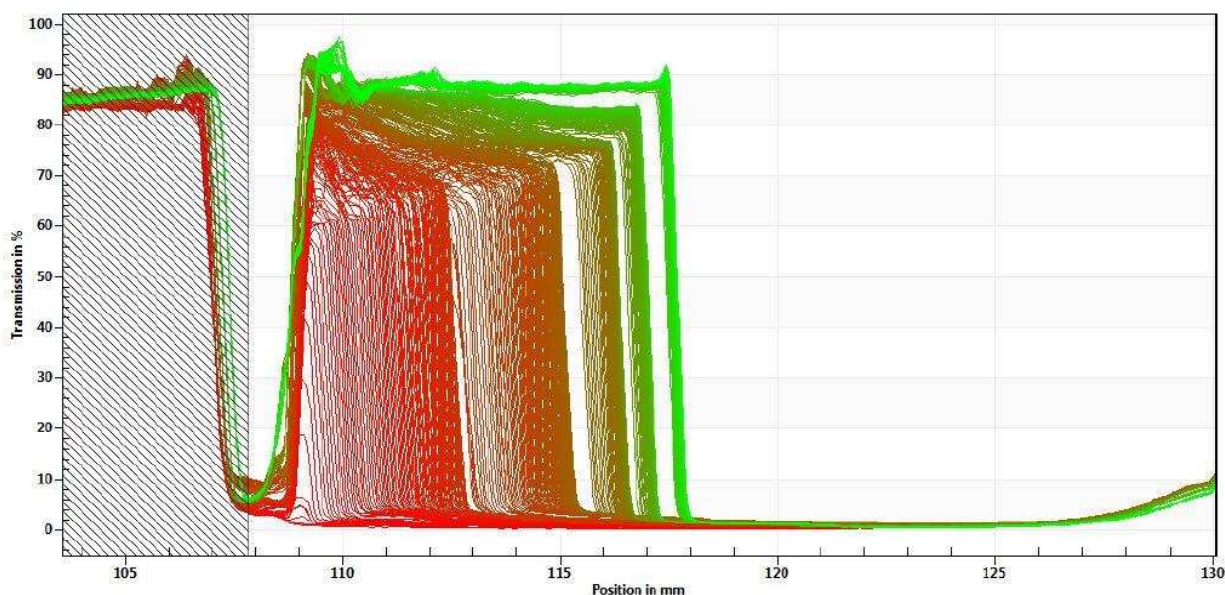


Figure 1. Transmission spectra as a time function for non-stable MR fluid (green lines mean the most actual value – the end of the experiment, red lines mean transmission spectra at the beginning of experiment).

Acknowledgements: This research project has been supported by project GACR 17-10660J “Studies on Magnetorheological Fluid with High Sedimentation Stability” and by project “Materials Research Centre at FCH BUT – Sustainability and Development” REG LO1211, with financial support from National Programme for Sustainability (Ministry of Education, Youth and Sports).

Inducing protein reentrant condensation with polyvalent anions

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Understanding how cosolutes influence protein-protein interactions is important for understanding protein behaviors such as crystallization pathways, liquid-liquid phase separation (LLPS) and liquid-solid phase separation (LSPS). Reentrant condensation (RC) describes the ability some polyvalent ions have to precipitate proteins at low concentrations and then resolubilise them at higher concentrations as shown in figure 1. Inducement of RC is dependent on a number of factors such as protein net charge, ion net charge, ion concentration and ion species. Trivalent cations such as yttrium (Y^{3+}) and lanthanum (La^{3+}) have been shown to induce RC of acidic proteins and their mechanisms have been studied extensively [1-2].

We have used protein solubility, static light scattering (SLS), dynamic light scattering (DLS), and zeta potential measurements to understand the molecular mechanism for RC by polyvalent anions such as pyrophosphate (SPP), tripolyphosphate (STPP) and phytic acid, which have been studied to a smaller degree than the cations. Figure 1 shows the phase diagram for lysozyme solutions with STPP.

Basic proteins have a net positive charge and repel each other through long-range electrostatics when no counter anions are present. The initial lysozyme concentration (precipitation) occurs when the polyvalent anions STPP/SPP interact with solvent-exposed basic residues via electrostatics, which neutralize the long-range repulsive interactions between lysozyme molecules and allows protein cross-linking (precipitation) to take place. Further increasing STPP/SPP concentration after this point causes resolubilisation because lysozyme net charge has been reversed from positive to negative. While this mechanism follows what has been proposed for the behavior of acidic proteins with trivalent cations, there are also fundamental differences. The precipitation of lysozyme occurs almost immediately when in the two-phase region and only LSPS is observed for the polyvalent anions. Interestingly, citrate does not RC of lysozyme at similar strengths of protein-protein attractions despite having a similar charge, size and shape to SPP. This disparity highlights the importance that ion-specific effects can have on protein solubility.

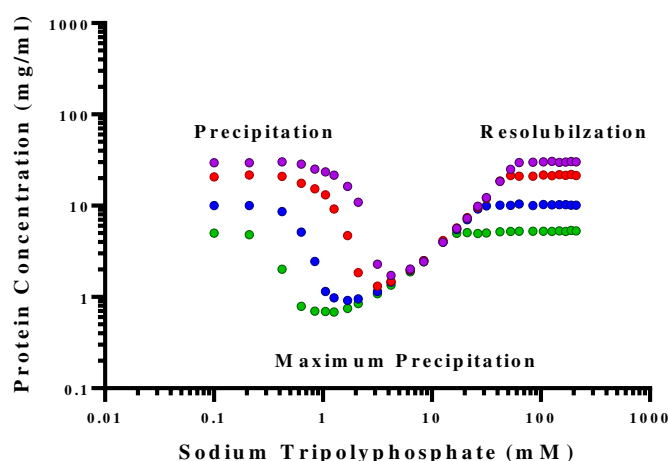


Figure 1. Data for lysozyme reentrant condensation induced by increase STPP concentration. Lysozyme concentrations are 5 (green), 10 (blue), 20 (red) and 30 mg/ml (purple) in 10 mM Tris pH 9.0.

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Supercharging proteins with polyvalent anions to offset aggregation

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Protein aggregation is a process that occurs in human disease and is a problem facing the development of next generation antibody therapeutics. Previous studies have shown that supercharging proteins by selectively mutating solvent-exposed surface residues to basic or acidic residues can greatly increase aggregation resistance [1]. Currently it is often near-impossible to modify the structure of a biotherapeutic once it has been developed. As such, companies look to optimize the formulation biotherapeutics are stored in by adding excipients such as salts, osmolytes and amino acids to improve solubility, stability and activity profiles [2].

Here we examine how the polyvalent anion tripolyphosphate (STPP) and monovalent NaCl modulate aggregation resistance of bovine serum albumin (BSA), human serum albumin (HSA) and ovalbumin. This was investigated through use of static light scattering (SLS), dynamic light scattering (DLS), zeta potential measurements and thermal ramp experiments to determine the onset of aggregation temperature (T_{agg}).

Figure 1 shows how the hydrodynamic radius (R_h) of ovalbumin changes with increasing temperature in the presence of STPP and NaCl. Increasing R_h values with increasing temperature is a sign that aggregation is occurring due to native proteins unfolding and associating with each other. The results show that STPP is more effective at increasing ovalbumin resistance to aggregation than NaCl is as the R_h values do not start to increase until higher temperatures are reached and the R_h growth rate is also slower in the presence of STPP. It should be noted that similar trends were observed for BSA and HSA with STPP and NaCl. Zeta potentials in figure 2 show that STPP supercharges ovalbumin and that NaCl has a minimal effect on ovalbumin net charge. We propose that polyvalent anions suppress aggregation by interacting with solvent exposed basic residues through electrostatic interactions which supercharge the native and unfolded protein states to increase protein-protein repulsion and reduce aggregation.

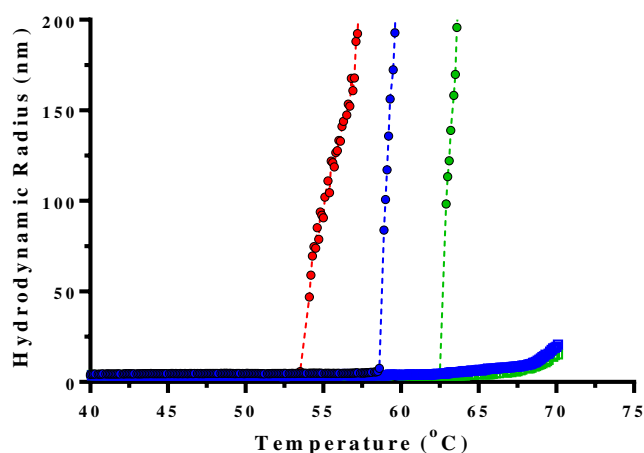


Figure 1. T_{agg} data for 5 mg/ml ovalbumin with 0 mM (●), 100 mM NaCl (●), 500 mM NaCl (●), 100 mM STPP (■) and 500 mM STPP (■) in 10 mM Tris at pH 7.0 (dashed lines are to guide the

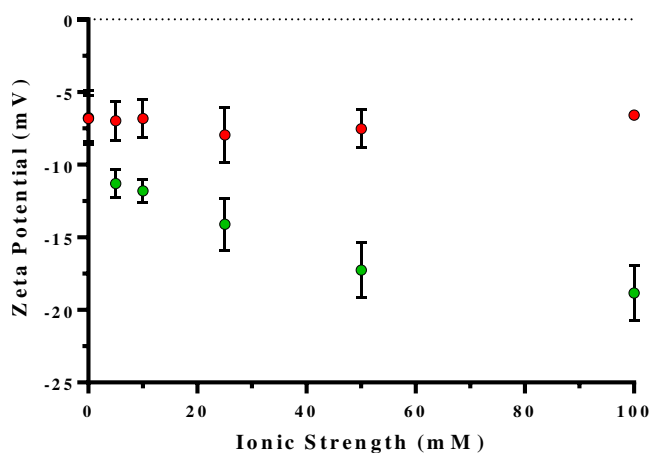


Figure 2. Zeta potential data for 5 mg/ml ovalbumin with increasing STPP (●) and NaCl (●) ionic strength in 10 mM Tris at pH 7.0.

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Salt-induced cluster formation of gold nanoparticles

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Colloidal stability plays an important role in soft matter science as well as in industrial and natural processes like cheese making, water treatment or the formation of river deltas. Derjaguin, Landau, Verwey and Overbeek (DLVO) explained the stability of colloidal particles as the result of a competition between attractive van der Waals forces and repulsive doublelayer forces. The increase in ionic strength for example can significantly reduce the repulsive forces and thus induce colloid coagulation.

In this contribution we present results from a study on the colloidal stability and the coagulation mechanism of gold nanoparticles that were functionalized with 11-Mercaptoundecanoic acid (Au@MUA). Coagulation of the particles was initiated by the rapid addition of salt. A combined approach of time-resolved Dynamic Light Scattering, Small-Angle X-Ray Scattering and UV-Vis spectroscopy was used to follow the process of coagulation. Rapid mixing of the compounds was achieved by a stopped-flow setup. The found cluster size could be directly correlated with the changes of the plasmonic properties of the nanoparticles during the coagulation.

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Tailoring the volume phase transition behaviour of core-shell nanoparticles

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Thermoresponsive polymers represent a versatile type of material which can be used in many applications like sensing, catalysis, separation and nanoencapsulation.

Polymers that display a lower critical solution temperature are in the focus of research since a few decades already. Consequently, the examples are numerous, with poly(*N*-isopropyl-acrylamide) being one of the widest studied polymers. However, the list of polymers, that display an upper critical solution temperature, is short. There are only a few systems, that display UCST behavior in water in a temperature range between 0 and 100°C, whereas the possible applications are as numerous as those of LCST polymers.

Our approach for the synthesis of core shell nanoparticles with a thermoresponsive polymer shell is based on a seeded precipitation polymerization [1]. During the polymerization process the chains grow to a critical length above which, at a certain temperature, the solvability becomes unfavorable due to enthalpic reasons and the polymer precipitates. By providing a cross-linker and surface functionalized nanoparticles, the polymer precipitates and binds covalently on these nanoparticles to form a cross-linked network on the nanoparticles' surface yielding core-shell nanoparticles [2]. By incorporating monomers that feature amine groups in their sidechains polymer shells can be realized that are sensitive to change in pH and also allow for relative simply postmodification. In particular, the postmodification is convenient to alter the response behavior of the polymer shells, e.g. from pH- to thermoresponsive.

In this contribution we present results from the synthesis of core-shell particles with silica nanoparticle cores and polymer shells of various composition. Dynamic light scattering is used to follow the steps of the route from the blank core, precipitation of polymer on the surface and postmodification of the polymer shell. Measurements at different temperatures allow to study the thermoresponsive character of the nanoparticles, i.e. to investigate the shell in the swollen and collapsed state, respectively.

As the phase transition temperature can be changed by the use of functionalization agent, the particles can be tailored for the desired use. By removing the core and tuning the volume phase transition temperature in the area of human body temperature, hollow thermoresponsive nanoparticles interesting for drug delivery applications are accessible.

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Hierarchically Ordered 2D Nanoparticles Providing Empty Liquid for the Formulation of Waterborne Coatings

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Application of 2D nanoparticles as lyotropic mesogens in waterborne and solventborne coatings is recently investigated [1-4]. It is shown that the transition from isotropic to ordered lamellar phases can assist the orientation of pigments [1-2] and enhance gas barrier properties [3]. However, despite the improved properties, it is known that liquid crystals, are not tolerant towards isotropic particles with regard to topological point defects [5].

In this research, we present novel anisotropic aqueous dispersions containing hierarchically oriented 2D nanoparticles. These waterborne dispersions provide empty liquid for accommodation of isotropic colloidal particles such as polymer chains with large variation of sizes [Figure 1]. It is observed that in sufficiently high volume fractions, platelets (with average lateral size of 300 nm) show up to four harmonic peaks in SAXS patterns ($d = 10$ nm) and appear as tactoids with d spacing up to 200 nm in cryo-SEM images.

Chemically, dispersions consist of α -zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α -ZrP) platelets, exfoliated by intercalation of alkanolamines in water. Colloidal stability and phase diagram of dispersions as well as the partial hydrolysis of platelets in basic milieu has been investigated. Additionally, it is shown that the empty space between the tactoids can be utilized for accommodation of organic species of coatings formulations by substitution of water with polymer dispersions.

Finally, we demonstrate the broad applicability of the approach and the transformation of the colloid states into organic coatings by real-time SAXS and TEM analysis which takes place through restacking of the α -ZrP platelets and structuring the film into an anisotropic morphology comprising aligned tactoids.

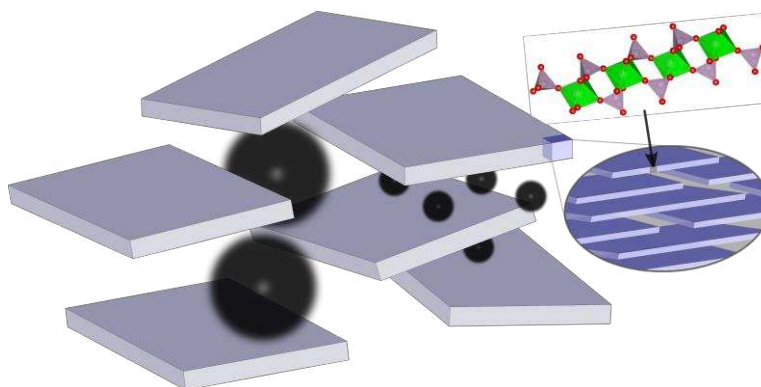


Figure 1 Hierarchical assembly of α -ZrP platelets into preferentially aligned tactoids with polymer colloids of different size accommodated in the interstitials.

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Development and characterization of food-grade olive oil-in-water nanoemulsions for the encapsulation of Vitamin D

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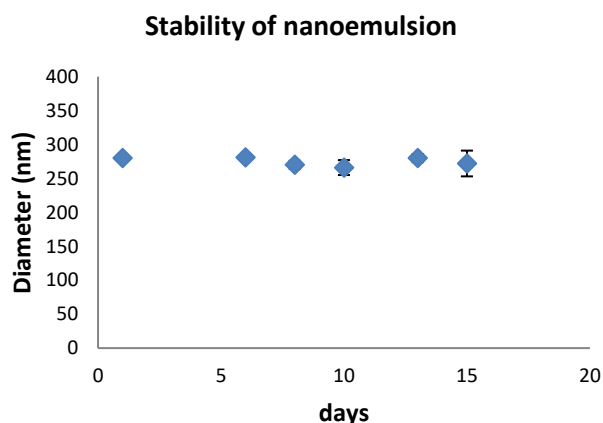
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In recent years, there has been growing public interest in a healthier lifestyle, with the food and drug industry turning to the development of biocompatible food-grade systems that will serve as carriers of various bioactive substances such as antioxidants, vitamins etc. Oral administration of encapsulated bioactive compounds at effective doses could provide a variety of health benefits [1]. Of particular interest is the development of nanoemulsions in which it is possible to encapsulate the desired substances, while offering advantages such as increasing bioavailability and solubility, protecting the functional substance from degradation and efficient delivery of active ingredients [2].

The purpose of the study is to develop and structurally characterize biocompatible, edible, non-toxic oil-in-water (O/W) nanoemulsions in order to encapsulate vitamin D, which is necessary for the proper functioning of the organism as it participates in a variety of functions. The proposed system consists of: an aqueous solution of calcium citrate as the continuous aqueous phase, a mixture of Tween 20 and lecithin as surfactants and extra virgin olive oil (EVOO) of high concentration of polyphenols as the dispersed oil phase. Vitamin D (cholecalciferol) was dissolved within the lipid phase prior to emulsification. The proposed nanoemulsions provide an innovative supplement of calcium and vitamin D combination with the aim to prevent of treat related micronutrient deficiencies.

Structural and antioxidant studies of the nanoemulsions were conducted both in the presence and in absence of the vitamin. Using the Dynamic Light Scattering Technique (DLS), the nanodroplet diameter, the polydispersity index, and the stability of the nanoemulsions over time were examined. Also, interfacial properties of nanoemulsions were investigated using Electron Paramagnetic Resonance (EPR) spectroscopy employing the amphiphilic spin probe, 5-doxylstearic acid (5-DSA) [3]. From the characteristics of the EPR spectra we have calculated the order parameter (S) and the rotational correlation time (τ_R) in order to investigate membrane dynamics and the degree of vitamin's embedment. Using EPR and the free radical TEMPOL we have also evaluated the antioxidant activity of vitamin D upon encapsulation in EVOO nanoemulsions.



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Electrophoretic mobility of latex particles: Effect of trivalent ions

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We have so far reported the results of the electrophoretic mobility (EPM) and charge reversal of latex particles in the presence of LaCl_3 or tetraphenylphosphonium chloride (TPPCL) [1-3]. Experimental results of carboxyl latex particles showed the charge reversal at lower pH in the presence of higher TPPCL concentration. Meanwhile, with higher LaCl_3 concentration, the charge reversal occurred at higher pH. The charge reversal of sulfate latex was found in the presence of TPPCL, and the concentration where the reversal occurred increased with the surface charge density. However, the effect of pH and surface charge on the charge reversal of sulfate latex bearing pH-independent surface charge has not yet been examined. In the present presentation, we show the measured results of EPM of three different sulfate latex particles with different surface charge densities. The measurements were carried out as a function of pH and LaCl_3 concentration.

The highly charged sulfate latex with a charge density of -43 mC/m^2 showed slight charge reversal to $\text{EPM} = +0.5 \times 10^{-8} \text{ m}^2/(\text{Vs})$ around 10 mM LaCl_3 at pH 4 (Fig. 1). Contrary to the case with TPPCL, with decreasing the charge density, the LaCl_3 concentration at the charge reversal increased and then disappeared at the lowest charge. While the sulfate latex bears pH-independent charge, the significant effect of pH on the charge reversal was observed. That is, the EPM of sulfate latex became over $+4 \times 10^{-8} \text{ m}^2/(\text{Vs})$ at pH 8 and higher. We presume that an ion-ion correlation model explains the charge reversal at low pH, and the consideration of adsorption of dissolved hydrolysed La species is crucial at neutral and high pH. Theoretical models captures our experimental trends of EPM by assuming plausible values of intrinsic energy of adsorption. We also discuss the applicability of simple theoretical models to describe the charge reversal.

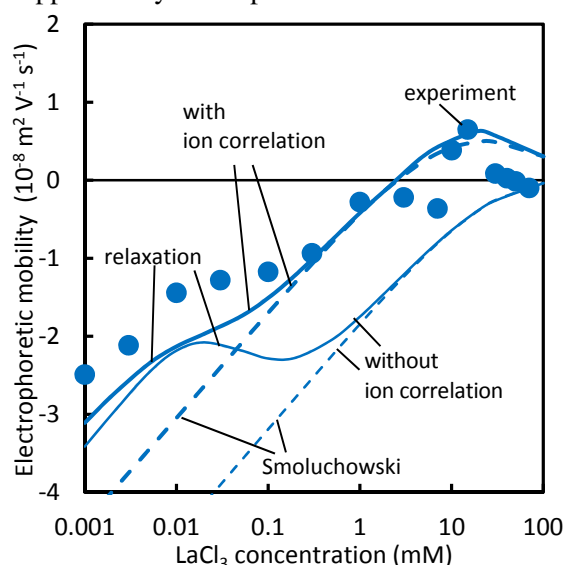


Figure 1 The relationship between electrophoretic mobility and LaCl_3 concentration for sulfate latex particles with the surface charge density $\sigma_0 = -43 \text{ mC/m}$. Symbols are experimental values. The Solid and dashed lines are theoretical values calculated by the CellMobility program and the Smoluchowski equation, respectively. The thin lines are calculated without ion correlation and heavy lines are obtained with ion correlation. Calculated values assume $\psi(x_s) = \zeta$.

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Microemulsions for fueling internal combustion engines

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The increased demand of fuel, the indiscriminate extraction, and depletion of crude oil reservoirs together with the mounting pollution and the rapid degradation of the environment are nowadays matters of worldwide concern. Those issues are good reasons to seek for 'green' fuels to replace diesel, and neat vegetable oils or their microemulsions are suitable candidates for this purpose.

The work presents innovative results on microemulsions alternative fuels prepared with rapeseed oil (RSO), diesel (D) or mixtures thereof, environmentally friendly anionic and nonionic surfactants, and cosurfactants. The water solubilization capacity of oil/surfactant/cosurfactant systems evaluated by pseudo-ternary phase (PTP) and Winsor (W) diagrams unveiled that extent of the single-phase microemulsion area (SPMA) depends on the nonionic surfactant (NS). The anionic surfactant (AS) alone does not make microemulsions. Addition of AS to NS decreases the SPMA, but SPMA increases by adding of cosurfactant. For D/RSO blends, the SPMA does not change as compared to diesel. In the PTP diagrams, addition of electrolyte decreases the SPMA. The tests of oil/water interfacial tension (σ_{ow}), oil and water solubilization parameter (SP_o) and (SP_w) and of particles' size (PS) show that the WIII microemulsions have minimal σ_{ow} values, and maximal of SP_o , SP_w and PS. The work stresses the relationships between the phase behavior and the microemulsions properties and emphasizes their best way for obtaining optimal fuels.

Preparation of Sulfonated Waterborne Polyurethane Dispersions by Acetone Process and Their Applications on Textile Substrates

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Different types of waterborne polyurethane (PU) dispersions were synthesized by using hexamethylene diisocyanate (HDI) and different types of polyols. In order to obtain environmentally friendly dispersions and reduce pollution caused by the solvents, acetone process was used. Since PU polymer chains are immiscible in water, sodium 2-[(2-aminoethyl)amino]ethane sulfonate, which is an anionic internal emulsifier, was used to associate ionic groups to the conventional PU structure.

Anionic PU dispersions were characterized by solid content, viscosity, pH measurements, mean particle size and particle size distribution. Moreover, chemical structure and thermal properties were determined by FTIR and DSC, respectively. The tensile properties and Shore A hardness of dispersion cast films were also measured. In the end, obtained dispersions were coated on textile substrates and final properties of the coated substrates were examined.

Acknowledgements: This work was financially supported by TUBITAK as TEYDEB project (Project No: 3170547).

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Does Length Matter?

Suitability of halloysite nanotubes in drug delivery applications

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In last decades, a large number of different colloidal systems are under consideration as innovative carriers of biologically active compounds as alternative to viral vectors. The ideal nanocarrier would require high target specificity, high loading capacity, good stability, slow and controlled cargo release. Liposomes, vesicles and nanoparticles have been effectively shown as nanocarriers [1]. Even if quite promising, these systems are not always suitable for large-scale applications. In this context, recently the halloysite nanotubes (HNT) have been considered as an effective alternative for a number of reasons [2]. Firstly, HNTs are hydrophilic aluminium-silicate tubes with a nanometer-sized cavity (*lumen*) which can easily filled with the desired drug. It is widely reported that the loading process can be easily performed in water. Moreover, as other nanoclays, HNTs are naturally abundant, cheap and biocompatible. Despite the numerous studies about HNTs, some simple questions are still to be solved. The high density of HNTs (2g/cm^3) produce annoying settling problems. Sedimentation can produce severe accumulation of HNTs in biological tissues [3]. In addition, commercial halloysite nanoclays are very polydisperse in length and diameter. As already observed for carbon nanotubes, cytotoxic effects are expected also for very long HNTs.

In order to improve their actual usability, a deeper knowledge of their behaviour in water dispersions is required. In this investigation, we used HNTs of different sources and purity. Aqueous dispersions were prepared with or without addition of salt and additives to monitor stability against aggregation and sedimentation. A very stable fraction was identified though Dynamic Light Scattering and microscopy measurements. This fraction is mainly composed of short tubes, freely diffusing in the solvent with low aggregation degree. These short tubes could have potential application as nanocarriers with high biocompatibility and low accumulation problems.



Figure 1. Effect of tube length and instability on settling and accumulation of circulating nanotubes in blood vessels.

Acknowledgements: The financial support from INAIL (BRIC02016 project ID 52) is acknowledged.

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Use of promesogenic ligands for preparation of liquid crystal colloid with barium hexaferrite nanoplatelets

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Barium hexaferrite (BHF) crystallizes in the form of thin hexagonal plates ($\text{BaFe}_{12}\text{O}_{19}$) and exhibits high magnetocrystalline anisotropy. It has a magnetic easy axis perpendicular to the basal plates' plane. When dispersed in nematic liquid crystal, the dispersion forms fluid ferromagnetic phase [1]. It was shown that surface modification of inorganic nanoparticles' surface with promesogenic ligands improves the colloidal stability of nematic liquid-crystalline suspensions [2]. Promesogenic ligands contain one or more mesogenic units, which also comprise the liquid-crystals' molecules, and are responsible for the liquid crystals' properties. Furthermore, promesogenic ligands present at the surface of nanoparticles affect anchoring and the alignment of nanoparticles in a liquid crystal.

Our purpose is to enable the dispersion of functionalized nanoplatelets in a liquid-crystalline matrix. We tried to achieve this using different ligands; a dendritic ligand with a phosphonic anchoring group and three mesogenic groups, and with a combination of dendritic ligand with shorter linear ligands. While hydrothermally synthesized nanoplatelets are dispersed in water at a pH of 3.5, the dendritic ligand is hydrophobic and soluble only in some nonpolar solvents. To disperse the bare BHF nanoplatelets in a nonpolar solvent it was necessary to hydrophobize them. Up to now, we studied two different procedures: 1) ligand exchange of ricinoleic acid at the nanoplatelets surface and 2) functionalization at a phase boundary a) with dendritic ligand and b) with combination of dendritic ligand and hexylphosphonic acid in molar ratio 1:4.

Pure dendrimer functionalization did not enable the dispersion of BHF nanoplatelets in liquid crystal 4-cyano-4'-pentylbiphenyl (5CB). On the other hand, nanoplatelets prepared by procedure 1) and 2b) dispersed in the isotropic phase of the liquid crystal, but aggregated when dispersion was cooled into nematic phase and redispersed again when it was heated above the nematic-isotropic phase transition temperature.

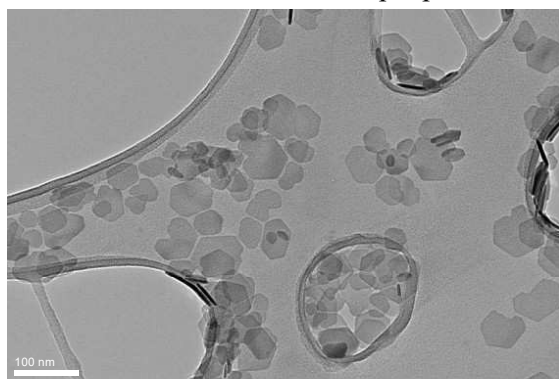


Figure 1. TEM image of BHF nanoplatelets.

Acknowledgements: The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P1-0192, P2-0089 and research projects No. PR-08415, J7-8267).

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Concentration dependency of aqueous ethanol pre-treatment for gelation of milk whey protein

-Ultrasonic and rheological analysis-

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Recently, we found that the gel hardness of milk whey protein was remarkably increased by aqueous Et-OH pre-treatment. In this time, we measured the changes in ultrasonic properties of milk protein solution with or without pre-treatment by various concentration of aqueous ethanol solution. The dynamic viscoelastic behaviors with temperature sweep were observed. Furthermore, we investigated the factor for showing the different texture depending on the ethanol concentrations using other chemical analysis (surface hydrophobicity of the protein solution, determination of content for SH and SS etc.) and secondary structure of the protein.

The milk whey proteins were suspended with or without aqueous Et-OH, and then evaporated the Et-OH from the suspension and determined the protein concentration by Lowry method.

When we compared to control (no ethanol treatment), we found that the pre-treatments for whey protein solution using 10, 25 and 50% aqueous ethanol solution gave distinct effects on the textures of protein gel by the heating and cooling process.

Although generally aqueous ethanol pre-treatment facilitated to the gelation of milk whey protein due to the partial denaturation, 10% aqueous ethanol had a bigger effects on the increment of gel hardness than that of 25% pre-treated one. However, the attenuation changes shows that the protein suspension was consisted from whey protein particle with similar diameter between 10% and 25% Et-OH pre-treatment before heating.

On the other hand, the surface hydrophobicity of 10% ethanol treated whey protein solution was smaller than that of 25% treated sample. These results suggests that other factors except for the unfolding of protein molecules also contribute to the gel formation depending on the Et-OH concentration.

The opposite cholesterol effects on the fluorescence anisotropy of DPPC liposomal bilayers

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Liposomes containing various amounts of cholesterol (CHOL) were fabricated from 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) in excess water. Effects of CHOL on liposomal bilayer ordering were then systematically studied by employing fluorescence polarization technique with Peltier temperature programmer using 1,6-diphenyl-1,3,5-hexatriene (DPH) as the probe. The experimental fluorescence anisotropy (FA) versus temperature plots of liposomal bilayers exhibited sigmoid gradient as they undergo a phase transition from gel-phase (L_β) to liquid-crystalline phase (L_α). The incorporation of CHOL in DPPC bilayer at temperatures below and above the main phase transition temperature (T_m) was found to decrease and increase, respectively, the ordering of the resulting bilayers (Figure 1). Disordering and condensing effects of CHOL may induce opposite influence on bilayer ordering depends on the temperature under considerations. As one of the consequences of the opposite effects of CHOL and therefore the formation of a single liquid-ordered phase (L_o) in the lipid bilayers, gradual disappearance of phase transition in DPPC bilayers with increasing CHOL concentration was evidenced by FA experiments of this work and differential scanning calorimetry (DSC) results as reported in the literature.

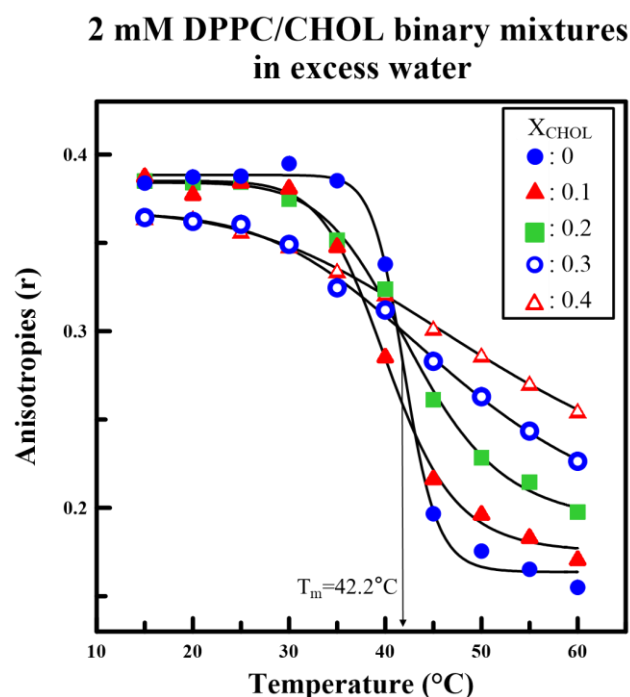


Figure 1. Effects of CHOL on the fluorescence anisotropy versus temperature plots of DPPC liposomal bilayers. The incorporation of CHOL in DPPC bilayer decreases and increases the ordering of the resulting bilayer at temperatures below and above, respectively, the phase transition temperature (T_m).

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From protein phase behavior to second virial coefficient

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We experimentally determined the phase behaviour and the interactions of protein (lysozyme) solutions under conditions favouring protein crystallization and metastable gas-liquid phase separation [1-3]. The phase behaviour as well as the interactions show striking similarities to those of colloids with short-ranged attractions. In particular, we find that the rescaled metastable gas-liquid binodals of protein solutions can be mapped onto those of square-well fluids [4]. Despite their much more complex interactions, protein solutions hence appear to also follow the extended law of corresponding states [5].

Moreover, we exploit this extended law of corresponding states and apply the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in order to infer the second virial coefficient B_2 from the phase behaviour, namely, the cloud-point temperature (CPT) [6]. This determination of B_2 yields values that quantitatively agree with results of static light scattering (SLS) experiments. Within this approach, the strength of the attractions is quantified in terms of an effective Hamaker constant, which accounts for van der Waals attractions as well as non-DLVO forces, such as hydration and hydrophobic interactions. This approach is based on simple lab experiments to determine the CPT and combined with the DLVO theory. Due to this simplicity, it can be applied to a wide range of protein-protein interactions including complex solution environments. This is expected to facilitate further biophysical research.

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Inorganic – Organic Nanoparticles: Interface Heterogeneity the Hidden Phenomena

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Modern application of multifunctional hybrid materials focus on a bottom –up approach according to which complex nanostructures are hierarchically formed by individual inorganic (metal, metal oxide) building blocks, stabilized by adsorbed organic ligands. In this strategy, resolution of a crucial task finding the proper balance between stability and reactivity of inorganic–organic colloidal nanoparticles requires comprehensive knowledge of ligand bonding mode and interface structure. Approach the one dominant among the majority of authors originated from Langmuir model of monolayer adsorption implying chemical bonding of ligand to energetically uniform surface and formation at higher concentration of secondary layer of ligand physically adsorbed on the primary one through the interpenetration of tails of primary and secondary layers [1, 2]. In this talk, we will argue that experimental data have sharply diverged from that simplified conventional understanding. We advocate more realistic model of adsorption accounting the fact that nanoparticles surface formed under highly nonequilibrium conditions due to artificial termination of crystal grows and freezing of irregular structure by adsorbed stabilizer. Silver-oleic acid capped nanoparticles was choose as a model for mono-and bi-layer ligand chemisorption [3]. FTIR spectroscopy, TGA and DTA data testify bidentate bonding carbocyclic oxygen atoms to Ag occupied 0,21 nm² per particle (which is close to [4]) and formation secondary layer at excess oleic acid (OA) content. The pattern of activation energy (E_a) versus mass loss (surface coverage) of OA can be regarded a fingerprint to determine the mechanism of chemisorption. Contrary to Langmuir, model, which predicts constant value of activation energy, E_a values calculated by Ozawa-Flynn-Yoll method [5], varies significantly with a fraction of thermally desorbed material, testifying increase in adsorption energy with surface coverage. Quantum chemical simulation leads farther insight into the mode of bonding and structure of adsorbed layer. OA interaction with Ag atoms results in charge density increase at metal surface and creation of negative electrostatic potential at carboxyl group owing to covalent bonding. Formation of secondary layer accompanied by redistribution of charge density: slight decrease in metal surface charge density, double decrease of charge density at C=C bond and strong increase in negative charge of carboxyl group of secondary layer. Complex variation of E_a with mass loss in presence of excess of OA reflects contribution of several factors: increase in E_a as OA molecules desorbed from sites with higher adsorption energy and corresponding variation in chemical bond strength in a secondary layer.

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From stable TiO₂ colloidal dispersions preparation to film formation from drying droplets

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Titanium dioxide (TiO₂) is a naturally occurring and commercially available metal oxide. Thanks to its high refractive index (2.5-2.7) and interesting optical properties such as UV light absorption and brightness. TiO₂ is widely used in a range of applications including paints, packaging and cosmetics. In a nanomaterial grade, with an average particle size below 100 nm, TiO₂ exhibits an enhanced photoactivity that can be triggered with UV light. However particles aggregation leading to a decrease in surface area can lead to a lower efficiency of TiO₂ as photocatalyst. Thus, controlling the synthesis in order to obtain stable colloidal is crucial in the optimization TiO₂ optical properties.

In this work, we focus on four main axes ranging from the preparation of colloidal suspensions of TiO₂, using titanium isopropoxide as precursor, to film formation from drying droplets of these suspensions:

- (i) We investigated the impact of strong (nitric acid) and weak acid (acetic acid) on the TiO₂ nanoparticles growth during sol-gel synthesis in low water content.
- (ii) Afterwards, we studied the impact of initial titanium dioxide precursor concentration synthesized TiO₂ nanoparticles by acid catalysed sol-gel method in aqueous medium resulting in TiO₂ dispersions with a concentration between from 0.5 to 5 wt%. The particle size measured by both DLS and SAXS gave an average particle size of around 50 nm as presented in figure 1.
- (iii) We also studied the effect of peptization on the colloidal stability on the final TiO₂ aqueous dispersions. It was observed that samples with peptization resulted in more stable suspensions than the one without peptization. In order to understand what occurred during the peptization in terms of particle size and zeta potential, we monitored the evolution of both parameters during TiO₂ synthesis using light scattering techniques.
- (iv) Finally, we followed the film formation by droplets deposition in order to investigate the flow dynamics in drying droplets of TiO₂ colloidal dispersions with different initial concentrations.

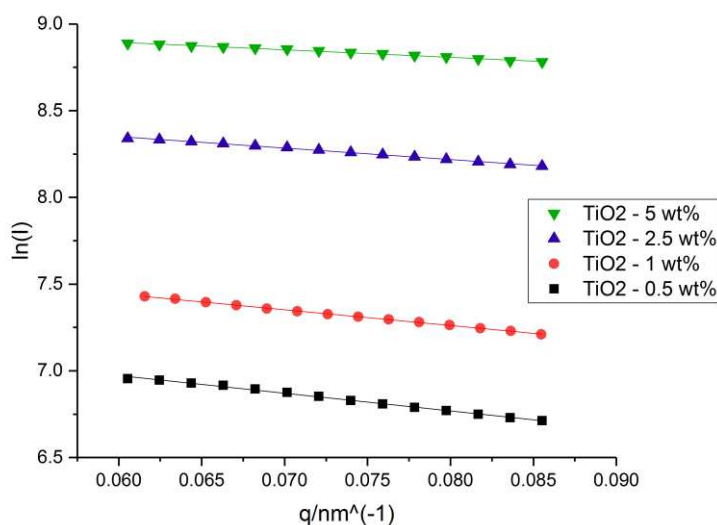


Figure 1. This represents the Guinier plots for TiO₂ dispersions at different concentrations extracted from SAXS experiments with synchrotron radiation. The linear fitting of for each concentration allow to extract the radius of gyration of the nanoparticles that is linked to the average particle size.

Polyelectrolyte-coated cerium oxide nanoparticles

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The research interest in cerium oxide (ceria) nanoparticles has been increasing recently due to their potential applications in various fields such as biomedicine and catalysis. In that sense, one of the main advantages is the biocompatibility of ceria nanoparticles [1]. In the field of environment and energy related applications cerium oxide's catalytic ability, which is largely affected by redox behaviour and is related to cerium's redox state, gets more and more attention. In many cases a stable dispersion of cerium oxide nanoparticles in a biological environment is needed. For reaching that aim particles coated with various polyelectrolytes are very promising. Therefore, the objective of this study is to synthesize and characterize ceria nanoparticles and to systematically investigate their interactions with polyelectrolytes. As a model polyelectrolyte strongly charged polyanion sodium poly(styrene sulfonate) (PSS) [2] was used. Cerium oxide nanoparticles were synthesized [3] and characterized by means of XRD, BF – STEM, DLS and zeta-potential measurements. Average diameter of ceria nanocrystals was estimated to be ≈ 5 nm. Isoelectric point of uncoated ceria nanoparticles was measured at two ionic strength values ($I_c = 0.01 \text{ mol dm}^{-3}$ and $0.001 \text{ mol dm}^{-3}$) and the obtained value was in both cases $\text{pH}(\text{iep}) = 6.7 \pm 0.1$. Hydrodynamic radius of the synthesized cerium oxide nanoparticles was investigated by dynamic light scattering at various experimental conditions. It was shown that the particle size depends on pH and on ceria mass concentration. After adsorption of PSS, polyelectrolyte-coated ceria nanoparticles were also examined using the above-mentioned methods.

In order to interpret the obtained experimental results by means of the modified Ohshima model for soft particles [4], mobility of ceria particles covered with PSS was determined as a function of ionic strength. DLS was used for determination of the hydrodynamic radius of ceria nanoparticles coated with PSS. Finally, on the basis of these results the electrophoretic softness parameter for ceria-PSS system and adsorption density value were determined and compared with the results obtained by classical adsorption experiments.

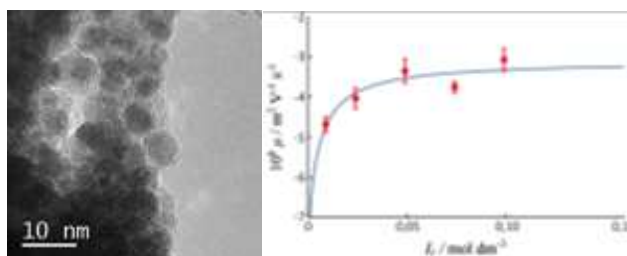


Figure 1. Polyelectrolyte-coated ceria nanoparticles and the dependence of their mobility on ionic strength.

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Preparation of composite zein nanoparticles with natural resins

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In recent years there have been worldwide tendencies to develop more efficient and safer technologies for application of various plant protection products (PPPs) i.e. pesticides, herbicides, antibiotics, hormones etc. being used for crops protection. One of the possibilities is nanoencapsulation of PPPs in bio-materials, such as biopolymers [1]. Encapsulation and controlled release of PPPs from nanoparticles can be even more challenging if compounds are lipophilic.

Zein, as highly hydrophobic biopolymer, can be one of the potential encapsulation agents for different lipophilic PPPs. It is soluble in concentrated aqueous ethanol (70% or higher) and can be precipitated in form of nanoparticles by antisolvent precipitation. Zein is non-toxic and completely biodegradable. Addition of different materials to zein nanoparticles in order to adjust their solubility in water has been investigated earlier [2-3]. In this paper, two natural resins – shellac and rosin, were used for that purpose. Both resins are also environmentally safe and biodegradable [4-5].

The objectives of this work were to prepare composite nanoparticles of zein with two different natural resins, and to investigate their stability and solubility against different pH conditions. Firstly, 2% stock solutions of biopolymers were prepared by dissolving zein and each resin at different zein/resin mass ratios (1/0; 0.8/0.2; 0/1) in 90% aqueous ethanol. Thereafter, nanoparticle suspensions were obtained by shearing stock biopolymer solutions into water under stirring. Zeta potential and particle size of thus prepared nanoparticles were determined. The results of presented work showed that pH conditions and type of resin affect stability and solubility of zein/resin nanoparticles.

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A semiempirical expression for the effective viscosity of multicomponent suspensions

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We propose a methodology to approximate the viscosity of multicomponent suspensions. The procedure consists in successive applications of expressions for the viscosity of binary mixtures, originally written as the product of monomodal stiffening functions. Its application to arbitrary mixtures requires the detailed knowledge of the geometry of the system in the form of size ratios and compositions. When this information is unknown the model can still be used as a fitting tool. With that purpose, the final expression is written in terms of an effective volume fraction that is further approximated by the use of a (1,2) Padé approximant. This approximation allows incorporating the crowding effects due to different species in a volume fraction dependent crowding factor that can be used as fitting parameter to match experimental or simulation data. We have applied the model to mixtures of particles with different sizes and tested its accuracy comparing with experimental results for the low-shear viscosity of bidisperse mixtures of spherical particles, with experimental results for the Bingham viscosity of a coal slurry, and with experimental results for the high-shear viscosity of polydisperse colloidal suspensions. The agreement with the experimental data is very good in all cases [1].

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Effect of hydrophobic block ratio PCL/PLA of amphipathic di block copolymers type PEO-PCL/PLA into DPPC Liposome

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In the present work, we show how different polymeric structures, in special amphipathic diblock copolymers, can interact with the lipid bilayer of large unilamellar vesicles of DPPC [1,2]. We report the effect of amphipathic diblock copolymers of the type AB, i.e., hydrophilic-hydrophobic diblock copolymers, where the hydrophobic block was poly(ϵ -caprolactone) and poly(lactic acid) at different ratio between them, i.e., hydrophobic block. The different systems studies were POE-PCL; POE-PLA and POE-PLA/PCL where PLA/PCL ratio was 1:1 and 4:1, on the dynamic and structural properties of L-alpha-dipalmitoyl-phosphatidylcholine (DPPC) large unilamellar vesicles (LUVs). Diblock copolymers proposed for this study are focused on the difference between PLA and PCL hydrophobic block, where a higher ratio of PLA/PCL, less flexibility of diblock copolymer, on the contrary, at lower ratio of PLA/PCL, less rigidity is observed. The difference of this behaviour are related to glass transition temperature (T_g) that for PCL is -60°C and for PLA is 43°C .

The interaction of copolymers upon DPPC LUVs was evaluated at low and high copolymers concentration. Different approach such as thermotropic behaviour from generalized polarization of Laurdan and fluorescence anisotropy of DPH, main phase transition temperature, relation between wavelength excitation and generalized polarization of Laurdan to evaluate the presence of segregate lipid domains, water outflow through the lipid bilayer and calcein release from DPPC LUVs were used.

Steady-state fluorescence measurements as a function of temperature show a typical behaviour for Laurdan and DPH, independent of type or ratio of hydrophobic block of copolymers. Furthermore, an increase of the rigidity of hydrophobic part of copolymers (higher PLA/PCL ratio) shows an increase of the T_m value of DPPC LUVs slightly $3-4^\circ\text{C}$ sensed by Laurdan at the interface of the bilayer, besides a decrease of water outflux and calcein release from the inside of the liposome.

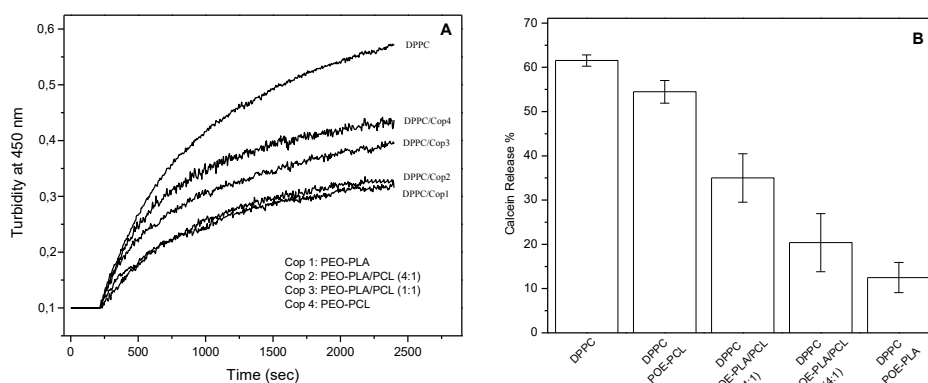


Figure 1. (A) Time-course of turbidity at 450nm and **(B)** Calcein Release Factor Percentage (RF%) from DPPC large unilamellar vesicles at different PCL/PLA ratio of hydrophobic block copolymers.

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Concentration and pH dependence of colloidal scale solute clustering within aqueous solutions of small organic molecules

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Aqueous solutions of well soluble molecules are usually assumed to be essentially homogenous systems with some degree of local structuring due to specific interactions on the sub-nanometre scale, involving the creation of, e.g. molecular clusters, hydration shells, etc., usually not exceeding several solute molecules. These small molecular structures (molecular clusters) are commonly observed (experimentally and theoretically) in aqueous solutions of many organic and inorganic systems.

The presence of colloidal scale (mesoscale) structures has been well established in aqueous solutions of various small molecules [1] and these clusters have been proposed to be involved in non-classical crystal nucleation mechanisms [2,3]. Clusters in solutions of amino acids have been reported to be thermodynamically stable and can be present in both undersaturated and supersaturated solutions with respect to the solid-liquid equilibrium [4,5].

We investigated concentration and pH dependence of mesoscale clustering in aqueous solutions of small organic molecules, including amino acids (such as glycine) and amines (such as triethylenetetramine), which are well soluble in water and have a range of charged states that can be adjusted by changing solution pH. We used Dynamic Light Scattering (DLS) and Brownian Microscopy/Nanoparticles Tracking Analysis (NTA) in order to measure size distributions and number concentrations as well as scattered intensities and optical contrast of mesoscale clusters.

Mesoscale clusters were present in undersaturated solutions at solute concentrations well below the solid-liquid equilibrium (saturation) concentration at a given temperature, with mean diameters within 200-400 nm. Scattering intensities and number concentrations increased with increasing solute concentrations, while the mean size of mesoscale clusters remained approximately constant.

When pH was varied in amino acid solutions, values away from the isoelectric point resulted in a decrease of the number concentration of mesoscale clusters. While the mean size of mesoscale clusters remained approximately independent of pH, scattering intensities decreased sharply as solution pH moved more than 3 units away from the isoelectric point in either direction. This change was closely correlated with the speciation of charged species, whereby the zwitterions predominate near the isoelectric point and positively and negatively charged species predominate at lower and higher pH, respectively.

We note that the mesospecies are not to be seen as a separate phase and the system is better described as a thermodynamically stable mesostructured liquid containing solute-rich domains (mesoscale clusters) dispersed within bulk solute solution [6]. At a given temperature, solute molecules in such a mesostructured liquid phase are subject to equilibrium distribution between solute-rich mesospecies and the surrounding bulk solution.

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Modulation of metallic oxide particle behaviour in a formulation: physico-chemical and/or sensory properties of emulsions as a tool to identify particles interactions within the matrix

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Particles of metal oxides such as silica (SiO_2), alumina (Al_2O_3) or titanium dioxide (TiO_2) are nowadays widely used in manufactured products. The interest of these solid particles lies in the possibility to vary their size (a few nanometers to several micrometers), their shape, and their state of aggregation, as well as their specific surface. In addition, these metal oxides are good candidates for surface modification (coating with other metal oxides, silanization) to also modulate their surface properties [1-2].

Thus, incorporated in a complex medium such as an emulsion, these solid particles, due to their varied physicochemical properties, will be able to interact with all the constituents of the matrix. This represents a subject of great scientific interest, from both applied and fundamental point of view. Depending on its surface properties, the particle can manifest more affinity with the continuous phase, the dispersed one, or can be placed at the interface [3]. In the latter situation, the particle can act as a surfactant and can even replace the molecular surfactants conventionally used.

The aim of this study lays on its multiscale approach: from microscopic scale through the investigation of the ingredients interactions (guided by the type of particle used) to macroscopic scale with the characterization of stable, homogeneous and totally emulsified systems (as it was a required condition to provide an adapted system for macroscopic evaluations). Rheological, textural and sensory behavior, as well as emulsion colloid size and size distribution, were used as a tool to identify the role of the particles on the matrix organization.

One objective was to find the emulsions optimal formulation process and composition to accomplish the desired requirements for this study.

The obtained results clearly showed the importance of the particle properties in emulsion formation and stabilization. Interactions created inside the matrix were governed by the specific surface and the coating type of the particles. Thus, the modulation of the emulsion can be possible relying on the particle/emulsifier/oil phase interaction and ratio.

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Effect of Cholesterol and Copolymers di and tri block upon water permeability and Calcein release from Liposome models

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Large unilamellar vesicles can be stabilized with different biocompatible, biodegradable and amphipatic copolymers, also functionalized with peptides u other molecular markers attached in the surface of the liposome system. These approaches would allow having a system that could be used as a good drug delivery [1]. Furthermore, it is in our interest to evaluate the effect of the presence of segregate domains in the lipid bilayer, rich in sphingomyelin and cholesterol, in the release of antitumoral drug. In this context, is in our interest to prepare a series of liposome models of POPC/SM/CHO at different mol ratio to obtain “detergent resistant membrane”, DRM, and “detergent soluble membrane”, DSM, [2, 3] in the presence at different di and tri block copolymers concentration to study their effect in the drug delivery.

Our result shown that the di and tri block copolymers, arranged as POE-PCL and PCL-POE-PCL, where POE (poly-oxide ethylene) is a hydrophilic part and PCL (poly-caprolactone) is the hydrophobic part, interact with lipid bilayers of different liposome model dispersions, and also they promote the coexistence of phase domains in the lipid bilayers determined by excitation spectrum of Laurdan [4]. Furthermore, DPPC LUV's at 18-mol% of CHO and in the presence of copolymers at different concentrations produce a delay in the release of water and encapsulated calcein from inside to the liposome.

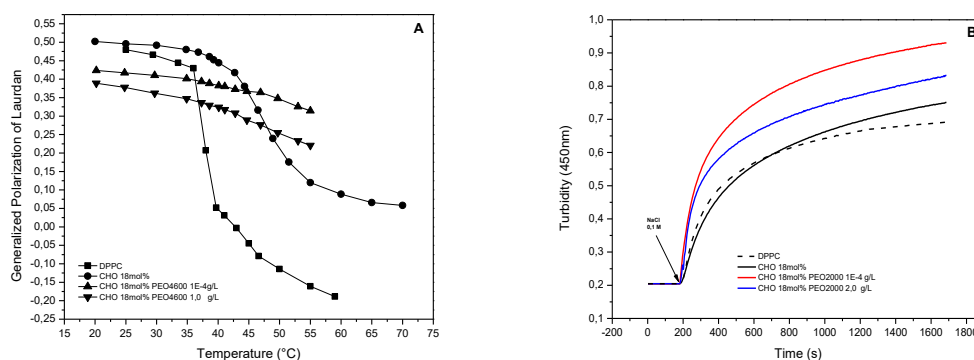


Figure 1. (A) Thermotropic behaviour of Generalized Polarization of Laurdan and **(B)** Time-course of turbidity at 450 nm of DPPC large unilamellar vesicles in the presence of 18 mol% of Cholesterol and tri-block copolymer tyhpe PCL-PEO-PCL.

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Structural characterization of triglyceride nanodispersions prepared by antisolvent precipitation

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The production of organic nanoparticles via antisolvent precipitation (AP) is a less-invasive and low-cost alternative to top-down methods like high-pressure homogenization (HPH) [1]. Thus, AP is of growing interest for the preparation of nanosuspensions of pharmaceutical ingredients [2]. For instance, triglyceride (TG) nanodispersions are under investigation as drug delivery system [3,4]. Here we report TG nanosuspensions synthesized by AP which have dimensions of ~ 25 nm and exhibit unknown structural characteristics. The morphology, the melting behavior and the molecular structure of the nanodispersions are analyzed by photon correlation spectroscopy (PCS), differential scanning calorimetry (DSC), cryogenic transmission electron microscopy (CryoTEM), small-angle X-ray and neutron scattering (SAXS, SANS) as well as wide-angle X-ray scattering (WAXS). In particular, the combination of SAXS and SANS studies allow the determination of the molecular structure within the interface between nanoparticles and the dispersion medium [5].

Fig. 1(a) compares DSC curves of TG nanodispersions prepared by AP and HPH, which show vastly differing melting behaviours. The melting peaks at ~ 55 °C in the curve of the HPH dispersion (dashed red line) are due to the well-known β -modification of TGs. For the AP dispersion (solid red line), however, there is a striking peak around 40 °C present, which we attribute to a fraction of very small TG nanoparticles with an unknown modification [6]. Fig. 1(b) plots SAXS (ID02/ESRF) and SANS (KWS-1/MLZ) data of a TG nanodispersion prepared by AP in its emulsion state. The simultaneous fits of the SAXS and SANS data indicate spherical core-shell particles with a total mean diameter of about 27 nm.

In conclusion, the AP-produced TG nanodispersions reported here exhibit extraordinary small particle sizes with a novel crystalline structure. Both the new crystalline structure and the small particle size make the dispersions of interest for pharmaceutical application and beyond.

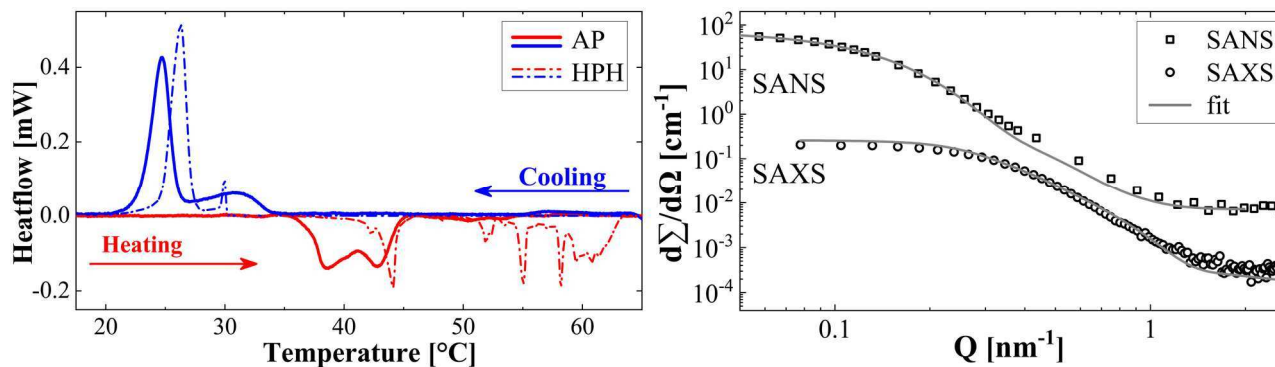


Figure 1: (a) DSC heating (red, bottom) and cooling (blue, top) curves of TG nanodispersions prepared by AP (solid lines) and HPH (dashed lines). (b) SAXS (bottom) and SANS (top) curves of a TG nanoemulsion prepared by AP. The grey lines are simultaneous fits to the SAXS and SANS data.

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Phospholipid vesicles can be converted into micelles by contact with a non-amphiphilic fluorocarbon gas

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It is well documented that phospholipid vesicles can be converted into micelles under the action of detergents such as sodium cholate and alkyl glucosides [1,2]. Understanding this vesicle-to-micelle phase transition is of interest for better controlling the dynamics of phospholipid aggregation[3] and membrane protein extraction [4], and for designing innovative vesicle preparation techniques [5].

We now report that transition of dimyristoylphosphatidylcholine (DMPC) vesicles into micelles can also be achieved by exposing an aqueous dispersion of these vesicles to perfluorohexane (*F*-hexane) vapour, although this fluorocarbon is highly hydrophobic, non polar and non-amphiphilic. *F*-hexane was introduced in the N₂ atmosphere overlying the phospholipid suspension. The transition was characterized by dynamic light scattering (DLS). In the absence of the fluorocarbon gas, the DMPC vesicles display a monomodal size distribution with a radius of 40 nm (Fig. 1a). By contrast, when *F*-hexane is introduced above the vesicle dispersion, the dispersions present a bimodal distribution (Fig. 1b). The first population corresponds to the vesicles (mean radius of 40 nm) and the second to micelles (mean radius of 10-20 nm). The kinetic evolution of the hydrodynamic radius was studied in the presence of *F*-hexane (Fig. 1c). These results were confirmed by cryo-transmission electron microscopy. This unexpected phenomenon was also observed with other phospholipids such as dipalmitoylphosphatidylcholine (DPPC). It was recently found that *F*-hexane gas markedly accelerates the adsorption of phospholipid vesicles to the interface [6]. We will discuss how the *F*-hexane-induced formation of micelles reported here, which diffuse faster and spread more swiftly at the interface than vesicles, could contribute to this accelerated adsorption. The implications for the use of easily retrievable fluorocarbon gases in the design of innovative lung surfactant substitutes are presented [7].

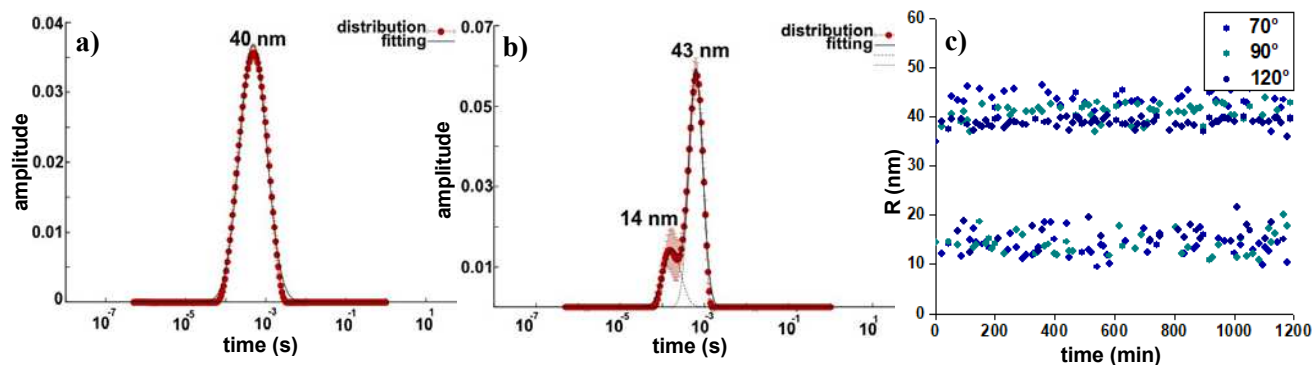


Figure 1. Distributions of hydrodynamic radii a) under N₂ showing vesicles (40 nm in radius) and b) under *F*-hexane-saturated N₂ (coexistence of micelles of 10-20 nm in radius and vesicles 40 nm in radius); c) Kinetic evolution of the hydrodynamic radius in the presence of *F*-hexane.

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Influence of salt on the stability of nanoemulsions: Ostwald ripening

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There has been considerable interest in the utilization of nanoemulsions as a delivery system for bioactive compounds. Essential oils are natural compounds that have shown distinct properties such as antimicrobial, antioxidant, and antifungal. Salt as a functional ingredient is widely used in most of the food products. In this work, influence of salt on the physicochemical stability of essential oil nanoemulsions was studied. The nanoemulsions of oregano, carvacrol, thymol, p-cymene, and sunflower oil stabilized using polysorbate 80 were prepared. The results obtained from solubility of the oils (fitted into the Setschenow equation) in water as the continuous phase of nanoemulsions and droplet size measurements suggested that the nanoemulsions containing the oil with lower solubility has more stability in the presence of salt. However, despite of the fact that in the presence of salt the solubility of the oil was lower, the nanoemulsions broke down due to the Ostwald ripening. Interestingly, the interfacial measurements revealed that the increase in the interfacial tension in the presence of salt led to a higher Ostwald ripening rate.

The results of this study provide crucial information for the first time about influence of salt on the stability of essential oil nanoemulsions, which are recently the subject of different studies.

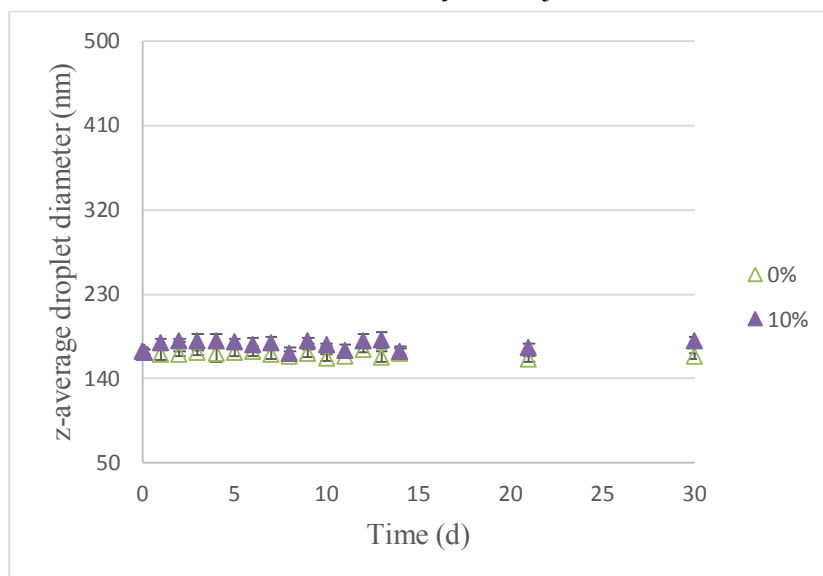


Figure 1. The droplet size variation of oregano nanoemulsions during long-term storage in the absence (empty symbols) and presence (filled symbols) of sodium chloride.

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Thermophilic poly(N-acryloyl glycineamide) microgels

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While lower critical solution temperature-type (LCST) thermosensitive behavior is utilised in many polymer and microgel applications, polymers showing upper critical solution temperature-type (UCST) have received considerably less attention.[1] Poly(N-acryloyl glycineamide) (PNAGA) is a non-ionic polymer that shows UCST-type of behavior in water and saline solutions. We report here the synthesis of PNAGA microgels that swell in water upon heating and their use as nanocatalyst hosts, Figure 1.[2]

The microgel syntheses takes advantage of the UCST-type phase transition behaviour of PNAGA. By performing the precipitation polymerization in water at sub-ambient temperature microgels with variable crosslinker content were prepared. The microgels show reversible swelling and shrinking upon change of temperature.

Silver nanoparticles (AgNP) were loaded into PNAGA microgels (Ag-PNAGA) for catalysis application. Ag-PNAGA retained the thermophilic behaviour of the PNAGA after the nanocatalyst synthesis. The catalytic activity of Ag-PNAGA was studied using nitrophenol reduction in presence of NaBH_4 as a model reaction and compared to corresponding poly(N-isopropyl acrylamide) microgels. The catalytic activity of Ag-PNAGA microgels increased especially at elevated temperatures due to their swelling leading to enhanced diffusion of the reactants.

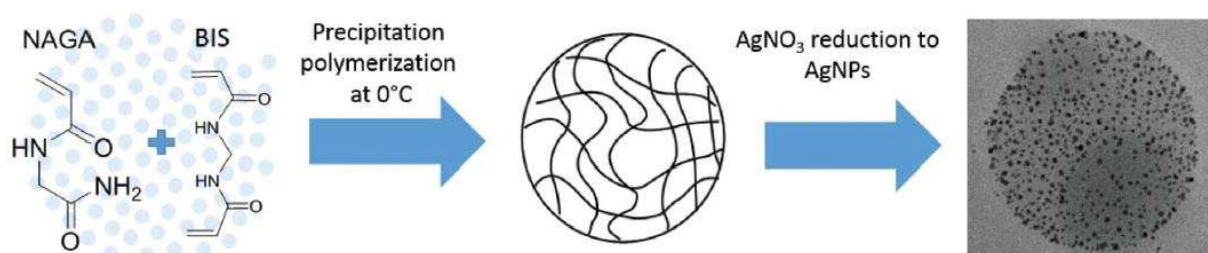


Figure 1. Synthesis route to PNAGA microgels and Ag–PNAGA hybrid microgels.

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Dispersibility in organic solvents of freeze-dried nanocrystalline cellulose

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Cellulose nanocrystals (CNC) are nano-sized crystalline rod-like particles, which can be easily isolated from renewable natural cellulose-containing raw materials by controlled acid hydrolysis. When used sulfuric acid, CNC form stable aqueous suspensions due to negatively charged sulfate ester groups at the NCC particle surface which cause electrostatic repulsion between the rodlike colloidal particles. The length of the anisotropic CNC particles is from 100 to 300 nm, the diameter is from 10 to 20 nm, depending on the raw material and processing conditions [1].

The main characteristics that stimulate the use of CNC are a rather large specific surface area, a very high modulus of elasticity, an anisotropic particle shape, a relative low density and a significant reinforcing effect at the low composite content. As one of the most abundant natural polymers and due to their superb mechanical properties and excellent biodegradability as well as biocompatibility, CNC have been regarded as an ideal reinforcing element for ecocomposites at a low cost.

A significant challenge in the handling of CNC arises when they should be dried from a suspension of well dispersed individual particles. Irreversible particle aggregation often occurs when the nanoparticles are dried, leading to loss of properties or functionality. Dispersibility is important for CNC because recovering the unique suspension and the particle properties is essential after the product has been dried for storage or transport [2]. Most applications require CNC to be delivered in dried form and redispersed at the site of use to minimize shipment size, weight, and cost. Drying also inhibits bacterial and fungal growth in the CNC and is frequently a necessary step for solvent exchange prior to dispersing CNC in organic solvents for chemical modification and in polymers for nanocomposites manufacture. However, dispersion of CNC is restricted to aqueous suspensions or dispersions in a few organic solvents with high dielectric constant. The main reason for such restriction is the electrostatic character of the suspension stability. In an apolar organic solvent, the electrostatic repulsion is inefficient and the establishment of strong hydrogen bonds between CNC leads to a rapid aggregation of the colloidal suspension.

Different chemical modifications of the CNC surface including noncovalent surface modification via adsorption of surfactants and polymer coating have been attempted to prevent aggregation and improve CNC redispersibility in organic solvents and compatibility with nonpolar or hydrophobic matrices in nanocomposites.

In this work, adsorption of polyvinylpyrrolidone (PVP) onto CNC was investigated for preparing redispersible freeze-dried CNC. Colloidal stability of the suspensions and the CNC particle size determined by light scattering were used as indicators of the dispersion quality. Results showed that the redispersity of CNC in organic solvent (propanol, dioxane, chloroform) can be significantly enhanced using a PVP (MW 40000) dosage of 50 wt%. Scanning electron microscopy was used to characterize morphology of the composites PVP/CNC. Thermo-gravimetric analysis and X-ray diffraction suggested that CNC crystallinity and thermal stability were not affected by the adsorption of PVP.

Acknowledgements: This work was supported by the Russian Science Foundation (grant number 17-13-01240).

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Microflows role during milk gelation

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Milk gels are by-products of cheese making and the final state of other milk products. Their formation involves a complex system of biochemical reactions and physical interactions between milk casein micelles. The micelles interaction first results in formation of di-, tri-, and tetramers of weakly-coupled casein micelles, further evolving into isolated loose fractal clusters of micelles. At the late flocculation phase most of the micelles are bound in such loose clusters. At this stage, when approximately 80% of the micelles surface in the cluster is free of glycomacopeptides, the “dense globule → molten globule” cooperative phase transition starts in the casein molecules forming the clusters [1].

The phase transition results in the ingress of water molecules and dissolved ions contributing to formation of new intra- and intermicellar covalent bonds. Energy sink into the clusters is caused by the micelles “molten globule → random coil” cooperative phase transition that is in turn due to the external conditions change.

Experimental studies carried out by us showed for the first time that at the stage of coagulation process of gelation the three-dimensional field of stochastic microflows occurs in milk. Micelles clusters should be considered as an essential element, causing and limiting the processes of heat and mass transfer in gel formation. Microconvective flows act over distances of several micrometers, with speeds of several micrometers per second and are modeled in the framework of microconvection theory. Our estimates are within this range, and it confirms the possibility of microconvection existence under the influence of the internal temperature gradients, concentration, density, viscosity and surface tension, resulting in a surface layer of casein micelle clusters. Theoretical analysis showed that the formation of the field of microflows is the result of the Ludwig-Soret effect and the Marangoni effect (Figure 1). The field of the microflows increases the number of interacting components in the structure of the gel per unit time (speed) and reduces the free energy of the system limited by a finite number of possible formed connections [2].

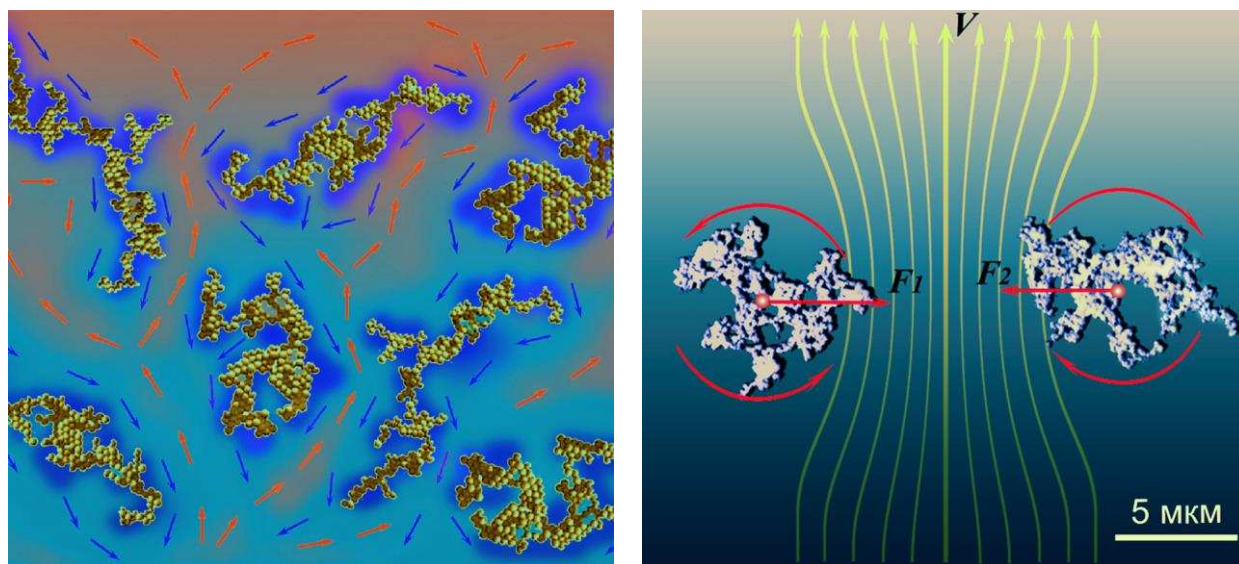


Figure 1. Microflows pattern during milk gelation

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Room-temperature synthesis of ultra-small colloidal $\text{LaPO}_4\text{:Eu}^{3+}$ and $\text{Tm}^{3+}/\text{Yb}^{3+}$, $\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{Ho}^{3+}/\text{Yb}^{3+}$ doped- REVO_4 ($\text{RE} = \text{Gd}^{3+}$, Y^{3+} , Lu^{3+}) multifunctional down-converting and up-converting nanoparticles

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The motivation for this work was to use low-temperature synthesis methods for preparation of $\text{LaPO}_4\text{:xmol\%Eu}^{3+}$ ($x = 0, 1, 5, 10, 15, 20, 30, 50, 75, 100$) and $\text{REVO}_4\text{:Tm}^{3+}/\text{Yb}^{3+}$ or $\text{Er}^{3+}/\text{Yb}^{3+}$, $\text{Ho}^{3+}/\text{Yb}^{3+}$ ($\text{RE} = \text{Gd}^{3+}$, Y^{3+} , Lu^{3+}) clear, colorless, water-based colloidal solutions of ultra-small, well-dispersed, stable nanoparticles which could be find applications in a various fields.

The water-based colloidal solutions with ultra-small, well-dispersed down- and up-converting nanoparticles were successfully prepared by the citrate route at room-temperature. High magnification TEM image and particle size distribution (Figure 1a and 1b) reveal that nanoparticles size is about 2 nm, and in accordance with the results obtained for crystallite size calculated from the X-ray diffraction (XRD) patterns. All XRD diffractograms showed the presence of single tetragonal zircon-type (space group $I4_1/amd$) GdVO_4 and monazite (space group $P121/m1$) LaPO_4 crystal structures. No traces of any impurity phases were noticed, indicating that any combinations of dopant ions were successfully incorporated into the host lattice. In addition, all optical properties (down-conversion and up-conversion emissions, the lifetimes as well as the Judd-Ofelt analysis) of the colloidal solutions with ultra-small up-converting nanoparticles were estimated.

In this comprehensive study, we have demonstrated that the different combinations of dopant (Tm^{3+} or Er^{3+} or Ho^{3+}) and co-dopant (Yb^{3+}) ions in REVO_4 ($\text{RE} = \text{Gd}^{3+}$, Y^{3+} , Lu^{3+}) nanoparticles can be optimized to enable multicolour (blue, green or red) up-conversion emission under NIR irradiation at 980 nm. Furthermore, the emission spectrum of ultra-small (2 nm) colloidal $\text{LaPO}_4\text{:Eu}^{3+}$ nanoparticles disclosed two intense broad bands centred at 459 nm (blue emission) and 550 nm (green emission), which can be attributed to defect emissions of host material. [1] No concentration quenching of Eu^{3+} emission was revealed up to to the stoichiometric material (EuPO_4). The absence of concentration quenching in this ultra-small nanoparticles can be ascribed to the phonon confinement, which foster non-radiative decays during energy migration between Eu^{3+} ions.

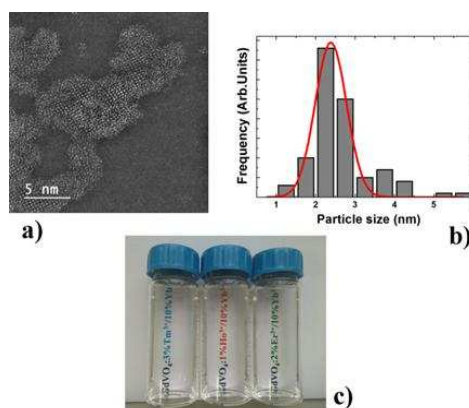


Figure 1. a) Representative TEM image of up-converting REVO_4 ($\text{RE} = \text{Gd}^{3+}$, Y^{3+} , Lu^{3+}) nanoparticles; b) their distribution and c) photograph of the colloidal solutions.

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Strong enhancement of the collective diffusion of quasi two- dimensional systems: trapped colloids and membrane lipids

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The collective dynamics of confined colloids [1] either close to interfaces due to electrostatics or trapped by optic forces (light) or by acoustic forces (ultrasound) etc., is strongly affected by hydrodynamic interactions with the embedding solvent. The so called quasi-2D dynamics [1,2] corresponds to particles which are confined to move in a plane but they are surrounded by solvent. In this configuration, the collective diffusion coefficient becomes anomalous and diverges as the inverse of the wavenumber, $D \sim 1/k$ [1,2,4]. This is a quite general phenomena [1] which has been also experimentally observed and/or predicted in other scenarios such as confinement in 1D and close to a wall, although with different low-wavenumber divergence-laws. Notably, we have recently shown that quasi-2D dynamics also rule the short-time collective motion of lipids in membranes [3] (and they might probably be also found in the case of membrane proteins). The enhancement of coherent motion can be understood from the hydrodynamic propagation of the confinement forces, which act on the particles in normal direction. These forces are immediately transmitted to the plane via the solvent's spreading of momentum lead by the Oseen tensor. In the plane, this collective drag acts like an effective repulsive force between the confined particles, leading to a strong correlation between displacements of distant particles (see Figure). I will first discuss the dynamics of confined and partially-confined colloids and their fluctuation spectra. Secondly, I will consider the short-time collective dynamics of **lipids** (Figure). Membrane simulations based on MD (Martini) and Brownian dynamics with hydrodynamics (BDHI) quantitatively agree with the quasi-2D theory, showing the same type of enhancement in collective motion of lipids at time scales below 100 ns; at larger times and Saffmann dynamics takes over.

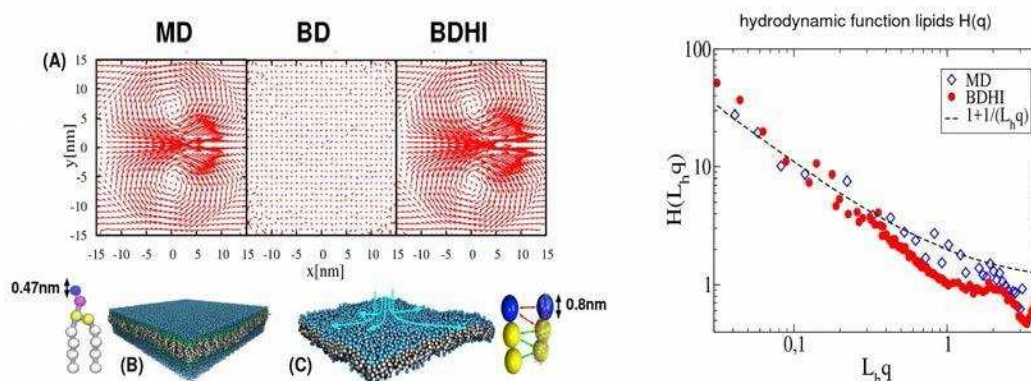


Figure 1. Left panel: velocity field for lipids relative displacements in the membrane obtained from MD (Martini) with explicit solvent, Brownian dynamics without hydrodynamics (BD) and with hydrodynamics (within the membrane and with the implicit solvent, BDHI). Right: Comparison of the hydrodynamic function $H(q)$ (proportional to the diffusion coefficient) obtained for MD and BDHI and with the quasi-2D theory (dashed line).

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Magnetorheology of magnetic colloidal gels

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The phenomenon of colloidal gelation is of great importance both from the standpoint of fundamentally understanding the non-equilibrium properties of colloidal dispersions, as well as for its implications in food science. Rheology is a very powerful tool to investigate the properties of colloidal gels. In particular, one important aspect of colloidal gels is the interplay between the structure of particles building up the gel and their interactions in determining the macroscopic mechanical properties of the gel phase. In order to gain better understanding on these important phenomena, in this work we have prepared magnetic colloidal gels, and performed a detailed characterization of their behaviour by means of magnetorheology. First, magnetic colloids have been prepared by miniemulsion polymerization of styrene, during which magnetite nanocrystals obtained by coprecipitation have been added to the styrene monomer. The resulting magnetic colloids have a size of about 100 nm, are electrostatically stabilized by SDS and are strongly responsive to magnetic fields, while keeping a superparamagnetic behaviour. Such magnetic colloids have been gelled in a rheometer equipped with a magneto-rheological cell, by using the procedure adopted in our previous work [1], which involves the screening of their charges via production of ammonia in the solution from urea catalysed by the enzyme urease. The sol-gel transition and the viscoelastic properties of the gel phase have been monitored by oscillatory rheology, through which the time evolution of the store and loss moduli have been monitored. Two situations have been considered: in the first one, the gelation process has occurred in the absence of a magnetic field, leading to conventional fractal colloidal gels, while in the second one gelation has been carried out in the presence of a magnetic field, leading to gels with a strongly anisotropic structure made of chains of the particles aligned in the direction of the field. Our system offers the unique possibility to observe how the mechanical behaviour of the gel changes when the magnetic field is turned on or off after the completion of the gelation process. In other words, it allows one to turn on and off the dipolar interactions acting between the particles, and to see this effect on the macroscopic behaviour of the system. Furthermore, the effect of the gel structure, controlled by keeping on or off the magnetic field during the formation of the gel can also be investigate. The effect of dipolar interactions, together with the gel structure, have been quantitatively assessed and interpreted by means of simple models accounting for the strength of the bonds among particles.

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Dynamics of sessile ferrofluid drops

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Ferrofluids are colloidal dispersions of magnetic nanoparticles in a liquid. The possibility of tuning the morphological and dynamical properties of the ferrofluids, taking advantage of their interaction with the magnetic field, is attracting a lot of attention because of its fundamental implications and wide technological applications.

In this presentation we will present different studies on the microfluidic properties of sessile ferrofluid droplets on open surfaces. First we will show how it is possible to tune the static shape the ferrofluid drops with the magnetic field (magnetowetting)[1]. It is found that the main wetting parameters (contact angle, contact line length and height of the drop) depend both from the gradient and the strength of the external magnetic field generated by permanent magnets. If the magnetic interaction is strong enough, it may led to the break-up the ferrofluid droplets in two or more daughters droplets. We have characterized this phenomenon by changing the nature of the surface and the magnetic interaction [2]. Finally, we will present a comprehensive experimental study of the interaction between gravity driven ferrofluid drops on very slippery oil impregnated surfaces in the presence of a patterned magnetic field. It is found that the drop speed can be accurately tuned by the magnetic interaction and, more interestingly, drops are found to undergo a stick-slip motion whose contrast and phase can be easily tuned by changing either the strength of the magnetic field or the ferrofluid concentration [3].

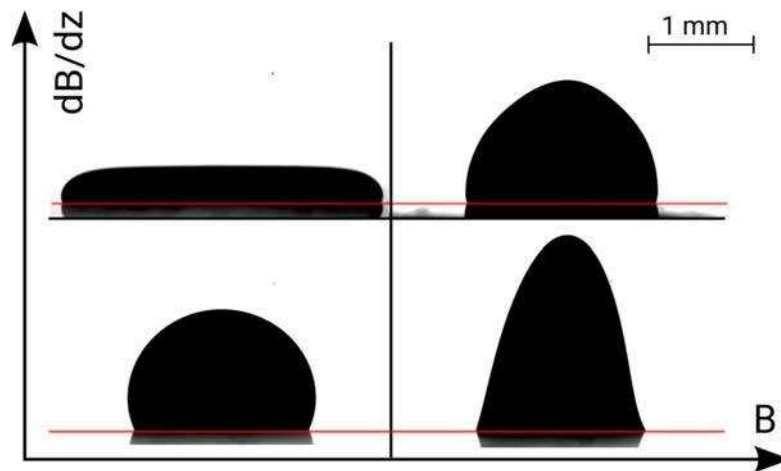


Figure 1.

Acknowledgements: we would like to thank Ali-Abou Hassan for the ferrofluid synthesis.

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Dynamics of Capillary Imbibition of Poly(ethylene oxide) Melts in Nanoporous Alumina

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Understanding the behavior of polymer fluids through nanochannels is not only of fundamental interest but also important for applications in nanotechnology. Nearly hundred years ago, Lucas and Washburn [1, 2] derived Lucas-Washburn Equation (LWE) for Newtonian liquids penetrating a cylindrical capillary with radius R . The penetrating length is proportional to $t^{1/2}$, t is the wetting time. Herein, we investigate the penetration of a series of entangled poly(ethylene oxide) melts within nanopores of self-ordered alumina. In general, the penetration follows $\sim t^{1/2}$ behavior according to LWE. However, LWE breaks-down because of differences in the prefactor. We observe a reversal in dynamics of capillary rise with polymer molecular weight. Chains with 244 entanglements or more display a faster capillary rise than theoretically predicted. Moreover, it is the first time to our knowledge that a slower capillary rise is observed for chains with 50 or less entanglements [3].

The reversal in polymer melt imbibition can be interpreted by the competition between a polymer dead zone next to the nanopore surface and the reptation of polymer chains under a pressure gradient [4]. The effect of dead zone results in a slower imbibition, *i.e.* an increase in effective viscosity; while, the effect of polymer reptation under pressure gradient results to a faster imbibition, *i.e.* a decrease in effective viscosity.

Lastly, we discuss the imbibition of PEO mixtures composed from long and short chains and show that it can result to the fractionation of short/long chains [5].

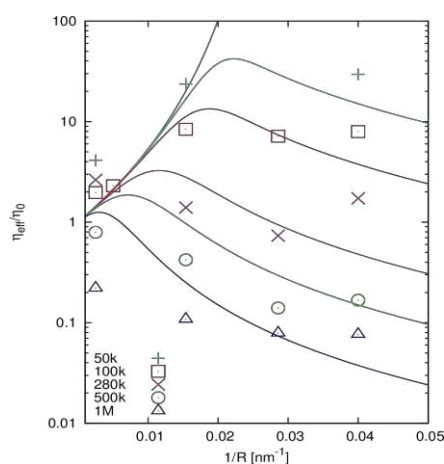


Figure 1. The comparison between theory (line) and experimental data (points) showing the ratio between effective viscosity (η_{eff}) and bulk viscosity (η_0) as a function of inverse of pore radius (R)

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Microscopic origin of flow in attractive colloidal glasses under shear.

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The key microscopic mechanisms defining the non-linear mechanics of frustrated states of attractive colloids are investigated using state of the art experiments and computer simulations. More specifically we present the connection between the structure and particle dynamics at the nanoscale, with the macroscopic rheological response for intermediate volume fraction colloidal gels and attractive glasses. We mainly focus on the way such systems yield under the application of steady or oscillatory shear. Start-up shear and large amplitude oscillatory shear tests, as well as shear cessation tests were probed. We discuss the phenomenology of two-step yielding, widely observed experimentally, its relation with quiescent microscopic dynamics and the underlying mechanisms affecting the relevant length- and time-scales during shear. For intermediate volume fraction gels, with large structural heterogeneities, Brownian Dynamics (BD) simulations reproduce well the steady state features but not the transient two-step yielding; the latter being crucially affected by hydrodynamic interactions (HI). On the other hand for more homogeneous attractive glasses BD simulations reproduce the two peaks in stress during start-up shear tests with good qualitative agreement with experiments suggesting that HI are not crucial. Structural analysis and microscopic particle dynamics obtained from BD simulations confirm that the first yield is related with bond breaking while the second yield point is primarily attributed to hard-sphere interactions during cage deformation and breaking. [1, 2].

We finally compare the internal relaxation and the linear viscoelastic properties of attractive glasses under shear with those of repulsive glasses [3], by Orthogonal Superposition Rheometry where a small amplitude oscillation probes a sheared attractive glass in the orthogonal direction.

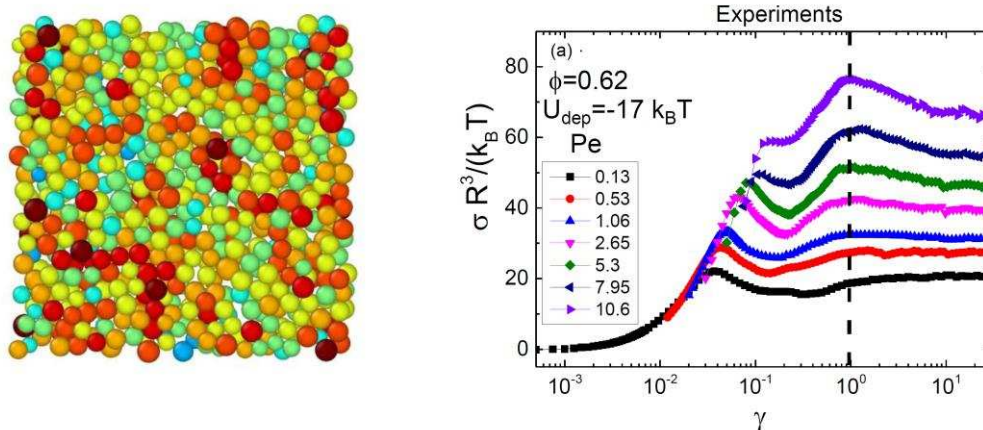


Figure 1. BD simulation snapshot (left). Two-step yielding in start-up shear in experiments (right).

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3D mobility of nanoparticles studied with liquid cell STEM

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Studying 3D self-diffusion of nanoparticles (NPs) in liquids, in real time and in real space, poses great challenges. The mobility of NPs increases with decreasing particle size, hence tracking of NPs becomes increasingly more difficult for smaller particle sizes. Liquid cell (scanning) transmission electron microscopy (LC(S)TEM) is a promising method for conducting such studies. However, up to now, most studies found diffusivities of NPs that were orders of magnitude smaller than theoretically expected. The main reason for this discrepancy is the electron beam-induced particle-window interactions that are essentially trapping the particles.

We have taken up the challenge to try to observe actual 3D diffusion (and ultimately 3D assembly) of particles (diameter 100-350 nm). In this work, we find conditions for which Brownian motion of particles is observable in LC(S)TEM and identify essential experimental parameters.

We found that NP-solvent combinations and low-dose imaging conditions ($\sim 1 \text{ e nm}^{-2} \text{ s}^{-1}$) are key parameters to ensure that the particles are not trapped in a potential well [1]. We show that 350 nm titania particles in glycerol carbonate do indeed exhibit Brownian motion and are not trapped in a potential near the windows. The measured mean squared displacement (MSD) leads to a diffusion coefficient ($D = 1.2 \cdot 10^{-2} \mu\text{m}^2 \text{ s}^{-1}$) of our 2D experimental data that corresponds very well with theoretical predictions for Brownian motion. Furthermore, the slope of the MSD in a log-log plot is close to unity, indicating Brownian motion instead of the anomalous diffusion often found in LC(S)TEM experiments [2]. Control experiments and further analysis were conducted to ascertain that the influence of the electron beam is minimized. We explain the reduced e-beam influence by analyzing the induced electric fields [3], and we briefly show that this low dose STEM technique can be applied to other particle systems as well.

We expect that, with the rapid improvements to EM detectors, scanning technology, and increasingly smart image reconstruction techniques, 3D NP experiments can soon be conducted for even smaller particle sizes, if the experimental parameters found in this work are taken into account.

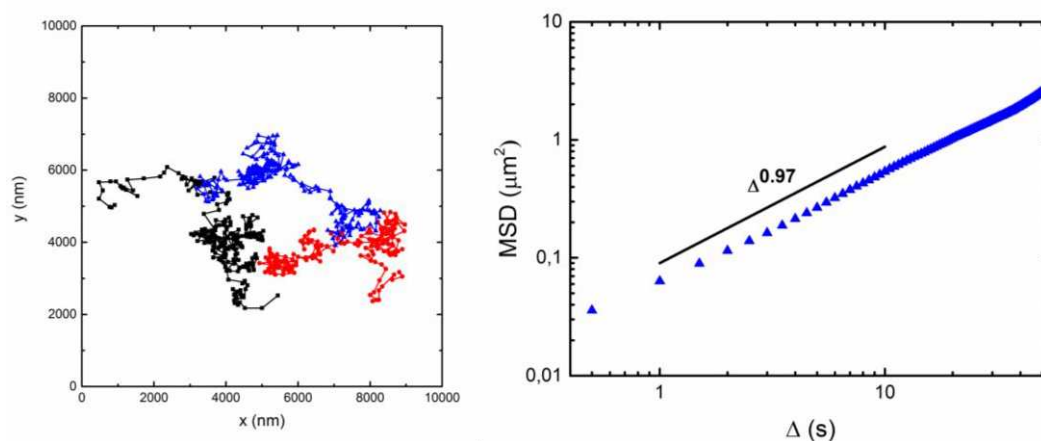


Figure 1. Movement of titania particles in LCSTEM. Left: Single particle tracks. Right: Averaged MSD.

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Swelling kinetics of *N*-*n*-propylacrylamide based microgels upon periodic pressure jumps investigated by time-resolved Small Angle Neutron Scattering

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Temperature responsive microgels are particles in the size range between 100 nm and 1 μm that undergo a reversible microphase separation at a specific temperature, the so called volume phase transition temperature (VPTT). Structure, size and phase transition properties can be controlled by the synthetic conditions, e. g. crosslinker content, surfactant concentration or different monomers/comonomers. This makes them outstanding candidates for various applications, such as drug delivery, catalytic particle carriers or nanoactuators. A precise understanding of the underlying processes is necessary to tune the network properties precisely for the different applications. Therefore, we investigated the swelling and deswelling kinetics of *N*-*n*-propylacrylamide (NNPAM) based microgels upon periodic pressure jumps across the phase transition by time-resolved small angle neutron scattering (SANS). Preceding photon correlation spectroscopy (PCS) measurements showed, that the phase transition shifts towards higher temperatures with increasing pressure, i.e. a swelling of the particles is induced upon compression. Due to the sharp phase transition [1], NNPAM based microgels are especially suited for this experiments, as both the swollen as the collapsed state can be accessed at the same temperature by applying different pressures. While the swelling occurred on a time scale of around 1 ms the deswelling was much slower (~ 10 ms). Together with static SANS and PCS spectroscopy we could show that the differences in the phase transition dynamics can be associated the underlying complex particle architecture, which exhibits a core region with a high density surrounded by a loosely connected shell.

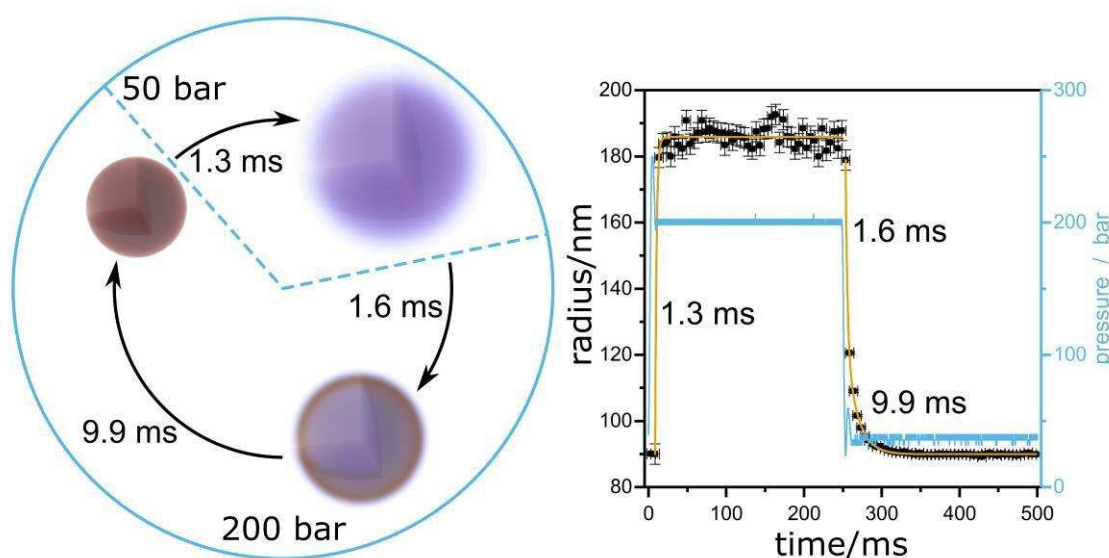


Figure 1. Schematic representation of the investigated phase transition (left) and the volume phase transition kinetics upon a pressure jump between 50 and 200 bar and vice-versa (at 22.8 °C).

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Magnetically driven omnidirectional artificial microswimmers

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Motion of microorganisms in water is governed by the hydrodynamics of low Reynolds numbers. In this regime, viscosity prevails over inertia and time-reversible motion does not generate net displacement. In order to move, microorganisms must break the symmetry by performing non-reciprocal motion.

Inspired by living microorganisms, in the past decade several artificial microswimmers have been either proposed theoretically or demonstrated experimentally. Here we present an experimental realisation of two new types of artificial magnetically actuated microswimmers that swim at low Reynolds numbers. The swimmers are composed of magnetic colloidal particles and are externally driven with a periodically modulated magnetic field that induces an alternating attractive/repulsive interaction between the individual beads. The superparamagnetic beads differ in size and due to the change in the field sequence, the drag on the swimmer components changes during the cycle, making the working cycle non-reciprocal.

The resulting asymmetry leads to a net translational displacement reaching velocities of up to 2 micrometers per second. The swimmers can be made omnidirectional, meaning that the same magnetic field sequence can drive swimmers in any direction in the sample plane. We demonstrate their omnidirectionality by guiding them through a circular microfluidic channel. Additionally, we use simple scaling arguments as well as more detailed numerical simulations to explain the measured velocity as a function of the actuation frequency [1].

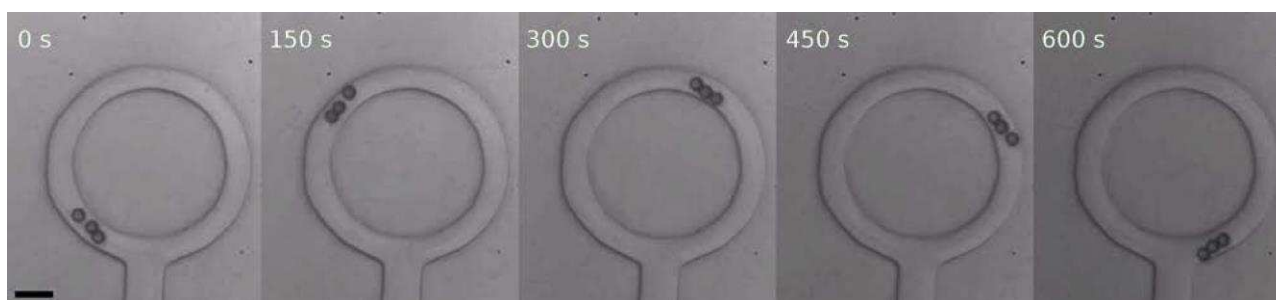


Figure 1. Demonstration of the omnidirectional swimmer moving through a circular channel. Its motion in the clock-wise direction is driven by a repeating magnetic field sequence. The scale bar is 10 microns.

Acknowledgements: The authors acknowledge the financial support from the Slovenian Research Agency (ARRS P1-0192, P1-0099 and J1-6724) and COST Action MP1305.

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Onsager's reciprocal relations in electrolyte solution. Sedimentation and electroacoustics.

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When an acoustic wave is applied in an electrolyte solution, water molecules and ionic solutes are set in motion. Ions get a velocity relative to water molecules, and two different ions get different velocities, because their masses and diffusion coefficients usually differ. This (small) difference in velocity induces an electric potential difference called the Ionic Vibration Potential (IVP). This effect is currently used as a method to determine the electrokinetic properties, especially the electrokinetic potential ζ , for the dispersions of colloidal particles. The use of acoustic waves is then a valuable advantage especially for dark or turbid samples. A new apparatus together with a reliable theoretical treatment were developed and thoroughly tested on simple electrolytes with a good agreement and without any adjustable parameter [1]. Several theories have been proposed over the years to predict the IVP have been proposed over the years to predict the IVP for high ionic strengths, taking into account non-ideal effects. In recent papers [2, 3], it is demonstrated that most of these theories are not consistent with Onsager's reciprocal relations. A new expression for the IVP has been presented that does fulfill the Onsager's reciprocal relations. We obtained this expression by deriving general expressions of the corrective forces describing non-ideal effects in electrolyte solutions. This new formulation also predicts the measured data in a satisfactory way.

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SAXS on a chip: from alignment phenomena at interfaces to dynamics of phase transitions studied with microfluidic devices

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The field of microfluidics offers attractive possibilities to perform novel experiments that are difficult (or even impossible) to execute using conventional bulk and surface-based methods. Such attractiveness comes from several important aspects inherent to miniaturization [1]. First, the flow of fluids under submillimeter confinement typically causes turbulence to vanish. This leads to predictable and controllable flow profiles, along with well-defined chemical gradients and stress fields that can be used for controlled mixing and actuation on the micro and nanoscale. Secondly, intricate microfluidic device designs can be fabricated to perform complex tasks, that require exquisite control of flow of several components and gradients, or to mimic real world examples with more realistic models. Thirdly, microfluidic devices are usually compatible with *in situ* or integrated characterization methods that allow constant real-time monitoring of the processes occurring inside the microchannels. Altogether, these characteristics provide researchers with a set of tools that allow both exquisite control of materials at the micro and nanoscale, and their observation.

In this work, we will focus on the use and prospects of combining microfluidic devices with *in situ* small-angle X-ray scattering (SAXS), and its enormous potential for colloid and interface science research. In a first example, we use this manipulation ability to create well-defined flowing interfaces to study the interplay between shear-flow forces and the structure of nematic liquid crystals and surfactant monolayers. By use of a microfocused x-ray beam applied *in-situ* on the microfluidic device we are able to determine the orientation field of the liquid crystal molecules, and how this orientation is influenced by the flow conditions and chemical nature of the interfaces [3]. In a second example, we study the lamellar-to-microemulsion transitions in the SDS-pentanol-water ternary system by mixing a lamellar phase with water or pentanol in a crossed microchannel configuration [4] (Figure 1). By manipulating the individual flow-rates, one can carefully tune the final composition and probe different time-scales of the transition with SAXS. The main findings show that the lamellar to o/w droplets transition (by mixing with water) occurs through a gradual stripping down of bilayers from the lamellar phase, whereas the lamellar to w/o reverse droplets transition (by mixing with pentanol) involves the formation of an intermediate lamellar phase.

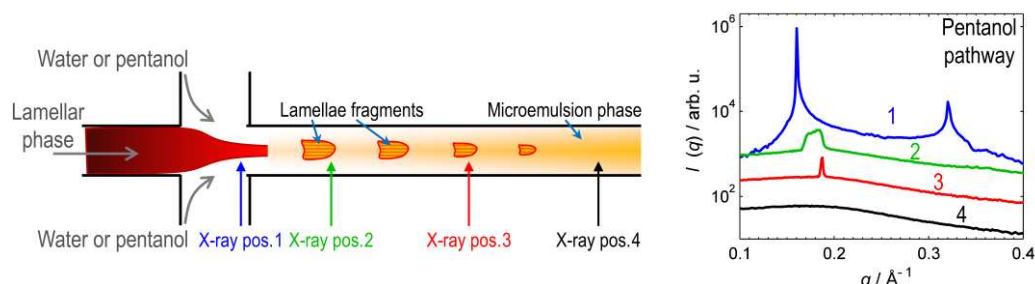


Figure 1. Schematic of the described microfluidic concentration-jump experiment (left) and representative SAXS patterns from different locations on the chip for the pentanol pathway (right).

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Displacement of Colloids in Liquid Crystals Induced by UV Light

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The motion of colloids in media is studied abundantly. It is often induced by Marangoni effect [1], electro-osmosis [2] and so on. In this study, we focus on the motion of colloids in liquid crystals [3]. Several research groups reported the transportation of colloids in liquid crystals by using the effects of heat [4], electric convection [5], defect [6] or light pressure. Here, we will show the displacement of colloids in liquid crystal at room temperature induced by UV light [3].

SiO₂ colloids ($\phi 10\ \mu\text{m}$) were dispersed in 4-Cyano-4'-pentylbiphenyl (5CB). This mixture was inserted into the cell, the surfaces of which were coated with rubbed polyimide and arranged in an anti-parallel way with a spacer of $50\ \mu\text{m}$. The motion of colloids was observed by a digital microscope while irradiating 365 nm light ($150\ \text{mW}/\text{cm}^2$) from the obliquely-upward direction.

In the irradiation of UV light, a colloid ran away quickly from the light and returned back gradually toward the original position by the extinction of the light [3]. We made the same experiments in various temperatures and found that colloids do not move when 5CB performs the isotropic state, while they move when 5CB performs the nematic state. The nematic-isotropic transition temperature of 5CB is around $35\ ^\circ\text{C}$.

We investigated the reason why the colloids moved. We focused on the photo-thermal effect in this system. To check that the present motion was able to be caused by the photo-thermal effect, the temperature of the sample surface was measured by the infra-red thermometer. During the irradiation of UV light, the surface temperature of the cell quickly increased by almost $1\ ^\circ\text{C}$. According to Weiss et al., the thermal expansion coefficient, α [$10^{-4}\ \text{K}^{-1}$], of 5CB increases in a divergent way just below the nematic-isotropic transition temperature [7]. And this divergent increase in α can transfer colloids through the volume expansion of 5CB. We also confirmed that the substance which performed the photo-thermal conversion in our experiments was polyimide.

Our system for extracting the motion of colloids is very simple. Therefore we can expect that our system should be helpful for the development of future soft actuators, because the present system does not need complicated designs and constructions.

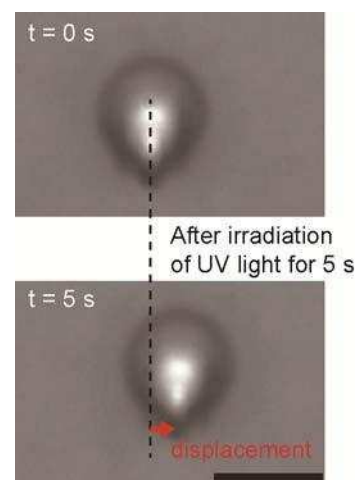


Figure 1. Displacement of a colloid induced by the irradiation of UV light for 5 s. The scale bar is $10\ \mu\text{m}$.

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Effect of large amplitude oscillatory shear on a lyotropic lamellar phase

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Lyotropic liquid crystals often show a rich phase behaviour and intriguing changes of the phase structure under shear. The most interesting phase is the lamellar one which can be considered, in a simplistic way, as a stacking of surfactant bilayers. Application of shear can lead to an alignment of the bilayers or to the formation of a defect structure that resembles close-packed monodisperse multilamellar vesicles also known as onions [1]. The response of lamellar systems to steady shear has been studied extensively, in particular, for the binary system triethylene glycol mono n-decyl ether (C₁₀E₃)/D₂O [2,3,4].

Here we report on the application of large amplitude oscillatory shear (LAOS) to the same system using rheo-NMR, rheo-SALS and bulk rheology to probe the structural changes. In this study LAOS deformation in a high-field NMR magnet [5] has been applied for the first time.

For the range of investigated strain amplitudes γ_0 (10 to 50) and frequencies ω (1 and 2 rad/s) the formation of lamellar vesicles is observed in all NMR and most SALS cases. In Figure 1, the characteristic changes of the ²H NMR spectrum of water, of the SALS patterns and of the rheological response can be seen. For LAOS the MLV size was found to mainly depend on the frequency, as opposed to previous steady shear experiments where the shear rate was the controlling parameter [3]. The onset of MLV formation under LAOS was primarily dependent on the applied shear amplitude. The process of onion formation appears to be retarded compared to the steady shear case.

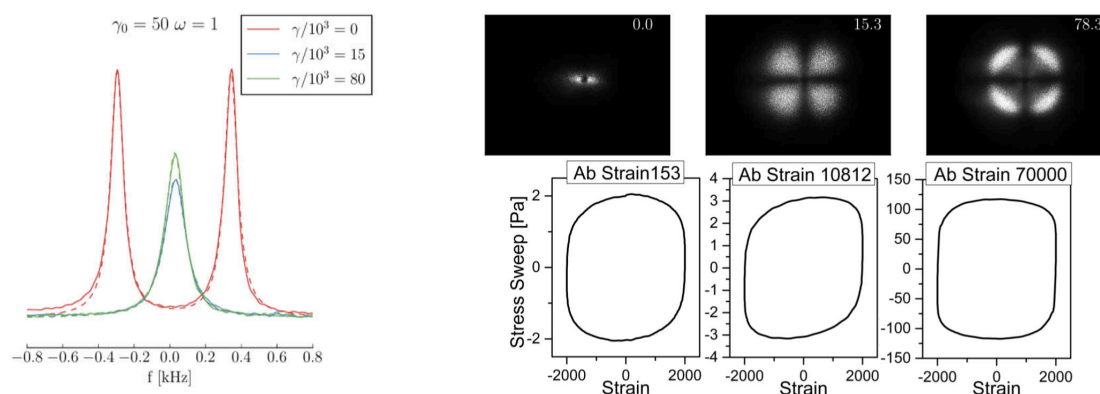


Figure 1. ²H NMR spectra of water (left), light scattering patterns (top right, $\gamma_0=20$) and rheological response (bottom right, $\gamma_0=20$) show the transformation from the aligned lamellar phase to multilamellar vesicles. γ denotes the accumulated absolute strain; the numbers given in the SALS patterns refer to $\gamma/10^3$.

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Abiotic vigorously motion of a vesicle under a pH gradient

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A biological system exhibits autonomous and oscillatory motions by utilizing a chemical potential difference that is formed by chemical reactions. As an example, white blood cells move toward inflamed sites by sensing irritant chemicals from the site [1]. In present study, we observed autonomous and oscillatory vesicle motions that are driven by a pH gradient. These vesicles are composed of oleate and oleic acid.

As the first example, a vesicle similar to a stomatocyte-like shape exhibit rhythmic shape changes under a pH gradient [2]. In this vesicle shown in Fig.1(a) the inner water is located at its one side (swollen-part), and a small hole exists in the centre of the swollen part. The opposite side of the vesicle is nearly dehydrated. This vesicle shows both of rotation of the entire vesicle and of reversal motion in which the inside and the outside of a vesicle are reversed. These motions repeat themselves many times. The size of the vesicle hardly decreases during these transformations. The motion can be explained by interplay between elastic energy of vesicle membrane and phoretic force due to pH gradient. The other example is that a desk-like vesicle exhibited the extrusion and contraction of a pseudopod-like structure (Fig.1(b)) [3]. This is similar to amoeboid motion. A pseudopod-like structure is always extruded toward a higher pH side. Therefore, the direction of this reversible pseudopod formation is controlled by the pH gradient around the vesicle. This reversible motion is repeated many times. The motion can be explained by the osmotic pressure across the vesicle membrane and its decay. A mathematical model that accounted for the osmotic pressure change reproduced the experimental results semi-quantitatively. As an extended system of this, the pH change leading to the pseudopod-like structure can be formed by the oxidation of glucose using an enzyme embedded in a vesicle [4].

The design of amphiphilic molecular assemblies with biomimetic motion may be applied for technological and medical applications of a molecular assembly. The present study may provide significant insight into the design of such biomimetic vesicles.

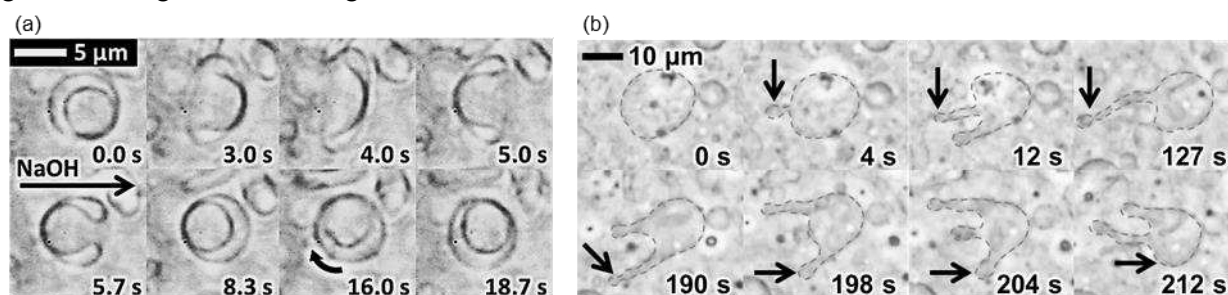


Figure 1. Time course of the vesicle shape change (a) and the reversible extrusion of pseudopod-like structure (b). (a) 1 M NaOH aqueous solution diffuses from the left side of vesicle, and the initial pH of vesicle solution is approximately 8.0. (b) 100 mM NaOH aqueous solution diffuses from the left side of vesicle, and the initial pH of vesicle solution is approximately 8.4.

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Effects of salt and fragrance-like molecules on formulation rheology

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Many personal-care formulations contain sodium lauryl ether sulfate (SLES; anionic) and cocoamidopropyl betaine (CAPB; zwitterionic) as main components. Here, we studied the effects of salt (NaCl) and fragrance-like molecules (FLMs) on the rheological properties of SLES-CAPB-containing solutions.

By varying the salt concentration, we constructed the so-called salt-response curve and observed a viscosity peak at nearly 400-500 mM NaCl; see Figure 1a. The peak position does not seem to depend on the total surfactant concentration or the weight fraction of SLES. Furthermore, we found that the zero-shear viscosity, η_0 , and the relaxation time, τ_R , pass through a maximum, whereas the elasticity, G_0 , increases monotonically as a function of the salt concentration.

We also investigated the effect of small FLMs on the rheological properties of SLES-CAPB-based micellar solutions. We demonstrated that such FLMs can act as thickeners or thinners depending on their structure and hydrophobicity; see Figure 1b and also [1]. If hydrophilic FLMs ($\log P < 1.5$) are added, η_0 and G_0 remain nearly constant. In the presence of FLMs with intermediate $\log P$ ($1.5 < \log P < 6.5$), η_0 and G_0 increase. In contrast, hydrophobic FLMs ($\log P > 6.5$) act as thinning agents and thus η_0 and G_0 decrease. These rules might be useful for the design of personal-care formulations that contain perfumes.

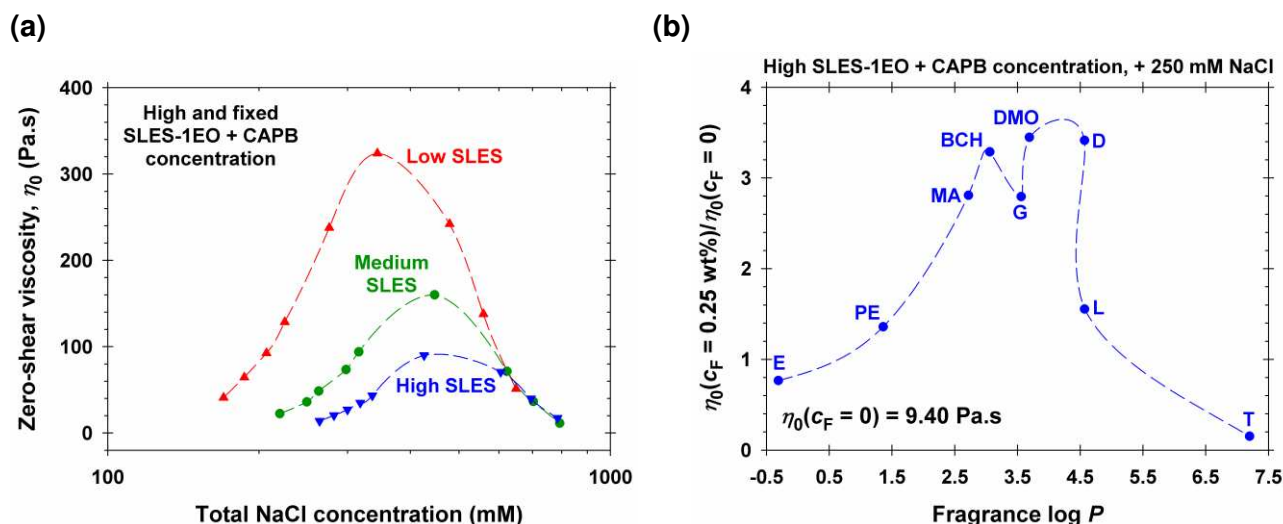


Figure 1. Effects of salt (a) and FLMs (b) on the rheology of SLES-CAPB-based formulations.

Acknowledgements: The study was supported by Unilever R&D. L.M.D. acknowledges financial support from project BG05M2OP001-2.009-0028 funded by the EU.

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Solute-Driven Colloidal Particle Manipulation in Continuous Flows Past Grooved Microchannels

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The integration of colloidal particle manipulation capabilities into microfluidic devices is a common feature of many lab-on-a-chip technologies for chemical and biological analysis. The most commonly employed strategies to perform particle operations, such as separation, filtration, trapping, focusing, and accumulation, are based on hydrodynamic, electrokinetic, acoustic, magnetic and optical effects. Recently there has been a growing interest in the use of diffusiophoresis – a phoretic phenomenon in which particle motion is induced by a solute concentration gradient – to manipulate colloidal particle in various applications [1-3]. The aim of this study is to explore diffusiophoresis to enable particle filtration, trapping, and accumulation within a microfluidic environment under continuous flow settings and in absence of any external force field. A Ψ -shaped microchannel, made of an optical adhesive glue and fitted with a micro-structured wall, was fabricated by photo-/soft-lithography techniques [4]. Electrolyte solutions were pumped into the device junction to generate steady-state salt concentration gradients enabling the manipulation of charged fluorescent colloidal particles. The spatial distribution of particles within the channel was characterised via fluorescence microscopy. This novel approach for particle handling by solute driven transport can unlock potential applications in point of care industry, drug delivery, biosensing and food industry.

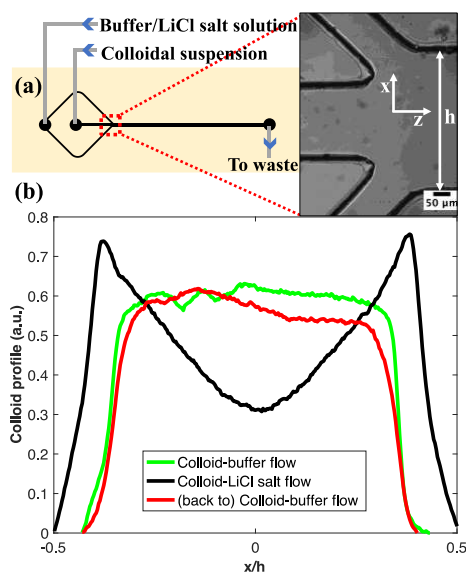


Figure 1. (a) A schematic of top view of microchannel fabricated using NOA 81 optical adhesive glue on a silicon substrate. Inset shows an optical micrograph of a junction of the lateral and central inlets through which a 10 mM Lithium Chloride (LiCl) salt solution and colloidal particle suspension (200 nm) in TRIS buffer (pH=9) are pumped respectively. **(b)** Experimental profiles of diffusiophoretic phenomenon in a microchannel on applying a LiCl salt gradient.

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Colloidal dynamics driven by confined cholesteric liquid crystals

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Energy landscapes have the ability to address and control the dynamics of colloidal particles. This feature can be employed as a useful tool for direct self-assembly of hierarchically organized structures, the most challenging goal in material science nowadays [1]. One of the possible examples for energy landscapes in soft matter are fluid interfaces, where colloidal particles migrate and reorient along the curvature gradients [2].

A similar environment which allows this sort of manipulation is liquid crystal. In nematic liquid crystal (NLCs) molecules show orientational order. When the nematic phase is confined in a vessel, anchoring conditions at the boundaries impose a series of distortions in the director field. As a result, the energy landscape is molded. The role of bend and splay distortions in presence of a wavy wall in NLCs has recently been exploited [3]. It results in a lock-and-key interaction: the particles have preferred location in the wall dales, where the maximum splay distortion is observed.

Here the study is extended to the case of chiral nematic (or cholesteric) liquid crystals (ChLCs), in the same vessel with undulated boundaries. ChLCs have an “intrinsic” twist distortion, which adds to the ones imposed by the solid boundaries. The cholesteric pitch p , i.e. the length scale over which the molecules twist by 2π , competes with the geometric length scales of the colloids or the topography of the boundaries, enriching the possible configurations. A 3-D control of the particle docking at the wavy wall is possible in ChLCs, and we observe a pitch-dependent docking mechanism. Depending on the pitch and on the pitch-to-sample thickness ratio the interaction can be attractive or repulsive, alternatively. Moreover, in proximity to a solid boundary the twisting LC introduces a vertical energy gradient, which allows to localize the colloid along the vertical axis. By tuning the pitch (i.e. changing the concentration of the chiral dopant), it would be possible to selectively promote or inhibit particle trapping at the docking site.

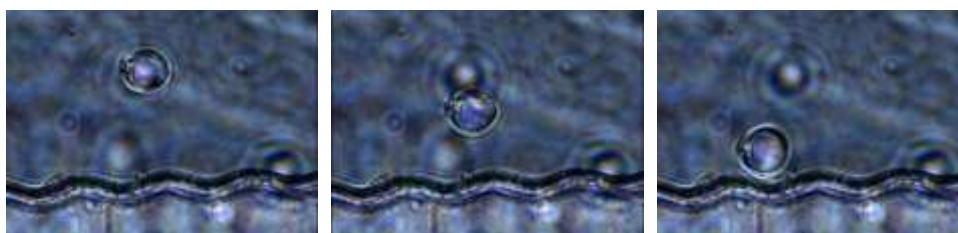


Figure 1. Docking of a spherical bead with homeotropic anchoring at a homeotropic wall in cholesteric liquid crystal (pitch 50 μm , cell gap 25 μm , particle diameter 15 μm).

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The structure effect of nonionic surfactants on the flavonoid incorporation into micelles - molecular dynamics studies

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Micellar mediated extraction (MME) is an alternative method to the classical extractions using organic solvents. In this method, an aqueous solution of surfactants is used as an eluent and the desirable substances are solubilized/adsorbed into the micelles. The nonionic surfactants exhibit the best solubilizing properties. The dissolving capacity of the surfactant solution depends on following factors: the structure and type of surfactant, the presence of electrolytes, presence of other organic compounds (e.g. polymers or monomers) and the temperature [1, 2]. Molecular Dynamic (MD) simulation study provided a series relevant clues for understanding the solubilisation behaviours of bioactive molecules in micellar systems and their underling mechanisms. Based on simulation of drug-Tween80 micelle system it was shown that the encapsulation process is predominantly driven by hydrophobic forces [3].

In this research the molecular dynamics simulations, used full atom approach to study the incorporation of chose flavonoid into nonionic surfactants micelles, were performed. The study focused on the aggregation of the series of polyethylene glycol ethers of fatty alcohols (C₁₀-C₁₈) in aqueous medium. The encapsulation behaviours of the flavonoid, the intermolecular interactions involved in the flavonoid adsorption processes, the structural properties of mixed nanomicelles, and the stability of flavonoid-surfactant micellar system were investigated.

Acknowledgements: The study was supported by Poland National Science Centre (Project MINIATURA: 2017/01/X/ST4/00508). Authors also acknowledge the computing resources from PL-Grid Infrastructure.

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Decay capillary flow of liquid crystals oriented by photosensitive surfaces and electric field

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Experiments with an arising of liquids in vertical capillaries of different cross sections are known as a well elaborated technique for a study of wetting processes [1]. In our experiments we apply this method to an investigation of rheological properties of nematic liquid crystals (NLC) contacted with the photosensitive inner surfaces of a flat capillary. The main idea of usage of such surfaces is to eliminate the non controllable influence of a nano relief on the wetting process, which takes place at rubbing treatment technique, previously used in similar experiments [2]. It makes possible to reveal the influence of surface anisotropy on the complicated behavior of a decay capillary flow of NLC. The additional usage of stabilizing electric field provides changes in the bulk orientation and the effective shear viscosity of NLC. It results in the essential slowing of the flow rate, as it is shown in Figure 1. The analysis of the static height of NLC rise at different surface orientations made possible to obtain the values of the corresponding contact angles. The dynamics of the capillary flow was analyzed in the framework of a model, previously applied to isotropic Newtonian fluids [1]. The role of specific hydrodynamic instabilities arising in shear flows of NLC [3] was also considered.

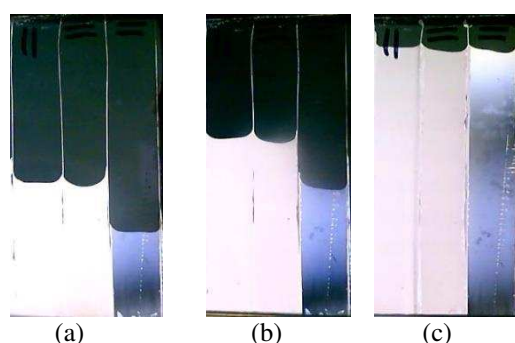


Figure 1. The images (in crossed polarizers) of the cell in the experiment taken at 75 s (a), 170 s (b) and 720 s (c) after beginning of a capillary decay flow of 5CB for the planar surface orientation along the flow (the left capillary) and perpendicular the flow (the central and right capillaries) with additional application of a stabilizing voltage (100 V, 5 kHz -right capillary).

Acknowledgements: This work was supported by Ministry of Education and Science of Russian Federation, identification number- RFMEFI58316X0058.

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Mechanism of the self-propelled motion of a sodium oleate tablet and boat at an oil–water interface using the quasi-elastic laser scattering technique

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The self-propelled behaviours of macroscopic inanimate objects at surfaces and interfaces are ubiquitous phenomena of fundamental interest in interface science. However, given the existence of a large variety of systems with their own inherent chemical properties, the kinematics of the self-propelled motion and the dynamics of the forces driving these systems often remain largely unknown. A tablet of sodium oleate, an anionic surfactant, is known to show self-propulsion abilities only at liquid–liquid interfaces such as water and oil [1]. However, to the best of our knowledge, a fully quantitative evaluation of this behaviour has not been carried out, with only one earlier study being available.

Here, we elucidate the kinetic mechanism of this system by quantitatively examining why sodium oleate tablets are only self-propelled at liquid–liquid interfaces [2]. We prove that the interfacial tension imbalance is the driving force of this motion through measurements of the time- and space-resolved interfacial tension distribution around a sodium oleate tablet at air–water and water–nitrobenzene interfaces using the non-invasive quasi-elastic laser scattering method (QELS). The sodium oleate tablet is self-propelled at the water–nitrobenzene interface due to an imbalance in the interfacial tension induced by the inhomogeneous adsorption of oleate/oleic acid molecules. On the other hand, the sodium oleate tablet does not exhibit self-propulsion on the water surface because the oleate molecules are uniformly adsorbed at the surface. Furthermore, to easily control the direction and speed of the motion and conduct a systematic study of its dynamics, we also designed a self-propelled sodium oleate boat floating at an aqueous solution–nitrobenzene interface in a loop.

The kinetics of the self-propelled motion of the sodium oleate boat is similarly studied by QELS measurements. The space-resolved interfacial tension at the front and back of the sodium oleate boat can be calculated from the time-resolved interfacial tension data in conjunction with the average boat speed in each lap as shown in Fig. 1. The interfacial tension difference between the front and rear of the boat is quantitatively identified as the force pushing the boat forward, although the Marangoni flow due to the uneven distribution of the interfacial tension behind the boat tends to decelerate the motion.

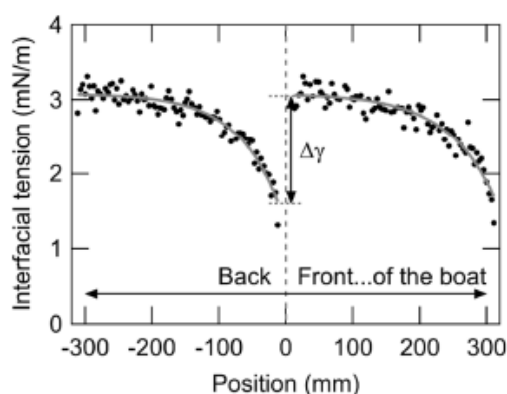


Figure 1. Space-resolved interfacial tension at the front (positive position values) and back (negative positions) of the self-propelled sodium oleate boat during two laps calculated from the time-resolved data.

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Functionalized and non-functionalized SBR latexes: Particle Size Distribution effects on oscillatory and steady shear rheology

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The use of SBR latexes is widespread in the industrial field; two examples of application are those of paper coating and foam rubbers for mattresses. SBR latexes are synthesized at industrial scale by emulsion polymerization, usually possess a unimodal, rather narrow, Particle Size Distribution (PSD) and are typically available for delivery at rather high concentration, close to 50% by weight in water. It is well-known that slight changes of polymer particles concentration or other parameters (like pH or temperature) may greatly influence the rheological behaviour of these systems. This implies a number of possible issues or opportunities when dealing with SBR latexes. Mastering the stability and rheological properties of such sensitive systems is therefore crucial for both the producer and the customer. In this work, we investigated the rheological behaviour of SBR latexes with and without Acrylamide functionalization. We explored the changes in latex dynamics and rheology obtainable modifying the PSD of functionalized and non-functionalized SBR latexes. We carried out an extensive rheological investigation in a wide strain, rate and frequency range, at two different concentrations, below but not far from the random close packing limit. Rheological measurements were performed with a RFS II (Rheometrics Inc.) strain controlled rheometer equipped with a coaxial cylinder geometry. Temperature was kept at 15°C throughout the tests and a thin film of silicone oil was poured on the free surface of latex in order to prevent water evaporation during measurements.

In fig. 1, the Small Amplitude Oscillatory Shear (SAOS) (Fig. 1a) and steady shear (Fig. 1b) results for three non-functionalized unimodal latex samples A, B, C together with a bimodal (D) sample are shown. In the figure legends, the PSD mode value is reported for each sample. The elastic modulus (Fig. 1a) shows a rather weak frequency dependence for unimodal samples, especially B and C. This strongly elastic behaviour at small strain is consistent with the high concentration of these samples. Bimodal sample D possesses a very different elastic modulus curve (Fig. 1a) in terms of both slope and magnitude in a wide frequency range. In accordance with literature [1], the steady shear stress (Fig. 1b) is reduced with increasing particle size. In Fig. 1b, we also compare the complex modulus G^* determined from linear viscoelastic SAOS data with the steady shear stress, τ . As expected, Cox-Merz rule fails for all samples. We used the onset and relevance of the G^* - τ discrepancy to characterize the transition from Brownian to advection dominated regime. Also from this viewpoint, sample D shows a clearly distinct behaviour as, only in this case, shear stress τ approaches G^* at the lowest investigated shear rates. Analogous results on functionalized systems will also be discussed.

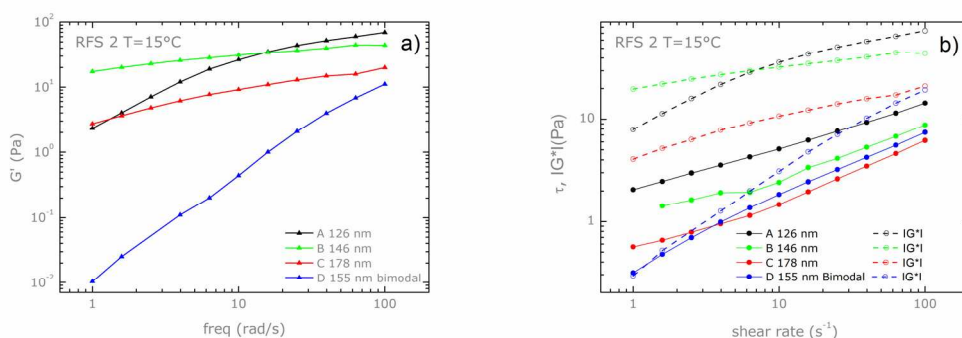


Figure 1: a) SAOS results for non-functionalized SBR latexes. b) filled symbols - stress from steady shear, empty symbols - complex modulus $|G^*|$ from SAOS for non-functionalized SBR latexes

Acknowledgements: A. Abbondanzieri is gratefully acknowledged for experimental support.

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Diffusion and Arrest of Ellipsoidal Particles in the Presence of an External Field

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Differential dynamic microscopy (DDM) has been recently developed to quantify the dynamics of submicron particles in dispersion from fluctuations of the intensity in optical micrographs. Although DDM is a powerful technique to measure anisotropic dynamics of concentrated suspensions, its full potential has not been exploited so far. Here we will present the dynamics of anisotropic ellipsoids over a large range of concentrations up to their glass transition using DDM. Prolate colloidal silica-coated hematite particles were used as a model system, and their ability to orient in a homogeneous external magnetic field was exploited to study the combined effects of shape anisotropy and orientation on their diffusion. The angularly resolved diffusion of the particles was measured to determine the particles hydrodynamic dimensions in the dilute regime to validate the technique for our experimental system. Upon increasing the amplitude of the magnetic field, the alignment of the particles perpendicular to the field is promoted, which is manifested by the stronger decoupling of the diffusion parallel and perpendicular to the field which start to diverge at higher concentration [fig.1a]. In this presentation, we will primarily focus on the field and concentration dependence of the short- and long-time diffusion coefficient and their connection to the phase behavior of these particles. Typical results for the high field case ($B \sim 350\text{mT}$) are shown in figs. [1b, 1c]. While the long-time diffusion coefficients at higher concentrations decrease dramatically, indicating that the system approaches a glass transition [fig. 1c], the short-time collective diffusion coefficient increases [fig. 1b], primarily reflecting the decrease in the static structure factor at low q -values typical for a repulsive system.

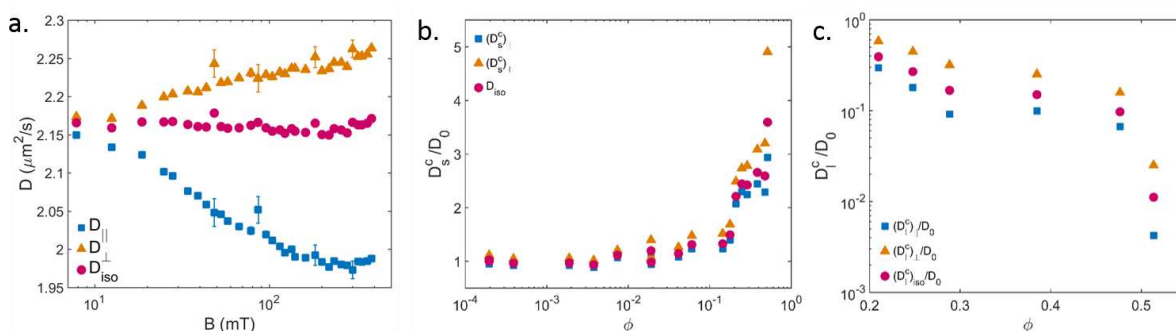


Figure1. (a) Decoupling of the diffusion coefficient along parallel and perpendicular to the applied magnetic field as a function of field strength for 0.1wt% of dispersion. (b) Variation of the anisotropic normalized short-time collective diffusion coefficients and (c) long-time diffusion coefficient as a function of the volume fraction.

Statistical analysis of Dynamic Light Scattering data: revisiting and beyond the Schatzel formula

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In his seminal paper published in 1990 [1], K. Schatzel provided a numerical expression for the full covariance matrix (and error bars) of the auto-correlation function estimator that is recovered in Dynamic Light Scattering experiment. Provided that the so called triangular average is properly taken into account, his formula was worked out without imposing any assumption on the sampling times, a requirement that is crucial when using multi-tau correlators where the sampling times might be comparable or even larger than the correlation time. In that same paper, K. Schatzel provided also an analytical expression for the covariance matrix (and error bars) for the specific (but quite common) case of a Lorentzian spectrum, where the correlation function is characterized by a single exponential decay function. However, this formula does not include the effects of the triangular averaging and, if used as is, gives highly inaccurate estimates of the error bars at lag-times comparable with the measurement time.

In this work, we solved this problem and worked out an exact analytical expression that generalizes the Schatzel formula for the specific case of a single exponential decay function. By the use of computer simulations we showed that this exact formula is capable the estimating quite accurately the covariance matrix and the error bars at all lag-times. The exact formula is also capable of describing the error bars in the case of a polydisperse sample, with polydispersities up to ~50-100%. Moreover, although not demonstrated, we showed numerically that that our new formula can also be used in the case of a single exponential decay cross-correlation function, provided that then average count rate is computed as the geometrical mean of the average count rates of the two channels. Finally, when tested on calibrated polystyrene particles, the new formula was to reproduce accurately the error bars obtained by averaging the experimental data.

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Rolling and ageing in soft adhesion of microparticles

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Immediately before adsorption to a horizontal substrate, sinking soft colloids can undergo a complex sequence of landing, jumping, crawling and rolling events. Using video tracking we studied the soft adhesion to a horizontal flat plate of micron-size colloids coated by a controlled molar fraction f of PLL-g-PNIPAM, which is a temperature sensitive polymer. It allows for sticking of colloids to the surface when the temperature is above $T_c = 32^\circ\text{C}$. In order to capture the very final events before the immobilization of colloids the T-ramp protocol was designed: the particles suspension is injected in the cell at room temperature, the temperature is increased at $10^\circ\text{C}/\text{min}$ up to $38^\circ\text{C} > T_c$, and kept constant until the end of the acquisition. Attraction between beads and the flat plate is thereby triggered by crossing the critical temperature $T_c = 32^\circ\text{C}$. 3D beads motion is real-time tracked using slightly defocus microscopy in parallel illumination decorating bead image with interference rings observed with video camera. Analysis of the tracking records indicates the Brownian rolling is the most relevant phenomenon in last moments before the immobilization. The experimental results are discussed in the framework of a simple theoretical model that includes ageing effects of the soft contact area between the microparticle and the flat substrate.

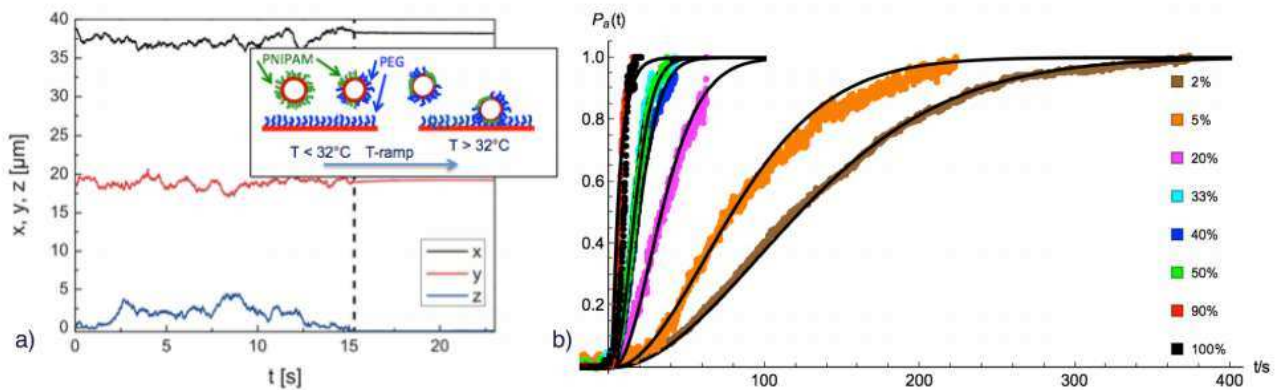


Figure 1. a) Typical 3D tracking record. Bead was captured irreversibly at $t=15.2$ s. Inset: schematic visualisation of temperature ramp experiment. b) Fraction of adsorbed particles as a function of time in a T-ramp of $10^\circ\text{C}/\text{min}$ between 26°C and 38°C , for a range of PNIPAM coverage ratios between $f=2\%$ and $f=100\%$. Solid lines are calculated using our theory in which f -dependence enters over a single scaling parameter [1].

Acknowledgements: This work was supported by ANR DAPlePur 13-BS08-0001-01 and program "investissement d'avenir" ANR-11-LABX-0011-01.

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Measurement of Kinetic Behaviour of Colloidal Particles in the Vicinity of Solid-Liquid Interfacial Boundary using Interference of Evanescent Waves

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We investigate electrokinetic behaviour of colloidal particles in the vicinity of a solid-liquid interfacial boundary. Colloids are expected to function as thermal transport media for a number of heat transfer applications. Nanofluids dispersed with nanometre-sized solid particles in water are reported to have higher thermal conductivities compared to the volume ratios. Micro-/nano-emulsions dispersed with micro-/nanometre sized phase-change materials are attractive for thermal storage medium. These colloids contain submicrometre-sized particles in liquid, and electrokinetic behaviour of the solute particles should play an important role in the heat transfer process between solid and liquid. However, experimental investigation of the behaviour still remains challenging due to the required spatial resolution beyond diffraction limit.

We developed a measurement system using evanescent waves generated by total internal reflections at a solid wall [1]. Unlike imaging technique such as micro particle image velocimetry (micro-PIV), the measurement is based on laser Doppler technique using an interference of a pair of coherent evanescent waves [2]. Resulting peak frequencies of the Doppler-shifted signals of colloidal particles correspond to their velocities parallel to the interfacial boundary, while the spreading of the frequency peak indicates the degree of Brownian motion in the measurement volume. The short penetration depth of evanescent waves overcomes the conventional diffraction limit and it allows the measurement of the particles within a few hundred nanometres within a solid surface. The thin measurement volume on the interfacial boundary is advantageous for measuring colloids with high densities, which cannot be measured with a micro-PIV.

Fig. 1(a) shows a schematic of the test section of the measurement system. The system provides the flow velocities of colloidal particles within about 300 nm from the glass surface. The measurement principle was confirmed and the performance of the system was characterized using particles attached on a scanning probe developed in our laboratory. Fig. 1(b) shows measurement results of electrophoresis experiment using aqueous solution of aluminium particles with a nominal diameter of 1 μm . The average result exhibits linear behaviour of the particle velocities and Doppler frequencies to the induced electric field.

Investigation is continued towards measurement of submicrometre-sized colloidal particles. We will report the details of the measurement system and latest results of the experiments at the conference.

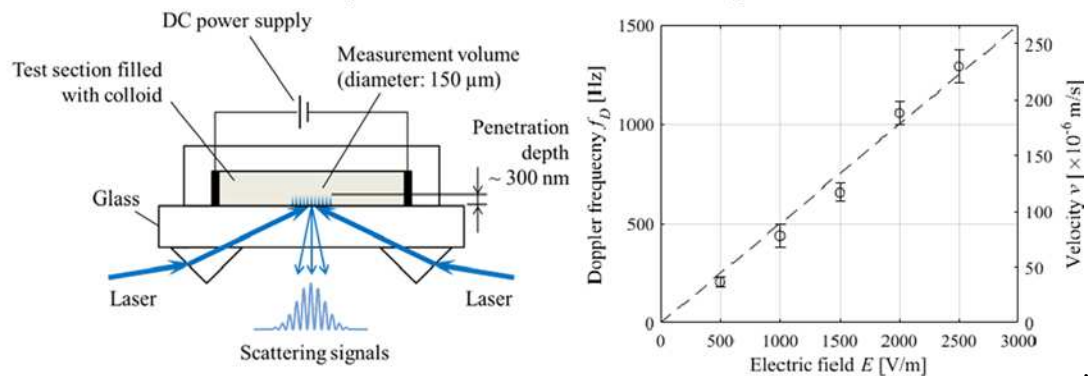


Figure 1. (a) Schematic of the test section of the measurement system based on laser Doppler technique using an interference of evanescent waves. The tangential velocities of solute particles of the test colloid are measured within about 300 nm from the glass surface. (b) The resulting Doppler frequencies and velocities of 1 μm alumina particles plotted against the induced electric field strength at the electrophoresis experiment.

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Dynamics in photoswitchable smart wormlike micelles

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The ability of photosensitive molecules such as ortho-methoxycinnamic acid (OMCA) to couple to surfactants such as CTAB and vary the polar head-group area by modulating the total charge has been exploited to produce smart micelles that can be optically controlled between two very different morphologies: a wormlike state, and a globular state [1]. The difference in viscosity between these two micellar states can easily reach up to 4 orders of magnitude. The mechanism underlying this transformation can be described in terms of the criterion for micelles shape introduced by Israelachvili, based on the ratio between polar headgroup area and the hydrophobic volume scaled by the hydrocarbon chain length [2].

With respect to other stimuli responsive wormlike micellar systems, CTAB-OMCA is of easy synthesis and based on cheap commercially available chemicals. Moreover, optical control offers a great precision in inducing localized effects. As such, numerous applications have been anticipated, among which are e.g. smart drug delivery and sensing [3]. However, to date, no real world applications have been developed and commercialized. This is in part due to lack of knowledge about diffusion process of macromolecules (such as drugs) or of nanostructures in these crowded and confined environments.

We shall report on a multiscale investigation of the diverse dynamical regimes (Reptation, Rouse, Brownian) in presence of tracer particles of different size and chemical nature (e.g. silica and gold particles of sizes from tens of nm to 500nm). The wide range of scales involved requires a combination of different techniques: imaging on the macro scale, dynamics investigation by Discrete Differential Microscopy (DDM) and Diffusing Wave Spectroscopy (DWS). DWS in particular is sensitive to tiniest motions and to faster time scales than those normally accessible by usual rheological techniques and by micro-imaging and related techniques.

It is expected that increased knowledge on the diverse dynamical regimes of smart wormlike micelles shall pave the way for real applications to precision drug delivery and sensing.

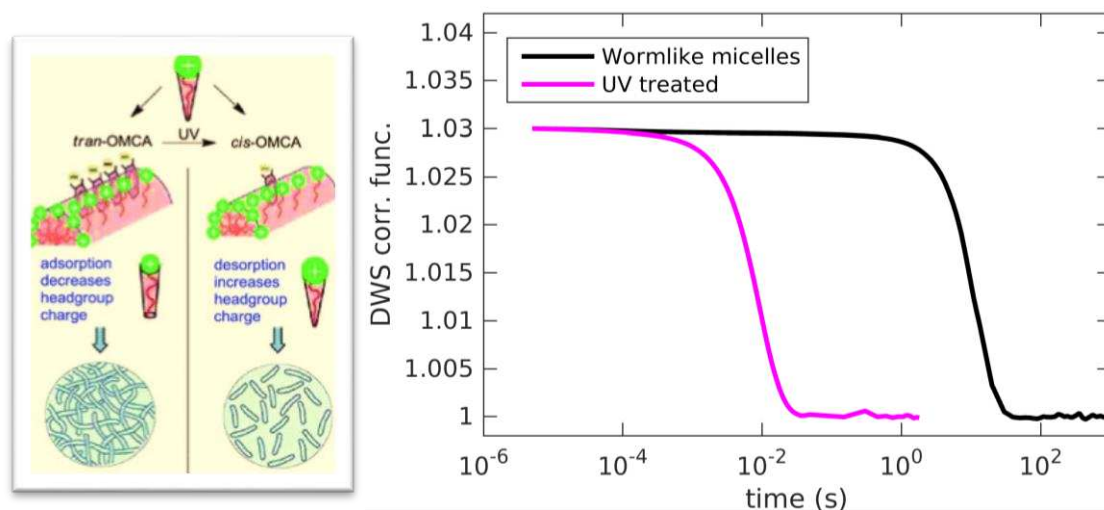


Figure 1. Left: the mechanism of conversion from wormlike to globular micelles (adapted from ref 3). Right: typical DWS result showing the different dynamics regime of a microparticle in photoswitchable smart wormlike micelles.

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Light-driven motions of asymmetric dumbbells in H₂O₂ solution

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Self-propelled particles (SPPs) have received attention in various application fields (e.g. drug delivery systems, non-invasive surgeries and motile sensors) because the motion of SPPs can be controlled by an external energy. Janus particles having a catalytic surface in one side have been studied as light-driven SPPs [1]. The Janus particles in hydrogen peroxide (H₂O₂) solution exhibited self-diffusiophoresis due to osmotic flow induced by a local reaction on the catalytic surface. In the present work, we prepared asymmetric composite dumbbells uniformly supporting photocatalytic nanoparticles on their whole surface to be provided with light-driven motion. Osmotic flow caused by the shape anisotropy in the solution could induce the self-propelled motion. The self-propelled motions with and without light irradiation were measured to examine the effectiveness of shape anisotropy for the light-driven motion.

Figure 1(a) shows the schematic procedure for the synthesis of the asymmetric dumbbells as the SPPs [2]. Submicron-sized silica spheres were coated with polymethyl methacrylate (PMMA) shell crosslinked with 3-methacryloxy-propyltrimethoxysilane (MPTMS). The dumbbells were obtained by protrusion of polystyrene lobe from the crosslinked polymer shell. The SPPs supporting magnetite nanoparticles were prepared by electrostatic heterocoagulation between anionic dumbbells and cationic magnetite nanoparticles. The motions of SPPs in H₂O₂ (5%) solution were observed with an optical microscope. The light wavelength was 510 nm or lower, and the light intensity was 3.7 mW/cm².

The STEM images of the asymmetric dumbbells (SPPs) are shown in Figure 1(b). Magnetite nanoparticles were uniformly supported on the whole surface of the SPPs. The SPPs exhibited propelled motion under illumination, whereas they exhibited Brownian motion without the light irradiation. The propelled motion caused gathering the SPPs, resulting in clustering of the SPPs in the solution. Interestingly, the clustered structures of the SPPs were redispersed again by turning the light off. The difference in motions of SPPs with and without light irradiation suggested asymmetric decomposition of H₂O₂ on the particle.

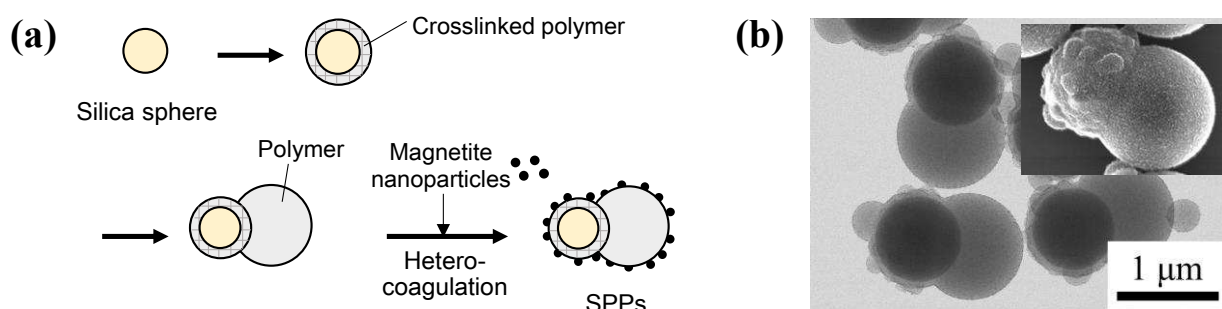


Figure 1. The schematic procedure for the synthesis of the asymmetric dumbbells (SPPs) (a) and STEM images of the SPPs (b).

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Wetting dynamics of polydimethylsiloxane mixtures on a poly(ethylene terephthalate) fiber

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Wetting dynamics drive numerous technological processes involving liquids in contact with solid substrates with a wide range of geometries. To describe the dynamics of wetting, two main theoretical approaches have been proposed: the hydrodynamic approach (HD) and the molecular-kinetic theory (MKT), which differ from each other mostly in the consideration of the channel of dissipation [1-3]. When applied to the spreading of droplets on a flat surface with vanishing contact angle (θ_i), the two models predict that θ_i varies as $t^{-3/10}$ and $t^{-3/7}$ for the HD and MKT, respectively [3]. It implies that the difference between these two regimes is not experimentally easily distinguishable. In contrast to the flat substrate, for the fiber geometry, HD and MKT respectively predict $\theta_i \sim t^{1/2}$ and $\theta_i \sim t^{-1}$ [4]. It suggests that, compared to flat geometry, it presents some advantages to use cylindrical fibers when the dissipation regimes have to be unambiguously distinguished.

This work therefore investigates the spreading dynamics, from an infinite reservoir, of one- and two-component polydimethylsiloxane (PDMS) liquids around a poly(ethylene terephthalate) fiber. Two types of PDMS with viscosities of 5 mm²/s (PDMS5) and 500 mm²/s (PDMS500) were selected to prepare mixture. Contact angle dynamics ($\theta_i \leq 45^\circ$) shows two different behaviors when the meniscus approaches equilibrium (Figure 1). The PDMS5 and 75/25 liquids show a slope of -1 (in agreement with MKT), whereas the others present a slope of -0.5 (in agreement with HD). The results indicate MKT and HD regimes exist during the spontaneous rise phenomenon. The frictional dissipation drives the low-viscosity liquid dynamics whereas the high-viscosity liquid dynamics are dominated by viscous dissipation. Interestingly, compared to the rise of pure PDMS liquids [4], the MKT/HD transition moves to a higher viscosity regime for the 2-component liquids, even though the surface tension (pendant drop test) and equilibrium contact angles (tensiometer test) are nearly the same for the considered liquids. Interfacial segregation of shorter molecules or precursor film may be responsible for this displaced transition.

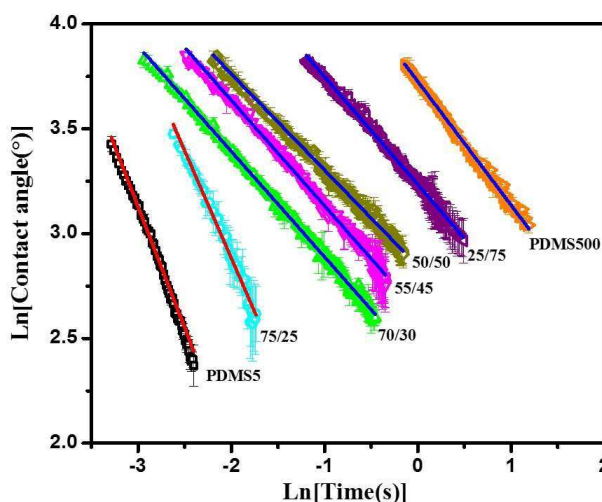


Figure 1. Contact angle relaxation ($\theta_i \leq 45^\circ$) vs. time for PDMS5, 75/25 liquid, 70/30 liquid, 55/45 liquid, 50/50 liquid, 25/75 liquid and PDMS500 on logarithmic scales. The 75/25 liquid means it contains 75 wt%PDMS5 and 25wt%PDMS500. The same naming way is applied to other liquids.

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Shear dependent network orientation in capillary suspensions

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The addition of small amounts of an immiscible secondary fluid to a suspension can dramatically change the rheological behavior of the suspension by inducing particle gelation or by reinforcing a weak network [1]. This transition is caused by strong attractive capillary force between the particles and two fluids producing a sample-spanning network. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles, and a capillary state when the bulk fluid is preferentially wetting.

These capillary suspension networks demonstrate a negative normal stress difference, from re-orientation of the flocs into the vorticity direction during shearing. Typically, systems with negative normal stress differences have either high volume concentrations ($\phi \sim 58\%$) and are shear thinning, or are shear thickening with very low particle concentrations ($\phi \sim 0.09\%$) [2-3]. In contrast, the capillary suspensions we report here have a 25% solid concentration and are shear thinning; a combination that has never before been reported in literature.

To investigate the network build-up systematically, we use strain rate sweep measurement with decreasing shear rate and report the corresponding normal stress differences. In the pendular state, the system undergoes a transition from a positive normal stress differences at the high shear rates to negative normal stress at the low shear rates. This phenomenon occurs due to the motion of particle networks, where the hydrodynamic force dominates and the flocs break-up at high shear rates. The remaining dimers and trimers tumble in the flow-gradient plane (Jeffrey orbits) and experience friction as they come into contact due to the capillary force. The network reforms and the size of the flocs grow as the shear rates decreases. The long, asymmetric flocs rotate to reorientate in the vorticity direction and this leads to a negative normal stress differences. Furthermore, we compare the rheological properties and images from confocal microscopy during shearing to gain insight into the network microstructure.

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Stimuli-responsive core-shell, hollow and Janus hybrid Nanoparticles

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The surface modification of inorganic nano-colloids with physically or chemically end-tethered polymer chains has gathered great scientific interest with a view towards new opportunities for constructing functional nanostructured materials. Advances in polymer chemistry have allowed control over the chemical composition, topology and function of the grafted polymer shell that govern the particle shape and interactions with the surrounding media, leading to complex structures and properties of the hybrid systems.

Herein, different types of hybrid nano-colloids, based on polymer chains grown from the surface of inorganic nanoparticles using surface-initiated atom transfer radical polymerization (ATRP), will be described. In the first example, multifunctional particles based on silica cores coated with pH-, temperature- and photo- responsive polymer shells will be discussed [1,2]. These core-shell particles were used for (i) the light-induced formation and disruption of responsive hollow capsules which are attractive for capture and release applications and (ii) the detection of biomolecules employing the inherent FRET behavior of the hybrid colloids (see Figure 1a). In the second part, responsive hybrid Janus nanoparticles comprising an inorganic silica core and a shell consisting of compartmentalized grafted polymer chains will be presented [3,4]. The synthesis of the nanoparticles was accomplished via a multi-step process commenced by a styrene/methanol Pickering emulsion using amine-functionalized silica nanoparticles ($D = 100$ nm) as the stabilizer, followed by the free radical polymerization of the styrene droplets to obtain silica nanoparticle stabilized polystyrene colloidosomes. Polymer chains were grown from one or both sides of initiator-modified Janus silica nanoparticles by a one- or two-step surface-initiated ATRP process. The asymmetric polymer decoration of the silica nanoparticles was verified by scanning electron microscopy, whereas the responsive aqueous solution properties of the hybrid nanoparticles were investigated by potentiometric titration, zeta-potential measurements and dynamic light scattering (see Figure 1b).

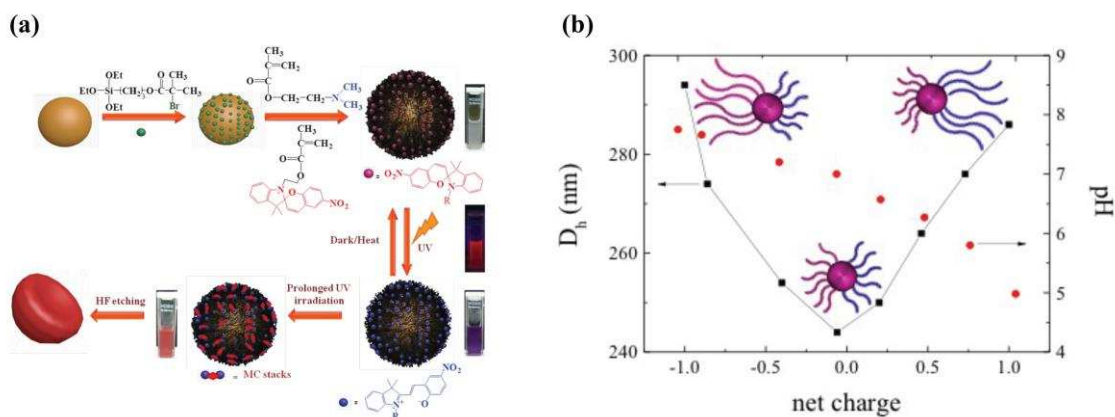


Figure 1. Synthetic procedure followed for the preparation of the pH-, temperature- and photo-responsive core-shell and hollow nanocapsules (a) and pH-responsive behavior of polyampholyte hybrid Janus nanoparticles (b).

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From surface forces and friction to local surface nanomechanical and wear properties

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Surface forces are of paramount importance for colloidal systems and for the adhesion and friction of macroscopic surfaces. In recent developments designated Atomic Force Microscopy, AFM, operational modes utilize fast collection of tip-surface force curves for extracting local surface mechanical properties, and AFM is also suitable for investigating local friction and wear. This presentation discusses these possibilities with focus on nanocomposites with applications for corrosion protection, where addition of nanoparticles strongly affects mechanical properties. Particle-polymer interactions will influence the properties of the matrix polymer next to the particle surface, providing different physicochemical properties than in the bulk matrix. To evaluate the properties of this interphase region remains a challenge. In this presentation we will discuss how different AFM methods can be utilized to probe the surface nanomechanical properties of nanocomposite surfaces, including the interphase region [1-3]. Our data demonstrate that the interphase exhibits a gradient distribution in surface nanomechanical properties, which weakly depends on the probing rate.

The presentation will also discuss local wear of an organic coating, and we will follow the development with increasing load. At low loads we find smooth friction and a smooth wear scar. As the load is increased stick-slip becomes prominent leading to formation of ripple structures in the worn area due to plastic deformation. The characteristic stick-slip length is very similar to the resulting ripple spacing as evaluated by 2D Fourier analysis. At even higher loads abrasive wear becomes dominant. Nanomechanical mapping of nanocomposite surfaces provide new insight into how the microstructure affects surface mechanical properties, including wear, which is of importance for the design and performance of such materials.

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Control over morphology and complexity of metal organic frameworks

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Control over size and shape of nano-micro objects is a pivotal point in modern colloid chemistry both for the investigation of fundamental aspects and for the material design. The synthetic tools to achieve such a control are well established for different classes of inorganic and organic materials and they have led to the enlargement of material properties and applications.

However size and shape control is still largely unexplored in the field of metal-organic frameworks (MOFs) where hitherto major efforts aimed at the design of the crystallographic structure [1]. In general MOFs produced by free modulator synthesis exhibit a non-homogeneous shape or simple polyhedral morphologies, usually reflecting the underlying geometry of the crystallographic structure. More complex synthetic routes such as interfacial synthesis, microemulsion preparation, additive dependent reactions and top-down fabrications have been mainly required for efficient and controlled process of shaping [2].

In contrast to this general trend we report on a free-modulator bottom-up approach that results in a tremendous variability of MOF morphologies as consequence of parameter variations involving just the typology of building blocks [3]. Moreover, keeping constant the typology of the building blocks and the crystallographic structures of the final MOFs, a further morphological variation can be induced through a low energy sonication of the solvent. Such a trivial treatment results in a drastic increase of the morphological complexity, leading to unique shapes not classifiable according to the conventional rules. As a remarkable example of this process, the case of prismatic MOFs is reported where solvent sonication triggers the increase of surface area through the formation of micro cavities extending through all the structure. Combining several microscopy and spectroscopy techniques, morphological and crystallographic characterization will be presented along with mechanistic insights.

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Anisotropic Superparamagnetic Supraparticles Prepared by Controlled-Evaporation of Nanoparticle Suspensions

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Superparamagnetic materials have drawn a great attention because they have numerous applications in the fields of micro-actuator, catalytic application, and drug delivery [1, 2]. However, the superparamagnetism is strongly size-dependent and only exists, in iron oxide, when the nanoparticles are smaller than 20 nm. To extend the superparamagnetic effect to micro/macro-size materials, superparamagnetic nanoparticles have to be assembled into more complex structures such as necklace-like wire [3]. These assembled materials can preserve and even improve their magnetic properties in comparison to the individual particles. Therefore, superparamagnetic materials prepared by the assembly of individual superparamagnetic nanoparticles have promising future in many applications.

Herein, we combined magnetic-guided assembly and solvent-evaporation assembly to arrange nanoparticles into various micron-size supraparticles with various architectures. These assembled supraparticles were prepared by the evaporation of an aqueous suspension of magnetic nanocolloids on a soot-templated superamphiphobic surface [4] in presence of an external magnetic field. The resulting supraparticles preserved the superparamagnetism of the original nanocolloids. Furthermore, the anisotropic shapes of fabricated particles can be tailored by controlling the evaporation process and magnetic field. We envision that such anisotropic materials with superparamagnetism can be used for the preparation of the next generation of actuators in a near future.

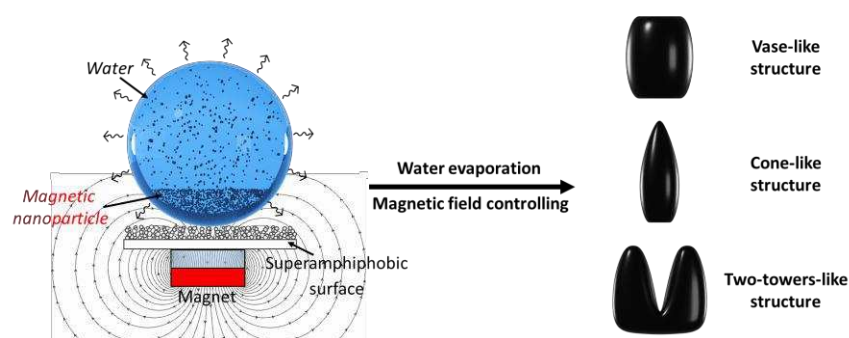


Figure 1. Scheme of fabricating macroscopic particles with mesoporous substructures, called supraparticles, by evaporating magnetic nanoparticles dispersion drop on a superamphiphobic surface. By controlling the drying process and magnetic field, supraparticles form different interested shapes in micron size.

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Optimization of method of synthesis of nickel nanoparticles with silver nanoshell for conductive materials

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Currently, most conductive materials for fabrication of electronic devices are based on silver nanoparticles (NPs), because of their high conductivity and oxidation stability. However, large-scale production of such devices requires low-cost inks or pastes. One of the suitable metals, which can be used as replacement of silver is nickel, due to its much lower cost and good electrical conductivity. However, Ni NPs are easily oxidized in air, resulting in poor conductivity. As a suitable option to overcome the high cost of Ag and to prevent the spontaneous oxidation of nickel, Ni-Ag core-shell nanoparticles can be synthesized. Several methods of synthesis of bimetallic nanoparticles have been proposed in recent years, nevertheless, the search for the technique of formation of low-cost, stable against aggregation and oxidation NPs, is still required.

In our research, Ni-Ag core-shell NPs were synthesized by using two methods. In the first, the three-step process of synthesis was used: (1) formation of a dispersion of Ni nanoparticles; (2) removing an excess of reducing agent; and (3) transmetalation (galvanic displacement) reaction, where surface of Ni NPs acted as reducing agent of silver ions. The Ni NPs were synthesized by the “wet” chemical method, i.e., by the reduction of metal ions by a proper reducing agent. Their properties (size, shape, degree of aggregation) were optimized by using various stabilizers as well as reducing agents. The Ni NPs with optimal size (~50 nm, Fig. 1A) were obtained when polyacrylic acid sodium salt and sodium borohydride were used as stabilizer and reducing agent, respectively. To remove the excess of reducing agent, the dispersion of Ni NPs was centrifuged and washed several time with deoxygenated water. After washing steps, the transmetalation reaction was performed by addition of silver nitrate, as the precursor of silver shell, to the dispersion of Ni NPs. In the second method of fabrication of Ni-Ag core-shell NPs, nickel NPs were first synthesized in the presence of excess of nickel ions and insufficiency of reducing agent to avoid the process of washing of nanoparticles. After that, the silver shell were formed by addition of silver ions. In this method the nanoparticles with the size of ~200 nm were obtained (Fig. 1B). The structure of Ni as well as Ni-Ag core-shell NPs were analyzed by UV-VIS spectra, X-ray Photoelectron Spectroscopy (XPS) and SEM analysis.

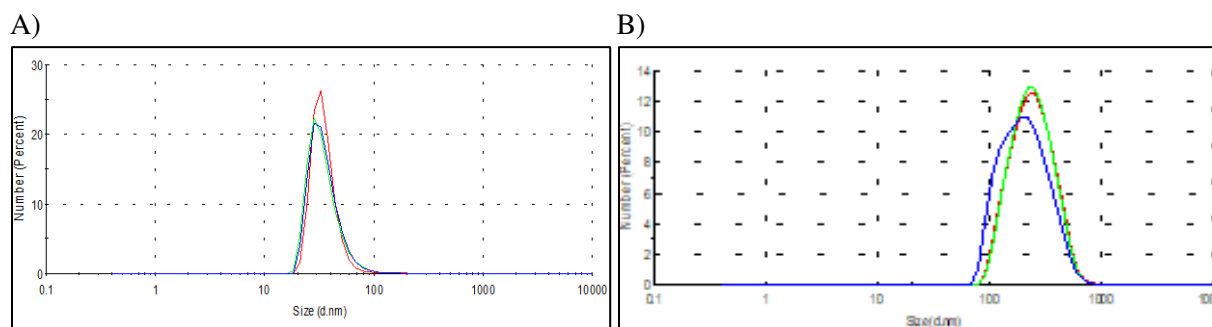


Figure 1. Size distribution of Ni-Ag NPs: first (A) and second (B) method of synthesis.

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cRAFTing nanomaterials: tailored structural and dynamic properties of hierarchical nanoparticle arrangements by controlling polymeric Architecture

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Because polymers from controlled radical RAFT polymerization inherently contain anchor moieties for the attachment to gold surfaces [1], they can be directly used as macromolecular ligand for gold nanoparticle modification. If these polymers are specially designed in addition, it is also possible to guide the formation of complex nanocomposites: Hierarchical arrangements of gold nanoparticles can be created and their internal structure can be manipulated in a directed manner by controlling the macromolecular architecture of the polymeric key components. We recently demonstrated the assembly of two types of gold nanoparticles into planet–satellite-type arrangement structures by RAFT star polymers [2]. Here, the well-defined macromolecular particle linker allows tight control of particle spacing in colloidal dispersion and after casting on surfaces [2,3].

This presentation will report a strategy for equipping these higher-order particle arrangements with stimulus-responsive properties [4]. This becomes possible using star block copolymers which—by virtue of their block structure—provide at the same time colloidal stability and responsive properties. The incorporation of responsive entities allows a reversible contraction and expansion of planet–satellite particle distances, as revealed by small-angle X-ray scattering.

Approaches toward anisotropic particle arrangements and their structural characterization will also be presented [5]. Using scanning transmission electron microscopy and electron energy-loss spectroscopy, we could show that phase separation of mixed binary polymer brushes on gold nanoparticles can lead to isolated polymer patches on the particle surface, i.e. Janus-type hybrid nanoparticles. If such polymer patch provides additional binding sites, site-selective attachment of satellite particles becomes possible, as depicted in Figure 1.

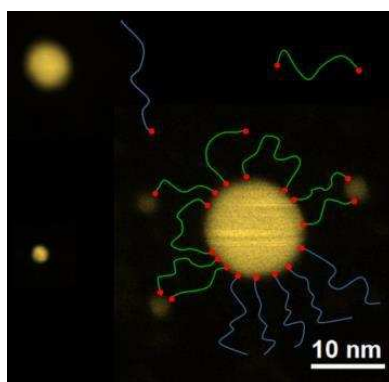


Figure 1. A schematic representation of phase separated mixed binary polymer brushes on gold nanoparticles and the selective functionalization of isolated polymer patches.

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Multifunctional mesoporous gadolinium-enriched TiO₂ microspheres can be simultaneously used for cancer diagnosis and treatment

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Gadolinium-enriched TiO₂ microspheres (beads) possess controlled multifunctional properties. Mesoporous semiconductor TiO₂ microspheres were enriched with gadolinium to improve their photoluminescence functionality and to make them applicable in optical and magnetic resonance imaging (MRI) due to improved spin relaxation for MRI. Additional applicability stems from the enhanced generation of reactive oxygen species (ROS) under UV-A light irradiation. Gadolinium-enriched microspheres were integrated into MG-63 osteosarcoma cell lines, which means they are biocompatible. The principal advantage of the use of gadolinium-doped TiO₂ microspheres is the possibility of their simultaneous use for cancer diagnosis (MRI) and treatment (ROS production upon UV irradiation). Namely, doped TiO₂ microspheres can be simultaneously used both for locating cancer cells (i.e. diagnostics via MRI) as well as for killing cells (i.e. therapy), which is the result of the formation of ROS when TiO₂ microspheres in cancer tissue are exposed to UV light [1]. The essential concept here is that cancer cells and normal cells have different dynamics of accepting TiO₂ microspheres. Cancer cells accept them faster (more) than healthy cells, which is fatal for cancer cells once exposed to UV-A light [1].

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Design of microscopic polymer materials by droplet microfluidics and additive manufacturing for cell-free biotechnology

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The structural diversity of natural and synthetic macromolecular building blocks allows for designing polymer materials with tailored size, shape, porosity, degradability, stimuli-sensitivity and stiffness [1], which have thus evolved as promising experimental platform in cell biology and cell-free biotechnology [2,3]. However, to process macromolecular building blocks into well-defined polymer materials with feature sizes from 1 to 100 μm , and spatial control over physicochemical / mechanical properties on the same length scale requires innovative fabrication strategies.

On this account, we utilize two methods: droplet microfluidics to fabricate polymer microgels swollen in water, and 3D printing based on micro-stereolithography (μSL) to fabricate polymer materials with micron- scale precision in bulk. Focusing on applications in cell-free biotechnology, we combine these methods to design experimental platforms for understanding and optimizing enzymatic cascade reactions in an artificial environment that still reflects key aspects of cellular life (e.g. diffusivity and spatiotemporal organization of reaction partners) [4]. For that, we immobilize enzymes in cell-sized microgels, whose polymer matrix is optimized regarding porosity and hydrophobicity to preserve enzyme conformation and activity. By loading these microgels into 3D-printed microbioreactors, we manipulate experimental conditions with spatiotemporal control within microseconds and micrometers, respectively (Figure 1).

The combination of μSL and polymer material design by droplet microfluidics provides the means to control biochemical reactions in a tailored microenvironment with reduced energy consumption and undesired side reactions towards tailored pharmacologically and technically relevant proteins and enzymes.

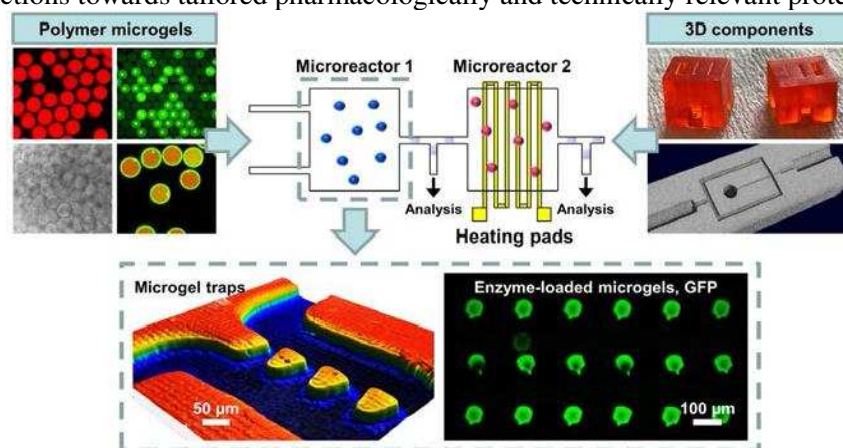


Figure 1. Microgels with tailored physicochemical / mechanical properties in 3D-printed microbioreactors.

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Liquid repellent surface mediated fabrication of superparticles

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Superparticles, which assemble colloidal particles into macroscopic structure, have attracted great interests due to their potential applications [1-2], such as catalysis, microfluidics, sensing, etc. To date, most of the superparticle fabrication methods occur in solution, such as template-based, kinetics-controlled, and thermodynamics-controlled growth [3]. In spite of being suitable for large-scale production, these approaches depend on chemicals, especially for size and composition engineering, which are unfavourable for environmental protection and energy consumption reduction. Therefore, developing new approaches to reduce or completely avoid the use of solvent, emulsifier or template is desirable. Recently, dry self-assembly has been introduced as a possible strategy for fabrication of superparticles, where superparticles are prepared by evaporation of sessile droplets containing colloidal particles on superhydrophobic surfaces [4-5]. However, one limitation of using such superhydrophobic surface is restriction to electrolyte solutions. Non-polar liquids or surfactant solutions will not remain in the Cassie state, and impale into the structures.

Superamphiphobic surfaces have become a better choice for superparticle fabrication, since they repel not only water but also nonpolar liquids, surfactant or protein solutions. Droplets on this kind of surfaces have high contact angle ($CA > 150^\circ$) and roll-off easily (tilting angle $< 10^\circ$) [6-8]. Herein, we prepared TiO_2 superparticles with hierarchical porosity by firstly constructing TiO_2 -PS binary superparticles on superamphiphobic surfaces, and then removing the PS phase by calcination. The obtained TiO_2 superparticles perform exhibit spherical morphology with the sizes easily controlled by regulating the concentration and droplet volume of mixed particle dispersions. The porosity of hierarchical porous superparticle is related to the volumetric ratio of TiO_2 to PS, and the size of macropores can be controlled by changing the size of PS particles. The hierarchical porous structures formed in the TiO_2 superparticles will be beneficial for potential applications in photocatalysis, sensing, separation, etc. Our approach for superparticle preparation not only avoids the expensive purification of a continuous aqueous phase, migration and ageing effects resulted from slow phase separation between particles and stabilizers, but also facilitates producing supraparticles with various sizes, compositions, and architectures by simple alternations without consuming chemicals and energy.

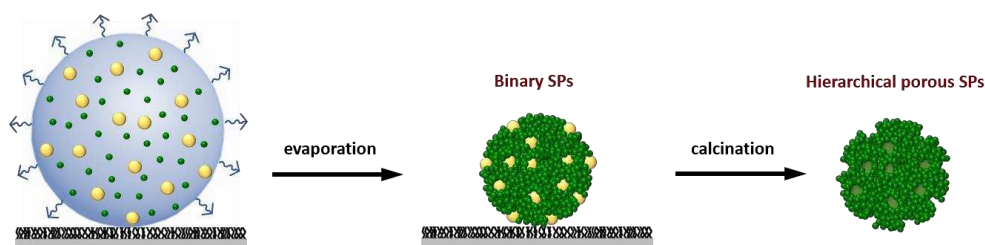


Figure 1. Schematic illustration of superparticle fabrication on superamphiphobic surface.

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Bio-inspired functional polyphenolic materials: meso- and nanoscopic determinants of the antioxidant activity

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With their distinctive carbogenic diversity and the tunable redox behaviour, natural phenolic compounds provide a unique reservoir of versatile, bioaccessible, biocompatible and biodegradable antioxidant systems for control and prevention of oxidative stress and unwanted aerobic degradation processes in biomedicine, food and materials science.

In this contribution, we investigate the electronic structure, mesoscopic organization and antioxidant activity of ten phenolic polymers biocatalytically produced from natural monomers, such as catechol, pyrogallol, resorcinol as well as gallic and p-coumaric acid. In all cases a black/dark brown and insoluble pigment is obtained, presenting broad-band UV/Vis absorption and a distinct electron paramagnetic resonance (EPR) signal. The last is due to free radicals associated with non-localized π system, stabilized by resonance in the polyaromatic centers. A deep analysis of the spectroscopic results shows a further stabilizing contribution to arise from supramolecular stacking, indicating that the mesoscopic arrangement of the polymers drives the electronic features of the pigment.

The antioxidant properties of polyphenol-based nanostructured materials were determined using four different assays. Polymers from gallic acid, pyrogallol and catechol displayed the highest activity in all assays. A clear correlation between the electron donor properties and the spectroscopic UV/Vis and EPR results was observed and interpreted [3].

In conclusion our study demonstrate that the antioxidant activity of polyphenols is intrinsically defined by the degree of electronic delocalization across the planar aromatic molecules as well as by their supramolecular organization. Since these properties can be finely tuned by an appropriate choice of the starting building block, our study paves the way to the molecular design of effective antioxidant materials based on this class of bioinspired polymers.

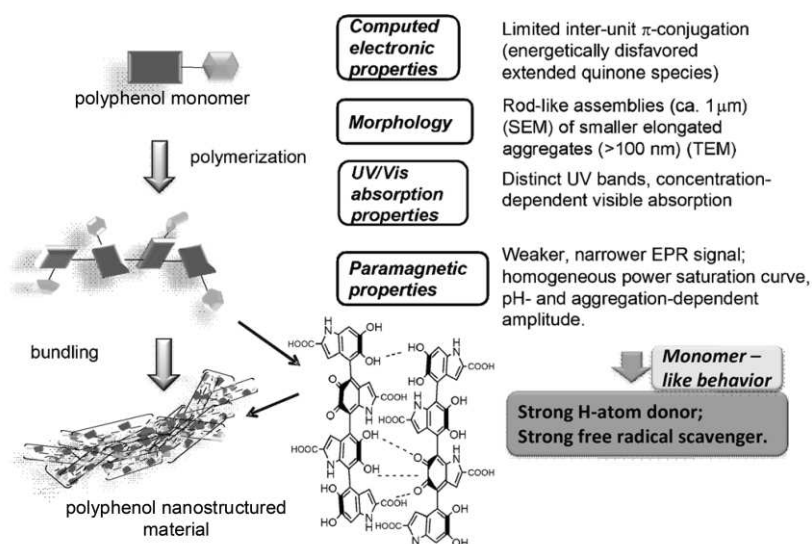


Figure 1. Example of function-structure relationship for the pigment from polyphenols.

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Curl it up: structure-directing polyelectrolytes aid the formation of polymer/mineral composite micro scrolls

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The Living organisms have developed elaborate mechanisms to construct intricately structured mineral architectures optimized at several hierarchical levels down to the molecular scale (e.g. bone, sea shells, siliceous sponge skeletons) and can exert an astonishing degree of control over the size, shape, texture and even polymorph of minerals. While Nature's dexterity in using organic matrices to generate bio-inorganic hybrid materials with internal interfaces on the nanometer level and a high degree of structural organization remains unmatched in synthetic systems, substantial progress has been made over the last years in translating some key concepts of biological mineralization into artificial materials. The implementation of such design principles holds enormous potential for the development of low-temperature routes to functional materials.

Our here presented research explores a bio-inspired approach, in which a cobalt(II) hydroxide carbonate precursor is precipitated in the presence of a range of contrasting synthetic water-soluble polymers, where the latter act as a mimic of the soluble structure-directing matrix associated with biological mineralization processes. Calcination leads to a pseudomorphic transformation of the precursors into the functional cobalt(II,III) oxide phase. Spinel-type Co_3O_4 finds applications in a wide range of technological fields, including gas sensing and clean energy conversion, where nanostructured Co_3O_4 may provide a cost-efficient alternative to Pt- and Ir-based catalysts for electrocatalytic water-splitting.

We demonstrate that extended mineral sheets with μm -thickness can be formed at the air-solution interface when precipitation occurs under slow diffusion conditions at room temperature [1]. Intriguingly, the film fragments isolated after drying characteristically show bent and even curled morphologies. In the presence of polymer additives this effect is substantially more pronounced such that micro scrolls composed of a polymer/mineral hybrid material are obtained. This remarkable observation motivated us to systematically investigate the film formation and curling behavior of basic cobalt carbonates precipitated via ammonium carbonate diffusion depending on the functionalization and concentration of the polymer additive as well as the interface geometry provided by the reaction container. The nanostructure of the scrolls is studied by small-angle-x-ray scattering complemented by electron microscopy with the aim to elucidate the structural prerequisites for a mineral to accommodate such a high degree of bending.

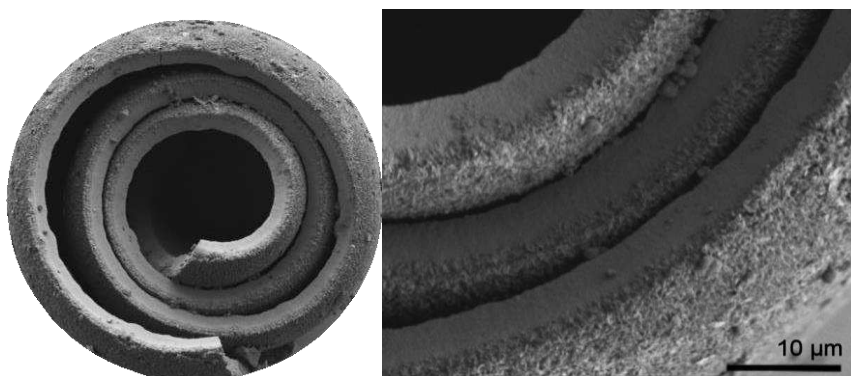


Figure 1. Strain-induced curling in mineral films with gradient structures induces micro scroll formation.

Acknowledgements: The German Research Foundation (DFG) is acknowledged for financial support *via* SFB 840.

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Controlled crystallisation using microemulsions

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Nanoquartz of varying size and perfection is required for toxicology studies aimed at understanding the role of silica in the lung disease silicosis. However, the crystallisation of α -quartz requires harsh conditions of 200-300 °C and 15-100 bar [1-2], where high growth rates prevent the selective formation of nm-sized quartz. We have shown that, remarkably, 2 nm-sized nanoquartz can be produced from microemulsions under ambient conditions (Figure 1.). This is the first non-biological reporting of quartz nucleation under such conditions. The 2 nm particles are then used to seed controlled hydrothermal syntheses of 5 nm nanoquartz particles under mild conditions of 175 °C and autogenic pressure. Accordingly, nanoquartz of varying size and degree of perfection is obtained exclusively for the first time. Furthermore, the nanoparticles affected the rate of formation of a β -enaminone, with an unexpected strong inhibition observed for the more structurally-perfect nanoquartz. A similar microemulsion-hydrothermal synthesis route may provide significant benefits in optimising industrial heterogeneous catalysts.

Ostwald's rules of stages states that metastable polymorphs crystallise initially before transforming into their stable forms [3]. This is because crystallisation is typically under kinetic control, highlighted by the infamous Ritonavir HIV drug which cost the pharmaceutical industry several hundred million dollars [4]. Our microemulsion-route provides a generic method to "leap frog" this usual polymorphic pathway by confining supersaturated solutions of the crystals' constitute molecules in microemulsion droplets. A crystal nucleus can only grow in an isolated microemulsion droplet to a limited extent before it depletes the supersaturation of the surrounding solution; this is signified by a minima occurring in the free energy curve at nm-sizes when the crystal nucleus in the droplet is surrounded by saturated solution (Figure 2.). Further growth occurs when this nucleus-containing droplet collides with a nucleus-free droplet and forms a transient dimer, thus allowing the nucleus to gain access to more growth material. If there is no pre-existing nucleus present when the transient dimer forms, crystallisation cannot proceed. Consequently, the ability to form a (near) stable crystal nucleus becomes the determining factor governing whether crystallisation occurs and hence thermodynamic control can be achieved. Several organic crystal systems (where under the same conditions metastable polymorphs form in bulk solution) will be discussed to demonstrate the generality of this approach, providing a crucial method that could be adopted in the pharma screening process of drugs.

The successful formation of nanoquartz highlights that our microemulsion methodology can be readily extended to inorganic materials with giant covalent structures. Furthermore, crystallisation of nanographite has also been achieved under ambient conditions using precursors that normally produce amorphous carbonaceous products.

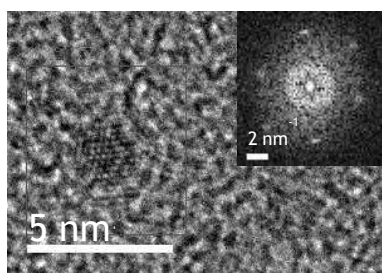


Figure 1. TEM micrograph of a 2 nm nanoquartz particle

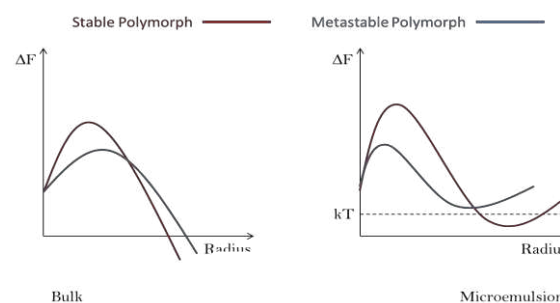


Figure 2. Free energy curves for crystallization in the bulk vs.in a microemulsion

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Hollow rods of high aspect ratio

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Rod-shaped particles are ideal anisotropic systems for studying the isotropic-nematic-smectic phase transitions. Micron-sized silica rods have been extensively employed as model particles in the investigation of such colloidal phase transitions, because of their facile synthesis [1] which also enables their labelling with fluorescent dyes [2] and the ability to visualize them using an optical microscope. However, one of the main drawbacks of these particles is their high density ($d \sim 2$ g/mL) which leads to the fast sedimentation of the colloids in common solvents such as ethanol, water, etc and renders the density matching of the system very challenging.

In this work, we describe the synthesis of core-shell rods, using a template-assisted hydrolysis-condensation method [3,4] or surface-initiated atom transfer radical polymerization [5] to grow a titanium dioxide or polymer shell onto silica rod particles. The challenge of the synthetic approach was to obtain individually coated rods, without any particle aggregation or side-nucleation. The importance of the surface properties for the successful coating of the particles was highlighted, and key parameters controlling the coating thickness were identified.

Next, the silica core was etched with a concentrated aqueous sodium hydroxide or hydrofluoric acid solution, to afford hollow titanium dioxide or polymer rod particles. The hollow rods were characterized using electron microscopy (see Figure 1) and spectroscopic techniques. The synthetic protocols were optimized to yield robust rod particles, and their characteristics, such as shell thickness, crystallinity, etc, were determined.

The hollow rod particles prepared by this method have a significantly lower density compared to their silica precursors, and therefore are advantageous for studying the liquid crystalline phase behaviour.

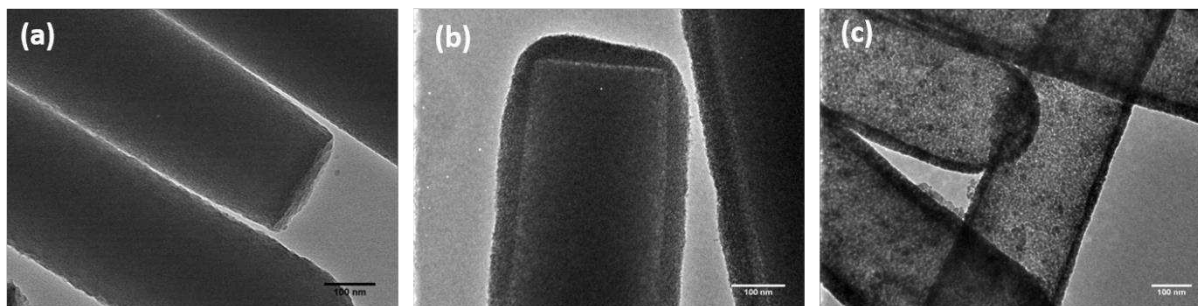


Figure 1. Silica rods (a), core-shell SiO₂-TiO₂ rod particles (b) and hollow TiO₂ shells (c).

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Self-assembly of nanoscale structures in deep eutectic solvents

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Deep Eutectic Solvents (DES) are a relatively new class of alternative solvents, formed by the complexation of various salts and H-bonding compounds to make a stable, room-temperature, partially-ionic liquid [1]. DES are rapidly gathering interest because of their potentially low environmental impact and tuneable nature. Accordingly, they can function as greener drop-in replacements for conventional solvents which offer enhanced functionality.

Our recent work has focused on the study of DES as neoteric green media for rationally-designed syntheses of nanostructured metal oxides with improved characteristics. We observed that modifying the physical properties of the DES choline chloride-urea, by introducing water as a co-solvent, allowed the morphology of the nanoparticles to be chosen. This allowed us to selectively produce 1D CeO₂ nanowires, highly active for the oxidation of CO to CO₂ for automobile emissions control purposes [2]. Atomistic modelling and neutron diffraction studies revealed the presence of potentially significant nanoscale structuring between the reactants and the DES. We have also developed a similar, simple DES-based methodology to produce haematite (α -Fe₂O₃) nanoparticles [3]. Tuning the hydration state of the solvent allowed for control over size and morphology, offering the opportunity to fabricate superparamagnetic nanoparticles for MRI, or photoanodes for the solar splitting of water to hydrogen, all in an environmentally-friendly manner.

While these developments demonstrate the potential offered by DES in the designer self-assembly of technologically-relevant materials, they also highlight our gaps in understanding of the fundamental self-assembly mechanics that are occurring. We therefore present here a total study of the kinetics of formation of iron oxide nanoparticles in a choline chloride-urea DES, using a variety of advanced multiscale time-resolved techniques to give a complete picture of the system, from beginning to end. Atomistic modelling of wide q -range neutron diffraction data reveals the initial structure of the solvated iron salt and the DES solvent structure itself, while time-resolved EXAFS measurements show the evolution of these solvated iron complexes and the initial steps in self-assembly that yield a colloidal phase of nanoparticles-in-DES. Finally, kinetic small-angle neutron scattering and total scattering measurements (Figure 1) show the evolution in size and shape of the produced nanoparticles, and how the concentration of iron and water affects these variables. Combined, the complementary characterisation shows the versatility of the novel DES-based synthesis methodology, which could not be determined with any single experimental technique.

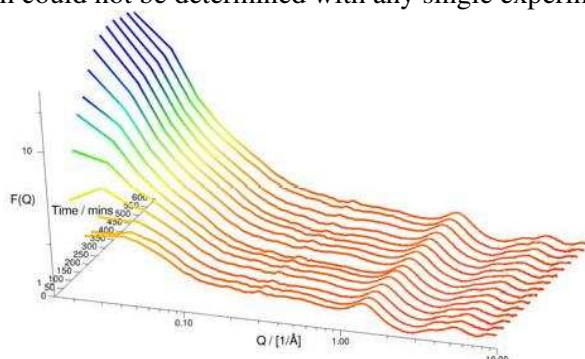


Figure 1. Time-resolved neutron total scattering measurement of iron oxide nanoparticle formation in DES; nanoparticle formation is seen as the growth in the low- q region.

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DNA-polyelectrolyte multilayers: Preparation and Sensing Applications

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Layer-by-layer (LbL) adsorption of polyelectrolyte multilayer (PM) presents a convenient general technique for surface functionalization. DNA adsorbed on PM by this method is functionally active: it is able to bind the complementary strand [1]. However, short oligo-DNAs present in solution, impeded the use of the technique in biosensing applications [2]. Here we show that the problem of interface stability could be circumvented by cross-linking of the PM-oligo interface and demonstrate the application of the method to study the organization of the immobilized DNA-duplex and specific DNA binding using localized surface plasmon resonance (LSPR) spectroscopy [3].

Surface functionalization included LbL adsorption of 3-5 layers of polyallylamine hydrochloride (PAH) and sodium polystyrene sulphonate (PSS) on substrates (glass, Au, and Ag nanoparticles (NPs) films) following adsorption of amine-terminated 23-base oligo-DNA. Stabilization of the system was achieved using covalent coupling of oligo-DNA and cross-linking with glutaraldehyde following the reduction with sodium cyanoborohydride. Oligo's used in experiments were labeled with Cy5 and WellReD D2 fluorophores allowing direct quantification of both surface coverage and hybridization yield and monitoring hybridization/release from the surface.

DNA probes immobilized on PM showed high (up to 10^{13} molecules/cm²) surface coverage and close to 100% hybridization yield. The amount of immobilized oligo-DNA after cross-linking practically did not change during multiple cycles of washing, drying, heating and cooling. Immobilized dsDNA and sequentially formed of complementary oligo's (Figure 1A) showed identical melting profile implying formation of double helix structure in both cases.

In experiments with Au NP and Ag NP films preparation of the interface and binding of analyte DNA was followed by LSPR spectroscopy. LSPR spectroscopy showed that both Au NP and Ag NP transducers are sensitive to binding of complementary strands (Figure 1B, C). The use of fluorophore-labeled oligo-DNA allowed evaluation of the coverage-dependent optical response of LSPR transducer. Control experiments with unrelated oligo as analyte show that stabilized DNA/PM interface rejects non-specific binding making it an attractive alternative in sensing applications.

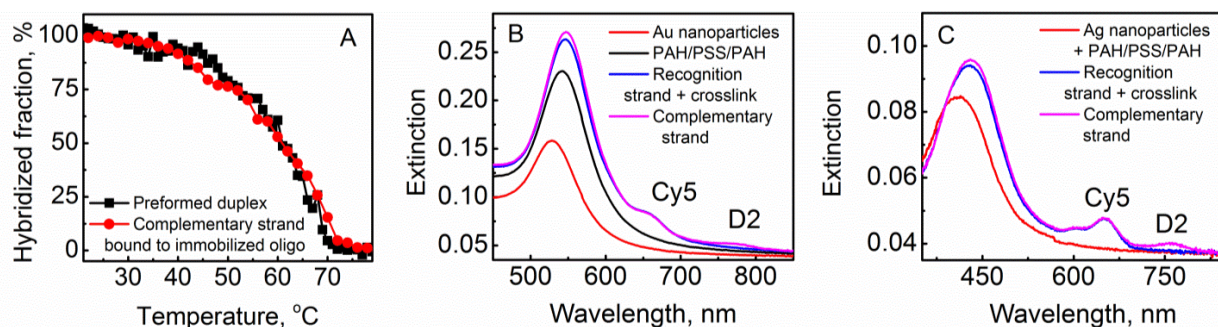


Figure 1. Denaturation of the DNA complexes immobilized on (PAH/PSS)₂PAH multilayer on glass (A), UV-Vis spectra of Au NP (B) and Ag NP (C) LSPR transducers during immobilization and cross-linking of the oligo-DNA labeled with Cy5 and binding of complementary oligo labeled with WellRED D2.

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*This work is dedicated to the memory of Prof. I. Rubinstein.

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Synthesis of nanostructured TiO₂ microparticles for photocatalysis

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TiO₂ is a versatile material that has been extensively researched for over three decades. It is widely used in a variety of applications and products in the energy storage/conversion and environmental purification including air and water purification systems, sterilization, photoelectrochemical conversion and water splitting. Because of its good chemical and thermal stability, easy synthesis biocompatibility as well as physical, optical, and electrical properties, nanostructured TiO₂ is of special interest as a photocatalyst or catalytic support material. When used as a photocatalyst the best results are obtained if the particles are suspended in a solution.

However, an additional step is then required to separate the particles from the solution after the reaction takes place. One of the important parameters for photocatalysts is their specific surface area. In order to increase it the particle size is usually decreased, with the most active TiO₂ photocatalysts having particle sizes in the range from 10 to 30 nm. Since filtration of nanoparticles is difficult and expensive, larger particles with a morphology that promotes a high specific surface area are desirable.

In this work we present a simple method to prepare nanostructured TiO₂ particles that could be of potential interest as photocatalysts or catalytic support. Even though the particle size is in the range of 2-5 μm the nanostructures that make up the particles ensure a large specific surface area with values above 300 m²/g. The powders were prepared from different titanium precursors using a hydrothermal method in a highly alkaline solution. Different morphologies can be prepared by adjusting the reaction parameters ranging from flower-like to highly compacted nanowires. The morphology of the prepared samples is stable and does not change after calcination at higher temperatures. The short reaction times, scalability and high concentrations of titanium in the reaction solution also allow for production of larger quantities of the powders.

The surface morphology of the prepared TiO₂ powders was examined using scanning electron microscopy (SEM) - Figure 1. To further characterize the samples, specific surface area for different morphologies was measured and the photocatalytic activity of the prepared powders was tested by degrading a model azo-dye pollutant under UV irradiation.

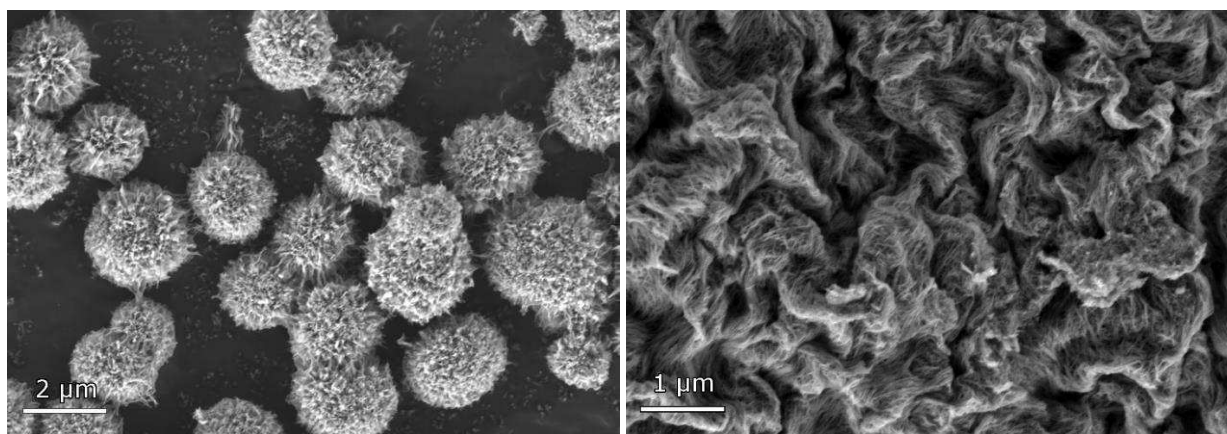


Figure 1. SEM images of the prepared TiO₂ nanostructured flower-like particles (left) and highly compacted nanowires (right).

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Active biohybrid coatings based on enzyme-loaded halloysite nanotubes

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Enzymes are frequently used as biocatalysts in various fields such as for biomedical treatment and chemical manufacturing [1,2]. However, native enzymes suffer from an often-limited recyclability and from their high sensitivity to the environment and operating conditions which can alter their properties. Therefore, many efforts have been made over the past decades to immobilize enzymes on or in nanocarriers, with the aim of increasing their lifespan by preventing their denaturation or to broaden their application range.

Halloysite nanotubes (HNTs) are natural nanotubular clays possessing a positively-charged lumen and a negatively-charged outer surface, making them suitable candidates for selective enzyme immobilization. However, the stability of HNT dispersions is limited as the particles aggregate rapidly and sediment [3,4].

Here, we investigate the use of HNTs as nanocarriers for enzyme encapsulation (Figure 1a). β -lactamase enzymes of different structure and molar mass (BlaP and L1) were chosen as model enzymes for the functionalization of the HNT lumen, while the properties of the outer surface of the HNTs were tuned by polyelectrolyte adsorption. Prior to their use, the HNT underwent an alkaline treatment to increase their stability in aqueous suspension and decrease their polydispersity. Then they were loaded with the enzyme (Figure 1b) and surface modified with polyelectrolyte layers. Depending on the applied polyelectrolyte dose, charge neutralization (aggregating system) or overcharging (stable dispersion) of the nanomaterial was observed. The enzymatic activity of the hybrid nanomaterial with and without a poly(ethyleneimine) coating was determined and compared to the one of the native enzyme, indicating efficient preservation of the activity. The enzyme-functionalized HNTs were then used as building blocks for the fabrication of coatings on model substrates, in association with a series of water-dispersible polymers; the enzymatic activity of the resulting films will be discussed depending on the composition of the film.

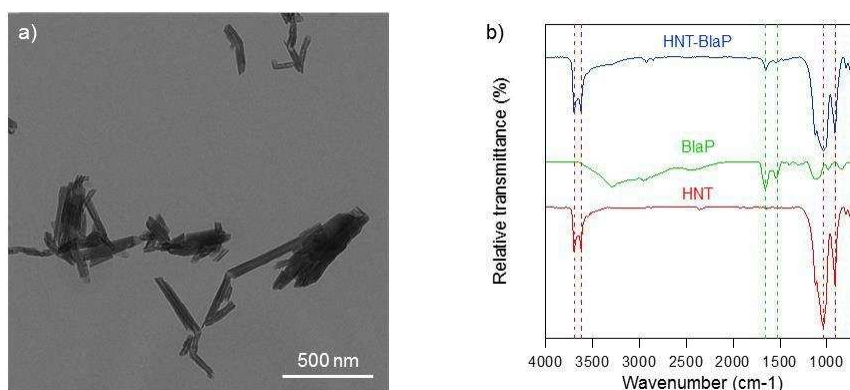


Figure 1. (a) Transmission electron micrograph of BlaP-functionalized HNTs and (b) InfraRed spectra of bare HNT, native BlaP and h-HNT loaded with BlaP (HNT-BlaP).

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Active nanocomposite with liquid inclusions of responsive colloids

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Nanocomposites exploit the properties of inorganic nanoparticles embedded in a matrix (usually a polymer) to enhanced optical responses, improve mechanical properties, or increase thermal stability [1-3], for example. Small particle concentrations are often sufficient for strong effects. Current research in the field of nanocomposites goes towards the control of the arrangement of particles inside the matrix [4]. Up to now, the arrangements of coupled nanoparticles embedded in nanocomposites are static, with no or minimal mobility of the particles in the cross-linked polymer matrix.

Previous work has shown how liquid nanoparticles dispersions can reversibly agglomerate after different stimuli (temperature, ion concentration, electric field strength, etc.) producing macroscopic changes in colour, reflectivity, and scattering due to plasmonic interactions between densely packed nanoparticles [5]. We have created active nanocomposites by combining the emulsion processing of nanoparticles with composite preparation to create a polymer matrix with liquid inclusions that contain particles dispersions. The liquid droplets provide mobility, drastically reduce the time required for switching between the different states, and increase the dynamic range of the switchable property. Remaining challenges include the long-term stability of the materials.

We present a hydrogel matrix with encapsulated oil droplets containing alkylthiol-coated gold particles that react to temperature changes by reversible agglomeration. *In-situ* small angle x-ray scattering during repetitive cycling between high and low temperatures was used to confirm that gold nanoparticles go from a fully dispersed to an agglomerated state in a fully reversible process. UV-vis spectrometry indicates that the change of the scattering of the nanoparticles is responsible for the transition of macroscopic properties such as color and haze.

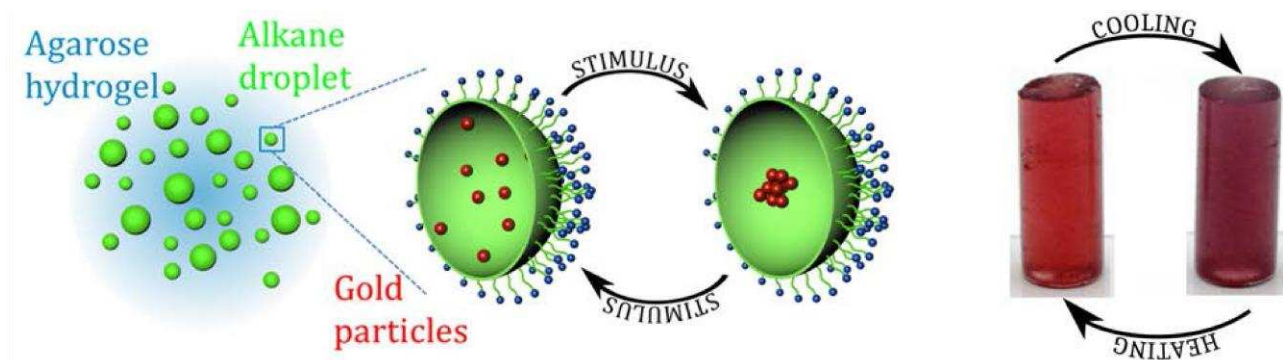


Figure 1. Schematic model (left) and real picture (right) of the nanocomposite showing the nanoscale and macroscopic differences between the two states of aggregation.

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Nitrogen-Rich Hierarchically Porous Polyaniline-Based Adsorbents for CO₂ Capture

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The heavy reliance on fossil fuels for our energy needs and its resultant high CO₂ emissions into the atmosphere has raised global concerns because of the implication of CO₂ in climate change and global warming. CO₂ capture from high emission sources is the immediate solution to reduce CO₂ emissions while searching for alternative sustainable energy sources. Unfortunately, till date, post-combustion CO₂ capture has not been deployed on a large scale due to corrosion problems and the high regeneration costs associated with the most mature amine absorption technology. There is therefore an urgent need to develop new materials and technologies, which can offer CO₂ capture at high efficiency, low costs and minimal environmental impacts.

We developed hierarchically porous nitrogen-rich carbon materials using a simple approach (Figure 1) and their application to CO₂ capture has been studied. The hierarchical porosity was obtained by the polymerization of aniline in the presence of the PS NPs resulting in 3-D frameworks with inter-particle mesopores. Subsequent chemical activation of the materials resulted in the creation of intra-particle micropores with significant increase in the surface areas and pore volumes, while also retaining high nitrogen contents.

The resulting materials were characterized by thermal gravimetric analysis, N₂ sorption, Hg porosimetry, FTIR and SEM. High porosities of up to 87% and surface areas up to 3244 m²/g were realized. Thermal gravimetric analysis (TGA) confirmed a very high thermal stability of the prepared 3-D microclusters up to 450 °C. High resolution XPS revealed the most important nitrogen functionalities are the amine and pyrrolic which were highest in the best performing materials. The high CO₂ adsorption capacities of up to 9.14 mmol g⁻¹ measured at 273 K and 1 bar are among the highest values reported for carbon-based materials. These values are also higher than that of similar materials without hierarchical pore structure. These properties demonstrate the potential for applying these materials in large scale, low cost post-combustion CO₂ capture.

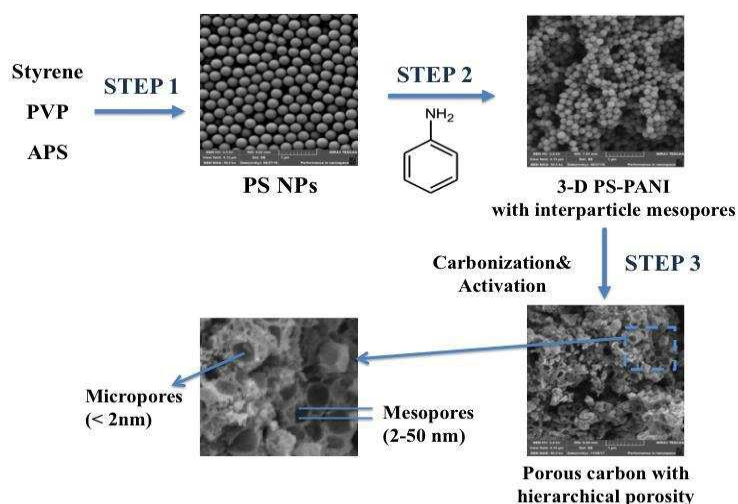


Figure 1. Procedure for the preparation of hierarchically porous nitrogen-rich sorbents for CO₂ capture

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Surface chemical patch formation and self-assembly investigated at the single-particle level

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Patchy nanoparticles offer the possibility for the spatial control of colloidal interactions and hence can enable the preparation of engineered bottom-up particle assemblies. Patch formation generally requires breaking of the homogeneous ligand shells that cover the nanoparticles. Careful ligand exchange might enable such surface chemical patch formation, whereby some inherent minor differences in the compactness or binding strength of the original ligands between certain regions of the particle surface get amplified.

We exploit the less compact nature of the initial CTAB ligand shell in the tip regions of gold nanorods prepared by seeded growth to site selectively modify the tips with cysteamine and to subsequently coat the side of the rods with (Figure 1.a). By monitoring the ensemble longitudinal plasmon resonance wavelength and electrophoretic mobility changes upon cysteamine addition, the concentration range for the tip-selective CTAB removal can be identified (Figure 1.b). Correlative peak-force AFM and optical scattering spectroscopy measurements have been performed on individual nanoparticles, characterizing exactly the same objects with the two different techniques. The AFM measurements have shown that for patchy particles prepared at near the saturation concentration of the tip region (10^{-2} mM) display well-defined structural inhomogeneity (Figure 1.c), which is not detected for significantly lower (10^{-3} mM) cysteamine concentration or for the reference particle coated homogeneously with PEG or MTAB. The single particle optical measurements (Figure 1.d) and the optical simulations agree well with the AFM results. In this regard, these recent results directly evidence the inhomogeneous ligand distribution on gold nanoparticles [1].

The inhomogeneous ligand distribution can be exploited for the spatial control of particle assembly. When such patchy nanorods are assembled with spherical nanoparticles having homogenous surface ligand shell, different heterotrimers or heterodimers (with two or one assembling sphere) can be obtained based on the balance of the dispersion, electric double layer and steric interactions between assembling particles [2]. By detecting the particle self-assembly in water at individual nanoparticles based on single particle scattering spectroscopy in a flow-cell, and performing simulations on the colloidal interactions, the fine details of the assembly mechanism can be captured as well [3].

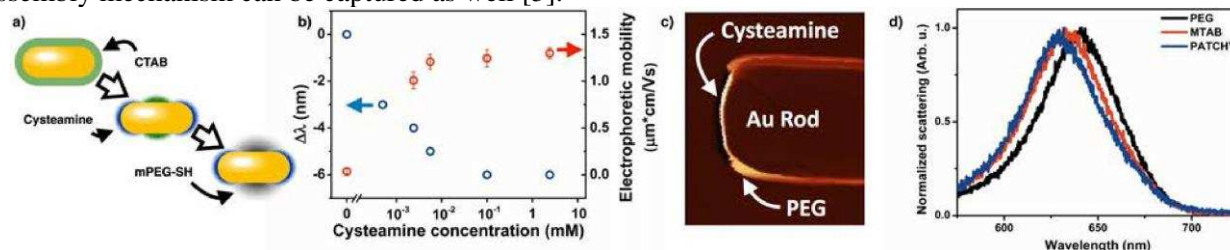


Figure 1. (a) Preparation scheme of the patchy particles by (b) fine-tuning the cysteamine concentration during the original CTAB capping ligand exchange. The well-defined surface chemical patches can be resolved in peak-force AFM images (c) and support the results of single particle dark-field scattering spectroscopy experiments (d).

Acknowledgements: The project was supported by the Hungarian Scientific Research Fund K-119532, K-112114, M-ERA.NET-WaterSafe (No. 39/2016).

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Release of spores from electrospun polyethylene oxide and chitosan/polyethylene oxide nanofibers

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Probiotics have recently been studied for the treatment of the periodontal disease since the reduction or the absence of beneficial bacteria turned out to be one of the crucial factors in pathogenesis of this disease. They suppress the growth of endogenous pathogens, prevent the infection with exogenous pathogens and additionally promote a beneficial host defense response [1,2].

With the aim to investigate the difference in release profile of potential probiotics, we incorporated the spores of the bacterial strain 25.2.M originating from oral microbiota of healthy volunteers and identified as *Bacillus* sp. in two different types of nanofibers. Polyethylene oxide (PEO) and chitosan/PEO (6/4, w/w) nanofibers were prepared by electrospinning of 4% (w/V) polymer solution with dispersed spores. The number of spores in polymer solution and nanofibers was determined by the drop plate method. To evaluate the release profile of spore-loaded nanofibers, defined amount of nanofibers was incubated in phosphate buffer (pH = 7,4) at 37°C, while shaking at 150 rpm. The number of spores released at different time points was determined by the drop plate method.

The PEO and chitosan/PEO nanofibers with spores were smooth and uniform with clearly visible spores incorporated (Figure 1). Their average diameter was approximately 200 nm and 100 nm, respectively. Comparison between theoretical number of spores in nanofibers (calculated based on number of spores in polymer solution) and experimentally determined number of spores in nanofibers (determined based on nanofiber dissolution) showed that spores were successfully incorporated in nanofibers and their viability was preserved. When exposed to aqueous medium, chitosan/PEO nanofibers released only 0.03% of spores in the first half hour and remained unchanged during next 14 days, whereas PEO nanofibers released 80% of spores in the first 30 min and all of them in the next hour. The controlled bacteria delivery can be achieved with the combination of both types of nanofibers.

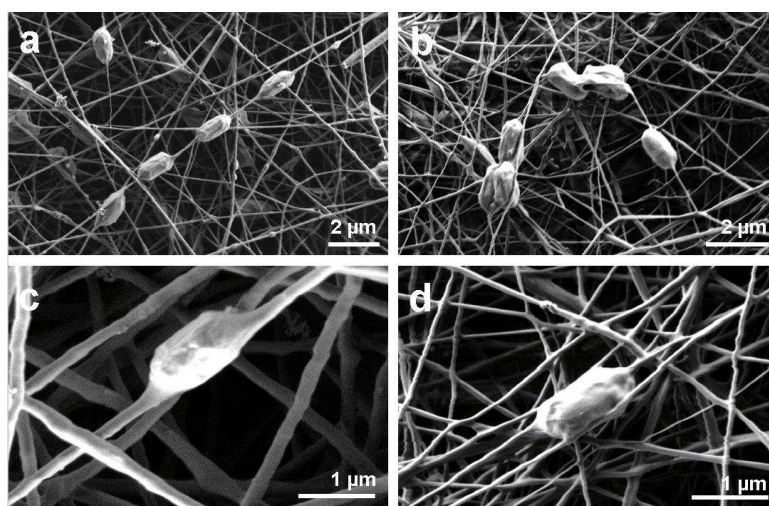


Figure 1. Spore-loaded (a, c) PEO and (b, d) chitosan/PEO nanofibers.

Acknowledgements: The work was financially supported by the Slovenian Research Agency through the research program P1-0189 and project J4-7640.

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Calcium carbonate porous microstructures biosynthesis: kinetic studies

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Calcium carbonate is a common biomaterial in Nature in a form of sea shells, avian eggs shell, otoliths and etc. [1]. Thanks to unique properties (high surface area, high porosity and non-toxicity) this material can find a wide application in industry as filler material for paints, pigments, coatings, paper and plastics, carriers of macromolecules and nanoparticles, templates for drug delivery or matrices for polymeric capsules [2, 3]. That is way for the last decade many researchers have tried to know the mechanism and mimic the biosynthesis of the biomaterials. It was found that in the formation of the mineralized tissues are involved biomolecules containing carboxylic, sulfate, hydroxyl, phosphate and amino groups [3]. Those biomolecules can bind metal ions and the crystals' surface, and control the growth of biomaterials with desired shape and polymorphs [4]. In literature several natural and synthetic compounds was tested as controlling biomaterials growth agents giving promising results.

The new aspect of this work is the use of biosurfactant in the formation of calcium carbonate particles. Studying literature, it was noticed that there is a lack of results considering the use of these molecules as additives controlling the growth of calcium carbonate. Compared to synthetic surfactants they are non-toxic, easy biodegradable, and can be synthesized from renewable waste. The application of these green surfactants molecules to control the morphology of calcium carbonate allows to develop the new eco-friendly technology of inorganic materials production.

The aim of this work is to investigate how the biosurfactant, surfactin, can affect the calcium carbonate microstructures formation. The kinetic of process was investigated by conductivity measurements. Also, the changes in calcium ions during the crystallization process were measured using ion-selective electrode. The morphology of crystals was analysed by scanning electron microscopy technique. The polymorph of precipitate was characterized using X-ray diffraction analysis. It was observed that surfactin molecules can retard the transformation of vaterite into calcite. What is worth to mention that after 24 h in the medium the porous crystals with pumice structure were formed.

Acknowledgements: The work was financed by the National Science Centre of Poland grant no. 2014/15/D/ST8/00544.

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Development of magnetically-responsive SPION-based nanospheres for drug delivery

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Magnetic drug targeting has proven to be an innovative strategy in a number of studies, especially in the field of cancer treatment [1, 2]. Thus, nanostructures based on superparamagnetic iron oxide nanocrystals (SPIONs) represent a very promising platform for development of novel drug delivery system. However, the individual SPIONs have only small magnetic moments, which are often too small to allow their effective magnetic manipulation [1]. This challenge can be overcome by assembly of multiple SPIONs into nanosized SPION clusters, nanospheres or magnetic nanochains [2]. Incorporation of 1-tetradecanol in magnetic nanospheres is expected to increase drug loading and enable hyperthermia triggered drug release, since 1-tetradecanol has melting point just above normal body temperature (38°C) [3].

The objective of this work was to prepare magnetic nanospheres based on SPIONs and 1-tetradecanol loaded with a model drug.

Preliminary results revealed the size of nanospheres to be about 100 nm. The method of passive drug loading during preparation of well-defined SPION clusters was used, which enabled successful drug loading. Various formulations of SPION-based nanospheres differing in proportions of 1-tetradecanol, SPIONs, and model drug were prepared and characterized. Drug loading was determined after disintegration of drug loaded nanospheres in ethanol with additional heating, sonication and mixing. The *in vitro* drug release experiments were performed in HEPES buffer, revealing rapid drug release from prepared nanodelivery system.

This work demonstrated that SPION-based nanospheres represent a promising nanomaterial for further development of a magnetically-responsive drug delivery system. However, the drug loading procedure should be further optimized in order to achieve controlled drug release. Furthermore, physical stability of drug loaded nanospheres in aqueous dispersions should be improved as well as their bioevaluation and safety studies should be performed.

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Development and characterization of hydrophilic polymer nanofibers with lipids as a delivery system for poorly water-soluble drugs

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Polymer nanofibers represent one of the newest nanomaterials [1]. They show a great potential as novel delivery systems for poorly water-soluble drugs [2]. The solubility and dissolution rate of incorporated drug can be increased due to specific characteristics of nanofibers such as very large surface area to volume ratio and high porosity of nanofiber mesh [3].

The aim of the present research was (i) the development of hydrophilic polymer nanofibers with selected lipids and incorporated model poorly water-soluble drug and (ii) the investigation of the drug release from produced nanofibers.

Nanofibers were prepared from a blend of hydrophilic polymers, selected lipids (mango butter, macadamia oil or cacao butter) and carvedilol as a model poorly water-soluble drug. Nanofibers were produced by electrospinning, being the most common method for preparation of nanofibers. The method enables one step incorporation of lipophilic compounds in hydrophilic poloxamer-based nanofibers. Morphology of nanofibers was characterized by scanning electron microscopy (SEM). SEM analysis revealed that incorporation of lipids (up to 17%, w/w) and model drug (up to 20%, w/w) in polymer matrix does not significantly affect the morphology of the electrospun product. Furthermore, the electrospinning of all investigated polymer solutions under optimal process parameters enabled the production of smooth, beadless, randomly oriented nanofibers with the average diameter between 400 nm and 500 nm. To evaluate the drug release from prepared nanofiber formulations a dissolution test was performed. The results revealed very fast drug release from all investigated nanofibers (total release in ≤ 20 min).

To sum up, the results have clearly shown that electrospun poloxamer-based nanofibers with lipids enable high drug loading and can be used to improve the dissolution rate of poorly water-soluble drugs. The research thus confirmed high potential of hydrophilic poloxamer-based nanofibers with lipids as a promising nanodelivery system for poorly water-soluble drugs.

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Comparison of cellulose-based filter surface modification methods with MTMS-aerogel structures

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In order to provide a high quality of fuel, new filtration techniques and separation materials are continuously developed. In the majority of automotive applications, the filter media consist of resin-impregnated cellulose papers. To enhance its long-time operation, hydrophobic materials should be characterized by self-cleaning properties and low adhesion of both solids and water droplets to the surface. A relevant combination of material structure with a modified surface is a route to obtain high-efficiency filtration materials [1]. In presented research, the material surface functionalization is realized in one step method, which utilizes hydrophobic aerogel spheres characterized by a hierarchical structure.

Aerogels are a group of highly porous materials characterized by excellent physicochemical properties such as low density, considerably high specific surface area and controllable wettability. There are many papers describing how synthesis conditions, drying method and precursor selection allow to control morphology of aerogel, which plays an important role in surface modification applications [2, 3]. This work is focused on different approach. Based on the same two-step acid-base aerogel synthesis method prepared from methyltrimethoxysilane (MTMS) precursor [4], three different modification procedures were proposed and their influence on material final surface properties has been examined.

First method is deposition of aerogel from the gelating solution for various volume ratios of MTMS to methanol under mixing conditions. As next, an aerodynamic method which relies on spraying of gelating solution directly on the material surface has been developed. Different gelation time and volume of reactive solution have been taken into account. Moreover, direct gelation of aerogel on the cellulose fibres, enhanced by ultrasonication is studied. Developed methods are compared in terms of obtained surface hydrophobicity, self-cleaning properties, coating uniformity and grade of pore blocking.

To characterize the properties of material, measurements of static contact angle (CA), sliding angle and contact angle hysteresis for water droplets are carried out. These parameters define the ability of the filter material to repel water, thus prevent its accumulation on the surface. Materials morphology analysis is performed by scanning electron microscopy (SEM).

The results show the influence of utilized modification method on obtained aerogel structure (Figure 1) and final surface properties of cellulose filtering material. It has been noticed that surface modification with aerogel can be a promising method to obtain cellulose-based material for fuel filtration.

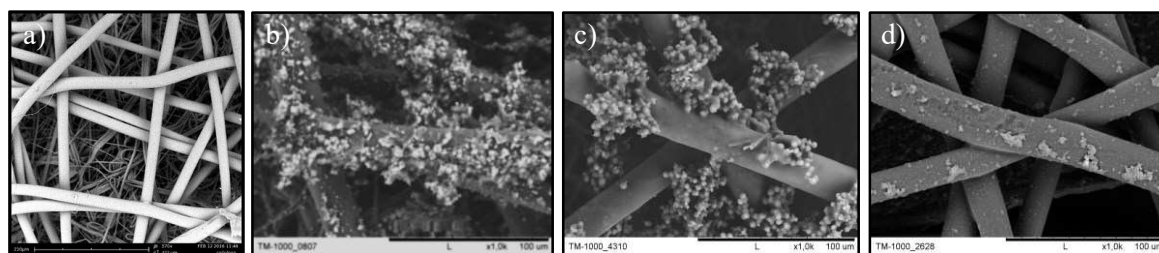


Figure 1. SEM images of cellulose fibres modified by MTMS-aerogel: a) reference material, b) deposition from gelating solution, c) sol-gel spray coating, d) direct gelation on the fibres.

Acknowledgments: This work was supported by NCBiR project “Oil removal from gas and liquid streams thanks to filter media modified by aerogel” LIDER/011/L-6/14/NCBR/2015.

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Structural and morphological properties of SiO₂ mesoporous materials with a range of pore diameters and volumes

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SiO₂ mesoporous materials present an interesting material because of its high surface area (up to 1000 m² g⁻¹) and tunable pore diameters, pore volumes and morphology with applications in fields such as drug delivery, catalysis and sensing. In order to obtain desired functionalities the structural, morphological and surface properties of mesoporous materials can be tuned by adjusting the synthesis parameters, such as the type of the surfactants and polymers used, pH and temperature of reaction mixtures, choice of silica precursor, addition of swelling agents, etc. [1].

In order to obtain materials with specific water sorption capabilities we have synthesized mesoporous SiO₂ material with a range of pore diameters (between 3 to 15 nm) with varying volumes of pores. We have studied the influence of the properties of the structure directive agents (such as the chain length of the alkyl group of the surfactant and the ratios of the poly(propylene oxide) and poly (ethylene oxide) chains in the triblock copolymers), the pH of the reaction mixtures and the addition of organic solvent on the properties of the synthesized mesoporous particles.

The pore size distribution was studied through N₂ sorption and small-angle X ray scattering (SAXS), while the morphological properties and orientation of the pores were studied via electron microscopy (FE-SEM, TEM). The water vapour sorption capabilities were examined via gravimetry and thermogravimetry with differential thermal analysis (TG/DTA) performed after exposure of the materials to a range of different relative water vapour pressures. The obtained materials exhibited different amounts of adsorbed water at specific water vapour pressures.

Acknowledgements: We acknowledge financial support from the Slovenian Research Agency through post-doctoral project No. Z1-8149 and research programme No. P1-0201.

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Charge properties of TiO₂ nanotubular structures in low salt aqueous solutions

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Specific and often enhanced properties of TiO₂ nanotubes make them suitable for various applications such as adsorbents for decontamination of different organic molecules and heavy metal ions. Furthermore, TiO₂ nanotubes could be used for degradation of environmental pollutants by exploiting its photocatalytic properties or even as carriers of various matter in a nanomedical application [1]. The majority of applications are conducted in aqueous media. Therefore, in order to understand and to successfully manipulate the mentioned processes, it is crucial to gain insights into charging phenomena of TiO₂ nanotubes. In this article, the surface charge properties of titania nanotubes in NaNO₃ solution were investigated through electrophoretic mobility and polyelectrolyte colloid titration measuring techniques. In addition, we used HR-TEM imaging to determine the morphology of TiO₂ NTs. A theoretical model based on the classical Density Functional Theory coupled with the charge regulation method in terms of mass action law was developed in order to understand the experimental data and to provide insights into charge properties at different physical conditions, namely pH, and NaNO₃ concentration.

intrinsic protonation constants and surface site density have been obtained. The electrostatic properties of the system in terms of electrostatic potentials and ion distributions were calculated and discussed for various pH values. The model can quantitatively describe the titration curve as a function of pH for higher bulk salt concentrations and the difference in the equilibrium amount of charges between the inner and outer surfaces of TiO₂ nanotubes. Calculated counterion (NO₃⁻) distributions show a pronounced decrease of NO₃⁻ ions for high bulk pH (both inside and outside of TiO₂ nanotubes) due to the presence of the strong electric field. With the decrease of bulk pH or the increase of the salt concentration, NO₃⁻ are able to accumulate near the TiO₂ nanotubes surfaces. The Donnan effect has been studied to the full extent [2].

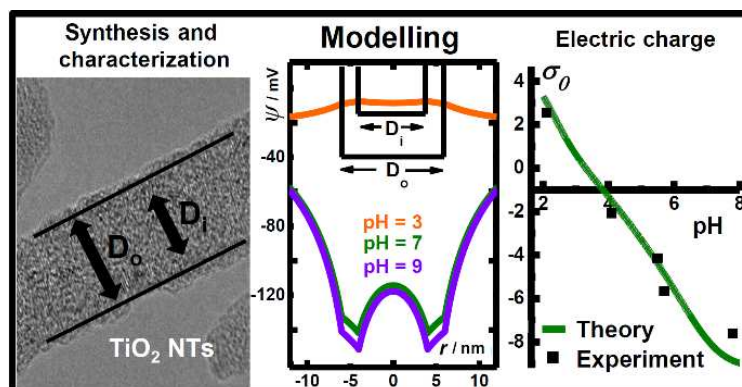


Figure 1: Schematic representation of step-by-step development of a simple but predictive theoretical model.

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Polysaccharide nanofibers – effect of high molecular weight poly(ethylene oxide) addition on electrospinnability

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Nanofibers have nanometer-sized diameter and can be used as drug carriers or as scaffolding material in the regenerative medicine. Their ultrahigh surface area, bioadhesion and structure resembling extracellular matrix are properties desired in wound healing. Additionally, they should be biocompatible, biodegradable, and with no adverse immunogenic response from the host. All these properties enable that the wound healing patch consisting of nanofibers does not have to be removed after treatment. Polysaccharides of natural origin are widely accessible and could be exploited for nanofiber production. However, the electrospinnability of such polymers is questionable [1-3]. Most polysaccharides are polyelectrolytes resulting in certain conductivity and surface tension properties of the solutions. They also have challenging rheological properties - gelling instead of elongation of jet into fibers. There are some options for enhanced polysaccharide nanofiber formation and most literature focused on alginate nanofiber production [1-3]. However, very few reached really high level of polysaccharide content (> 80 %, w/w) and rarely any research tested also other polysaccharides.

The aim of this research work was to produce nanofibrous mats from polysaccharides (i.e. alginate, pectin, chitosan) with the help of high molecular weight poly(ethylene oxide)s (PEOs; M_w : 2 - 8 million (M) Da) to determine how they can affect the electrospinnability of the polysaccharide solutions and morphology of nanofibers. Rheological properties (viscosity, storage and loss moduli) as well as conductivity of solutions were measured and morphology of nanofibers with SEM was examined.

In overview, high molecular weight PEOs improved electrospinnability of polysaccharides; however the highest molecular weight (8MDa) had just the opposite effect (Figure 1). With use of PEOs 2MDa and 4MDa we could effectively increase the mass fraction of natural polymer which was our overall goal. We discovered that solutions with lower electric conductivity were electrospun more effectively but also other variables should be taken into consideration. With varying the alginate, pectin or chitosan concentration, PEO content and PEO M_w we were able to find optimal formulations for all three tested polysaccharides resulting in nanofibers with high content of a biodegradable polymer that would provide efficient scaffolding material.

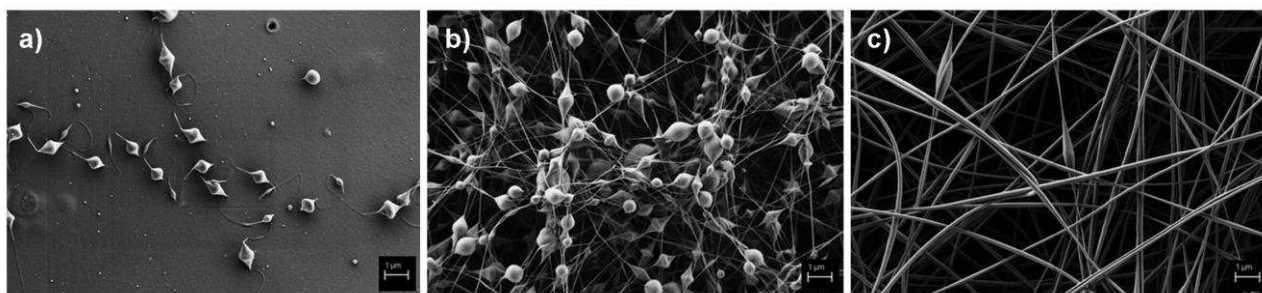


Figure 1. SEM images of three different electrospun formulations: a) 3.5% alginate:PEO 8MDa solution (2:98 (w:w)), b) 2.5% alginate:PEO 2MDa solution (8:92 (w:w)), c) 3.5% alginate:PEO 2MDa solution (8:92 (w:w)).

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Phosphonic acids as selective functionalizing agents: a study on halloysite surface modification based on model oxides

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Phosphonic acids are hetero-organic compounds bearing a C-PO(OH)₂ group, which are known for adsorbing covalently on oxide substrates and can be used to create self-assembled monolayers. Their selectivity towards certain oxides [1] can be exploited for the selective functionalization of inherently dual systems, such as halloysite nanotubes. Halloysite is a polymorph of kaolinite which naturally wraps itself to form nanotubes. Its numerous fields of application range from polymeric nanocomposites with superior mechanical and thermal properties, to catalysis and drug delivery [2]. Halloysite is one of the few nanotubular systems presenting an inner lumen and an outer surface characterized by different surface charge and structural composition: the inner lumen exposes aluminum hydroxyl groups, while their outermost layer is silica. This characteristic structural ambivalence holds potential for the separate modification of the two surfaces, which can thus be assigned different tasks. However, precisely defining the nature and location of molecule adsorption is a complex matter and the selective functionalization of halloysite inner and outer surfaces has been scarcely investigated in the literature [3].

In this work, the surface modification of halloysite with octylphosphonic acid (OPA) was investigated together with the functionalization of purposely prepared model oxides mimicking the inner and outer nanotube surfaces. Evidence of the preferential location of the OPA molecules in the halloysite inner lumen was gathered by both comparative studies on the model oxides as well as direct measurements on the functionalized nanotubes. Furthermore, the effect of the surface charge of the oxide on the functionalization efficiency and reversibility was investigated in detail. The isoelectric point of the oxide plays a major role in determining a stable OPA adsorption, as proved by functionalization isotherms on the model oxides measured at different pH values. An amphiphilic oxide (TiO₂) was also investigated as a reference [4]. The pH-triggered selective release of the adsorbed OPA molecules could be obtained and release conditions were determined for both the halloysite nanotubes and the model oxides.

The combination of the inner location of the functionalizing agents and the pH-dependent reversibility of their adsorption make of the phosphonic acid-functionalized halloysite nanotubes promising candidates in numerous fields.

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Hybrid polyelectrolyte films with embedded nano-objects as the antibacterial coatings

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A variety of biomedical devices, materials and drug delivery systems are used in direct contact with biological fluids. There are a number of problems associated with such use of materials. One of the most significant is associated with the fact that on the surfaces exposed to solutions containing biological material the process of biofouling occurs. Therefore, the development of the “antifouling” coatings protecting against non-specific protein adsorption, bacteria and fungi colonization [1] is an important area of the research within a broader field of biointerface science. New multifunctional coatings should combine passive components, as anti-adhesive layers, and active components that provide fast response of the coating properties to change occurring either in the matrix of those multifunctional coatings (e.g. local pH change, bacteria activity) or in the local environment (temperature, humidity).

The polyelectrolyte films were formed via Layer by Layer (LbL) approach, which is a sequential adsorption of the oppositely charged nano-objects. This method is considered as one of the most promising techniques of surface modification, including formation of multifunctional coatings with a wide range of possible applications, including: antibacterial coatings, selective membranes, biosensors and drug delivery systems [2].

The goal of this work was to build up functional multilayer thin films with metal/metal oxide nanoparticles with antibacterial properties (ZnO, Cu/CuO, Ni/NiO) and with graphene oxide(GO)/graphene. Applying polyelectrolytes of natural origin with confirmed antimicrobial electrolyte activity (chitosan, fucoidan) for multilayer construction, we expected synergistic effects between nanoparticles and polymers in action against various bacterial strains. Functionalization of the multilayers with PGA-g-PEG copolymers additionally enabled the reduction of the adhesion of bacterial cells to the modified surfaces as immobilization of neutral hydrophilic polymers, as poly(ethylene glycol) (PEG), at solid surfaces is one of the promising methods to reduce non-specific adsorption of proteins or microorganisms. Formation of coatings were studied using physicochemical methods: QCM-D, SEM, UV-Vis absorption spectroscopy and Zeta Potential measurements. The microbiological tests for various bacteria strains were performed using fluorescent staining and microscopic technique. Activity of the samples was tested on bacterial strains *Staphylococcus aureus*. It was found that nanocomposite films have antimicrobial properties, which makes them very interesting for a number of practical applications e.g. prevention of microbial colonization on treated surfaces.

Acknowledgements: The work was partially supported by the statutory subsidy for ISCS PAN and the Research Project for Young Employees of ICSC PAS.

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Tuneable photonic properties of particle-in-cavity nanostructures

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Nanostructured gold surfaces exhibit interesting optical properties which differ from those from bulk materials. One of them is the localized surface plasmon resonance, which becomes apparent when an external electromagnetic field incident on metal elements (metal nanoparticles or nanovoids) induces electron cloud delocalization. Optical response is originated from the strong localized metal absorption when the frequency of the electromagnetic field becomes resonant with the coherent electron motion. One interesting issue concerning the photonics of surfaces is the optical properties modulation through external inputs. In this context, merging of metal and smart-soft-polymer technologies to make hybrid systems leads to successful results. We present here novel nanovoid structures stuffed with soft polymer particles as well as with metal-polymer hybrid particles. The resulting photonic response is sensitive to external stimuli such as temperature and pH due to the change in the refractive index of the polymer network.

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Stability of silica nanoparticle gels

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An area of application for silica sols is the grouting (sealing) of narrow fractures in tunnels to prevent water ingress [1,2]. When used for this purpose the silica sol is mixed with a salt solution leading to gel formation in a predetermined time. Silica sols have only recently been used for this purpose and knowledge of the long term stability and functionality of silica gels in a grouting environment is therefore relatively unknown.

In order to evaluate the long term stability and behaviour of silica gels in different water compositions and pH new test equipment was designed and built. This allowed water to pass through the gels at a certain pressure and the resultant leached water was analysed using ICP-AES. Results of simulated leaching experiments gave valuable information regarding the kinetics of dissolution with respect to ionic composition and pH of water.

Simple theoretical predictions of the life time of gels with a volume of 100 mL revealed total lifetime between 200-400 years [3]. This is well within expected lifetimes for construction materials. The use of KCl as accelerator was shown to extend the lifetime compared to NaCl accelerator. Since KCl is a more effective accelerator allowing for more silica content in the gels leading to lower flow rates through the silica gels. Also, an increase in leach water pH only had a minor impact on the gel dissolution since the silica gels were shown to buffer the water to approximately pH 10.

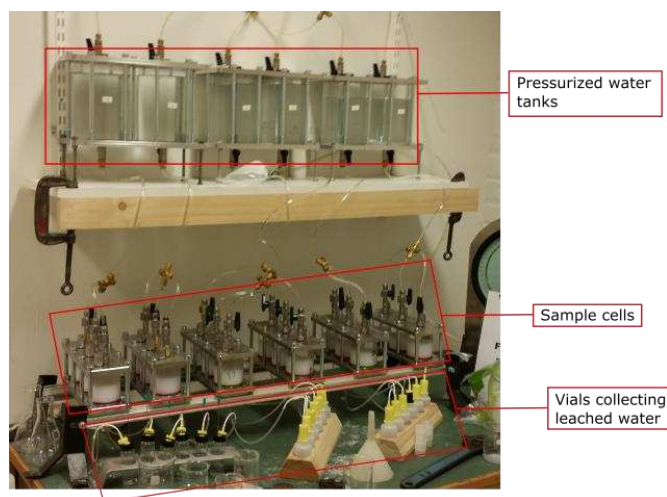


Figure 1. Picture of the long term stability test equipment in use. The pressurized water tanks contain the leach water of different ion composition and pH. This water is lead into the sample cells holding the 100 mL silica gels. The water passes through the gels and is collected in vials.

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Sub-micron core-shell mesoporous silica particles as a new generation for HPLC applications

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Mesoporous silica particles (MSPs) composed of solid core and porous shell are packing materials to efficiently separate chemical substances in high performance liquid chromatography (HPLC) [1]. Although core-shell MSPs with a diameter of *ca.* 2.7 μm are commercially available [2], recent reports employ sub-2 μm smaller particles as promising packing materials [3]. In this study, sub-1 μm core-shell MSPs with various shell thicknesses were prepared with our method that enables facile control in performance-determining shell parameters such as shell thickness and pore structures [4]. The particles obtained were subjected to HPLC test for separating hydrophilic solutes.

Figure shows sub-micron core-shell particles (Run A) prepared according to the previous method [4]. Silica shells with a thickness of 42 nm were uniformly formed on the silica cores with an average diameter of 725 nm. Table summarizes the physical properties of core-shell particles obtained at different numbers of particle numbers (N_p). Shell thickness (T_s) was increased by decreasing N_p and well controlled by the concentration ratio of silica source (TEOS) to N_p . Since few difference in porosity was observed among the three particles, mesoporous silica shells were successfully formed with a constant density and similar mesostructures. The core-shell particles obtained were then used for separating hydrophilic solutes by HPLC. A part of the results was shown in Table. As T_s decreased, retention time became shorter and theoretical plate number increased under tolerable column pressures in this HPLC test. The HPLC test shows that sub-1 micron core-shell MSPs are good candidates for packing materials to improve HPLC performance.

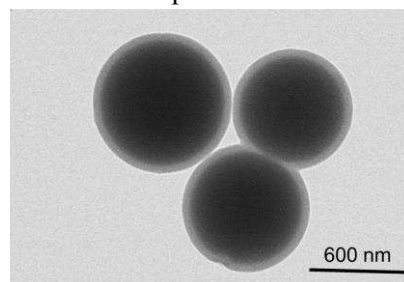


Figure 1. TEM image of core-shell MSPs prepared in Run (A)

Table 1. The physical properties of core-shell MSPs obtained by silica coating on solid silica cores with an average diameter of 725 nm at 35 °C and HPLC results using cytosine as analytes

Run	N_p [particles/ m^3]	T_s [nm]	D_p [nm]	d_{BJH} [nm]	S_{BET} [m^2/g]	Theoretical plate number [-]	Retention time [min]	Column Pressure [MPa]
(A)	1.5×10^{13}	42	809	2.8	157	12234	2.1	16.9
(B)	1.0×10^{13}	58	841	2.8	155	8708	2.3	13.4
(C)	6.4×10^{12}	88	901	2.5	239	4904	3.0	12.1

Synthesis conditions: [TEOS]/[CTAB] = 60/20 (mM/mM), $[\text{NH}_3]$ = 10 (mM), $[\text{EtOH}]/[\text{H}_2\text{O}]$ = 5/38 (M/M)
TEOS: Tetraethyl orthosilicate, CTAB: Cetyltrimethylammonium bromide

Measurement conditions of HPLC: Column size: 2.1 mm I.D. \times 50mm, Velocity: 0.21 ml/min,
Mobile Phase: Acetonitrile/0.1 M Ammonium formate aq. = 88/12 (v/v)

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Structural assessment of natural filler/polymer composites utilising their water diffusion coefficient

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Great attention is paid to polymer composites at the moment in order to introduce specific functionalities to a flexible, light-weight, chemical resistant and easy-to-process matrix. Carbon nanotubes (CNTs) are typically added to polymer matrices to create flexible and conductive materials for use in automotive applications or to improve the mechanical properties of structural materials [1]. The distribution of particles within the polymer is key to achieving the required functionalities in both cases, highlighting the importance to characterise and control it.

For electrically conductive composites, a connected network of fillers (percolation) is necessary to conduct charges throughout the material. Network formation can therefore readily be evaluated by measuring the electrical conductivity as a function of filler content, where a sharp transition between insulator and conductor can be observed around the percolation threshold. To assess the percolation threshold of non-conductive species for mechanical strengthening, rheology is often employed. A steady increase in modulus or viscosity is typically observed as a function of particle concentration due to their hardening effect. At the percolation threshold an additional increase can be observed as the fillers start to interact, the transition, however, can be very subtle [2]. Natural fillers such as cellulose, hemp or bamboo fibres are currently of great interest as they are renewable, readily available and inexpensive. They are typically non-conductive and therefore determination of the percolation threshold can be challenging [3].

Difficulties in determining the arrangement of particles within the composite, can hinder the understanding and development of novel composites. A new approach to assess the percolation threshold of polymer composites containing natural fillers was therefore investigated. This involved the evaluation of the water diffusion coefficient (D) as a function of particle loading. Under the assumption that moisture transport through the hydrophilic particles is favoured over the transport through the hydrophobic matrix, D becomes a convenient parameter to assess the dispersion state, where better connections will lead to faster moisture transport.

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Structural and electrosurface properties of iron – containing nanoporous glasses in KNO₃ solutions

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The development of new composite nanomaterials with predetermined characteristics is one of the purposes of modern chemistry. One of the classes of such nanomaterials are materials that have magnetic properties - powder magnetic sorbents, inorganic membranes, multiferroics, etc. The use of magnetic sorbents will help solve the problem of extracting the sorbent from the liquid phase by means of a magnetic field, without filtering and centrifuging the dispersions. High-tech materials should possess chemical, thermal and microbiological endurance, be environmentally safe and suitable for repeated use. These requirements are met by high-silica porous glasses (PG), whose magnetic properties are ensured by the introduction of iron (III) oxides in the charge when making alkali-borosilicate glasses.

The structural (volume porosity, structural resistance coefficients, tortuosity coefficient, mean pore radius, specific surface area) and electrosurface (surface conductance, counterion transport numbers, electrokinetic potential) characteristics of high-silica micro- (mean pore radii about 2 nm – MIP) and macroporous (mean pore radii about 15 nm – MAP) glasses of different composition (not containing 8V and containing magnetite (Fe₃O₄) Fe-4) have been studied in KNO₃ solutions (10⁻¹-10⁻⁴ M).

A study of the PG's pore morphology is an important problem, because their structure parameters, including the pore inhomogeneities, affect the sorption, capillary, diffusion, adhesive, optical, and other properties. The structural resistance coefficient (β), which reflects the contribution of the nonconducting skeleton to the electrical conductivity of the membrane, for the containing a magnetite phase MIP and MAP porous glasses was significantly higher than for the base 8V PGs.

The results of the study have shown that the efficiency coefficients α (equal to the ratio of the specific electrical conductivities of pore and free solutions) obtained for MIP and MAP glasses of both compositions were close in KNO₃ solutions. The values of α decrease with increasing electrolyte concentration and pore radius in accordance with the decrease in the contribution of ions of double electric layer (DEL) to the electrical conductivity of the pore solution. It was found that the values of the transport numbers of potassium counterions (n_+) also practically do not depend on the composition of the MIP and MAP PGs. As the concentration of the electrolyte increases, the values of n_+ decrease in accordance with the decrease in the contribution of ions of DEL to membrane transport processes.

The values of the electrokinetic potential were found by the method of streaming potential. A comparison of the concentration dependences of the electrokinetic potential for membranes shows that the chemical composition of the MIP glass practically does not affect the values of the ζ -potential in the neutral pH range. It was found that with the dilution of the electrolyte ($C < 10^{-2}$ M), the values of the zeta potential decreased for both types of MIP glasses. This can be explained by the fact that when the electrolyte is diluted, the degree of swelling of the secondary silica in the pore channels increases, which leads to a displacement of the slip plane from the solid surface to the center of the pore channel, and, consequently, to a decrease in the values of the zeta potential. Electrokinetic potentials of MAP glasses increased with electrolyte dilution in the investigated concentration range (0.1-10⁻⁴ M) in accordance with EDL theory. The obtained results also indicated that $|\zeta|$ values of MAP Fe-4 membranes is larger than zeta potential of MAP 8V membranes.

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Uptake of vapor of FeCl_3 by porous silica

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Porous silica adsorbs vapor of FeCl_3 at 200-250 °C and produces a light-orange material. Uptake of water vapor at room temperature by silica with pre-adsorbed FeCl_3 results in hydrolysis of the chloride, and the material turns yellow, and finally it turns brown on heating at 150 °C. A series of Fe-modified silicas with 10-30% of iron oxide with respect to silica by mass was prepared from SBA-15 and from Kieselgel fein from Merck. Similar method was previously used to modify silica with other metals [1]. The coloration of silica in the presence of Fe makes this possible to control the uniformity of distribution of Fe in the bed of silica powder. Such a control of uniformity is not possible with Al and Ti-modified silicas, which are colorless.

The of Fe-modified silicas were characterized by specific surface area, total pore volume and micropore volume, Mossbauer spectroscopy and ζ potential. The specific surface area and pore volume linearly decrease with the amount of Fe in the composite material. The Mossbauer spectroscopy did not detect the presence of any crystalline Fe compound in the materials containing less than 15% of iron oxide with respect to silica by mass. This result suggests that iron is uniformly distributed over the surface of pores. This suggestion is further corroborated by the study of ζ potential of dispersions of original and Fe-modified SBA-15. Namely the presence of iron did not result in a shift in the isoelectric point to high pH. Such shifts occur when metal oxides are deposited on the external surfaces of silica particles.

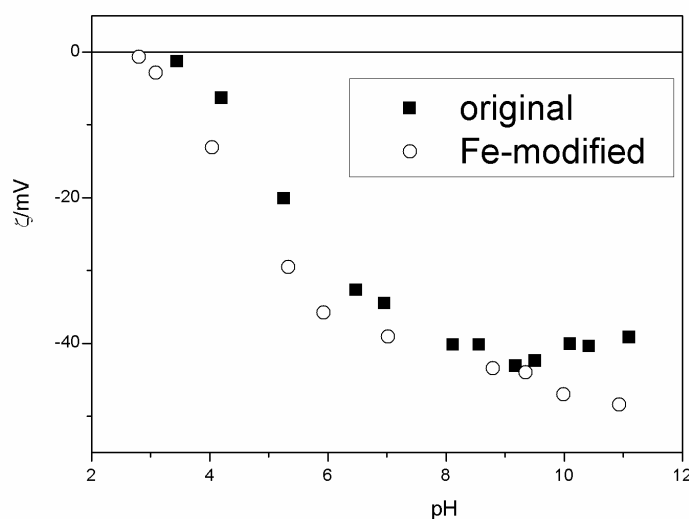


Figure 1. ζ potential of original and modified SBA-15.

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Synthesis of fluorescently-labelled magnetic composite particles using double electrostatic heterocoagulation

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Magnetorheological Fluid (MRF) is a dispersion of magnetic particles in a nonmagnetic medium. The viscosity of MRF can be controlled by application of magnetic field due to the chain formation of magnetic particles in MRF. MRFs have been studied as functional fluids applicable to dampers and surface polishing. In some reports [1] motions of magnetic particles in MRF were directly observed with a fluorescent microscope. Fluorescent dyes have been commonly employed as labels for the magnetic nanoparticles although they are easily quenched by long irradiation of excitation light. In the present work, ZnO nanoparticles are focused on as a less quenched fluorescent label to observe the magnetic particles with a fluorescent microscope. Electrostatic heterocoagulation between nanoparticles and support particles was effectively used for preparation of fluorescently-labelled magnetic composite particles.

Figure 1(a) shows the schematic procedure for the synthesis of the fluorescent and magnetic composite particles. SiO₂@magnetic nanoparticles were prepared by electrostatic heterocoagulation between anionic submicron-sized SiO₂ particles and cationic magnetic nanoparticles. SiO₂@magnetic nanoparticles were coated with SiO₂ shell. Finally, ZnO nanoparticles were supported on the SiO₂ coated particles via electrostatic heterocoagulation. Both magnetic and ZnO nanoparticles were surface-modified with a cationic silane coupling agent.

The SEM image of the fluorescent and magnetic composite particles are shown in Figure 1(b). The composite particles had surface roughness caused by electrostatic heterocoagulation of magnetic and ZnO nanoparticles. They were monodisperse with a coefficient variation of 3.5%. The magnetic responsivity of the composite particles was examined by using a permanent magnet. Six minutes after the application of magnetic field almost all the composite particles were collected in the suspension, indicating that they have high responsivity to the external magnetic field. A clear fluorescent image of the composite particles showed a sufficient amount of ZnO nanoparticles supported on the SiO₂ shell. These results demonstrated that the double heterocoagulation was effective for preparation of monodisperse composite particles with two different functions.

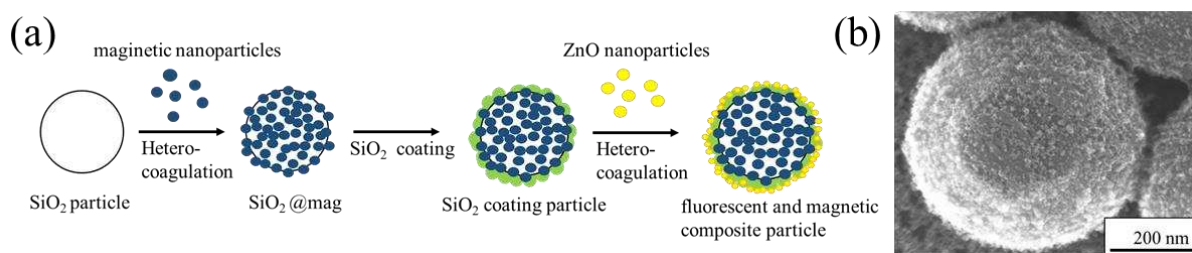


Figure 1. The schematic procedure for the synthesis of composite particles(a) and SEM image of the particles(b)

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Molecular dynamics simulations of interactions between carbon nanotube coated with poly(ethylene oxide) and oligopeptides

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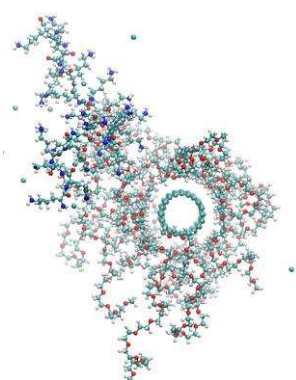
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Presently, carbon nanotubes (CNTs) belong to the most important building blocks in nanotechnology because of their excellent electronic, thermal, and mechanical properties. Thus, CNTs are extensively studied from the viewpoint of their potential applications in composites, electronics, computers and hydrogen storage [1]. In nanomedicine the applications of CNTs include biosensors, biomolecular recognition devices, molecular transporters, and cancer therapy and diagnoses [2]. The interactions of CNTs with proteins attract attention of scientific community since it plays important role in biochemical processes in biological systems. In case of undesired protein adsorption, CNTs are coated with the protective layer of polymer chains. Thanks to its biocompatibility and nontoxicity poly(ethylene oxide) (PEO) is frequently employed for this purpose.

The molecular dynamics simulations have been performed to study the interactions between PEO-modified CNT and oligopeptides composed of 24 amino acids of different affinity for water. Specifically, oligoglycine and oligovaline represent small and large nonpolar protein moieties, respectively, while oligoserine represents small neutral polar moiety. Oligoaspartate and oligolysine serve, respectively, as representatives of negatively and positively charged polar protein moieties. In order to address the effect of PEO coverage on the interactions between CNT and different oligopeptides the interactions between oligopeptides and uncoated CNT are also investigated. In addition, the effect of water and NaCl at physiological concentration is scrutinized. The radial density distribution of grafted PEO chains and water molecules, the distance of oligopeptides from the coated and uncoated CNT as well as the effect of the CNT on the conformation of oligopeptides are evaluated.

This study is meant to contribute to understanding of the complex interactions between proteins and PEO coated CNTs in biological systems and to uncover the function of PEO, water, and salt in these interactions.

a)



b)

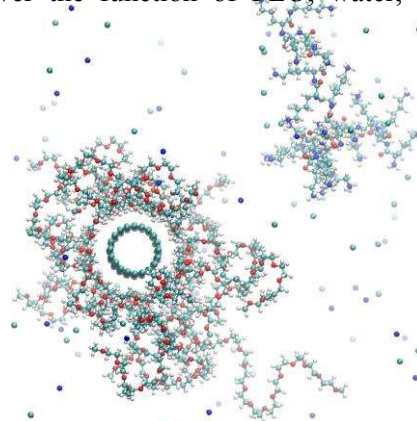


Figure 1. PEO-modified CNT interacting with oligolysine in water under salt free conditions (only the counterions Cl^- are considered) (a) and in water solution with physiological concentration of NaCl. Water molecules are omitted for the clarity.

Acknowledgements: This work was supported by grants SRDA-15-0323, VEGA 2/0055/16, VEGA 2/0098/16, Z.B. also thanks to FCT/MEC through national funds, and cofinanced by the European Union (FEDER funds) under the Partnership Agreement PT2020, through projects UID/QUI/50006/2013, POCI/01/0145/FEDER/007265, and NORTE-01-0145-FEDER-000011 (LAQV@REQUIMTE).

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Green Synthesis and Catalytic Properties of Hollow Polystyrene Microparticles Covered with Bimetallic Nanocrystals

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When compared to freestanding nanocrystals, supported nanostructures typically show several advantages including better stability and reusability as well as ease of handling. In the current work, a green approach using a nontoxic reducing agent and environmentally benign solvent medium was developed to produce hollow polystyrene (PS) microparticles covered with bimetallic nanocrystals. PS microparticles embedded with silver (Ag) nanocrystals were prepared by carrying out an in situ reduction of silver precursor on the PS microparticles and were used as seeds. These seed particles were dispersed in two ethanol-water mixture samples, one containing HAuCl_4 precursors and the other K_2PtCl_4 precursors, and transformed into hollow PS microparticles covered with bimetallic Au/Ag and Pt/Ag nanocrystals, respectively, as a results of the galvanic replacement reaction and the uptake of continuous phase by the particles. Based on our results and observations, a plausible mechanism for the formation of the hybrid microparticles was proposed. These microparticles exhibited high activity at low concentration and excellent reusability as catalysts for the reduction of p-nitrophenol by sodium borohydride.

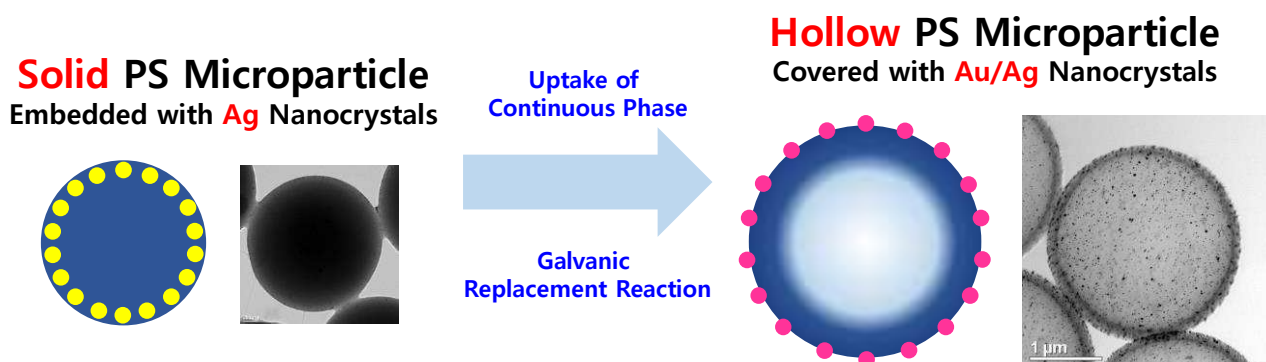


Figure 1. Schematic illustration of the formation of hollow PS microparticles covered with bimetallic nanocrystals

Acknowledgements: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2017R1E1A01074445).

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Single-step synthesis of hollow dimpled polystyrene microparticles

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The design and preparation of hollow non-spherical microparticles are of great significance for their potential applications, but the development of a facile synthetic method using only one production step remains a great challenge. In the current work, hollow dimpled polystyrene (PS) microparticles were synthesized using a one-step dispersion polymerization method that adopted the mono-phase polymerization system, without using any template. During the reaction, the solid spherical particles transformed into hollow particles, which then underwent a buckling process to form the hollow dimpled PS microparticles. The average diameter of the microparticles and the degree of concavity of the dimpled surface can be tuned to some extent by varying the reaction conditions. The experimental results revealed that ammonium persulfate (APS), which served as an initiator and as a co-stabilizer, played a critical role in the formation and growth of the PS microparticles. The hollow dimpled PS particles produced in this study were quite uniform, enough so that they could assemble into a close-packed lattice, and they showed excellent stability with regards to their dispersity and shape. This study not only advanced our understanding of the roles played by APS in dispersion polymerization, but also provides unprecedented opportunities to synthesize polymer particles with controlled nanostructures.

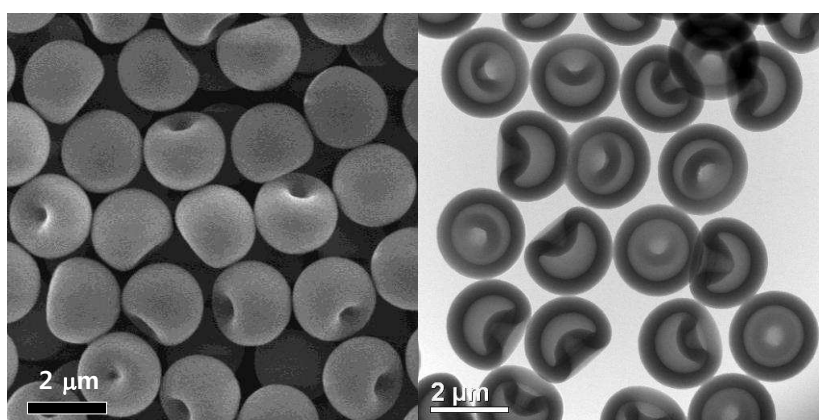


Figure 1. SEM and TEM images of hollow dimpled PS microparticles

Acknowledgements: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2017R1E1A01074445).

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Tuning the antifouling activity of bacterial S-layers by means of controlled degradation.

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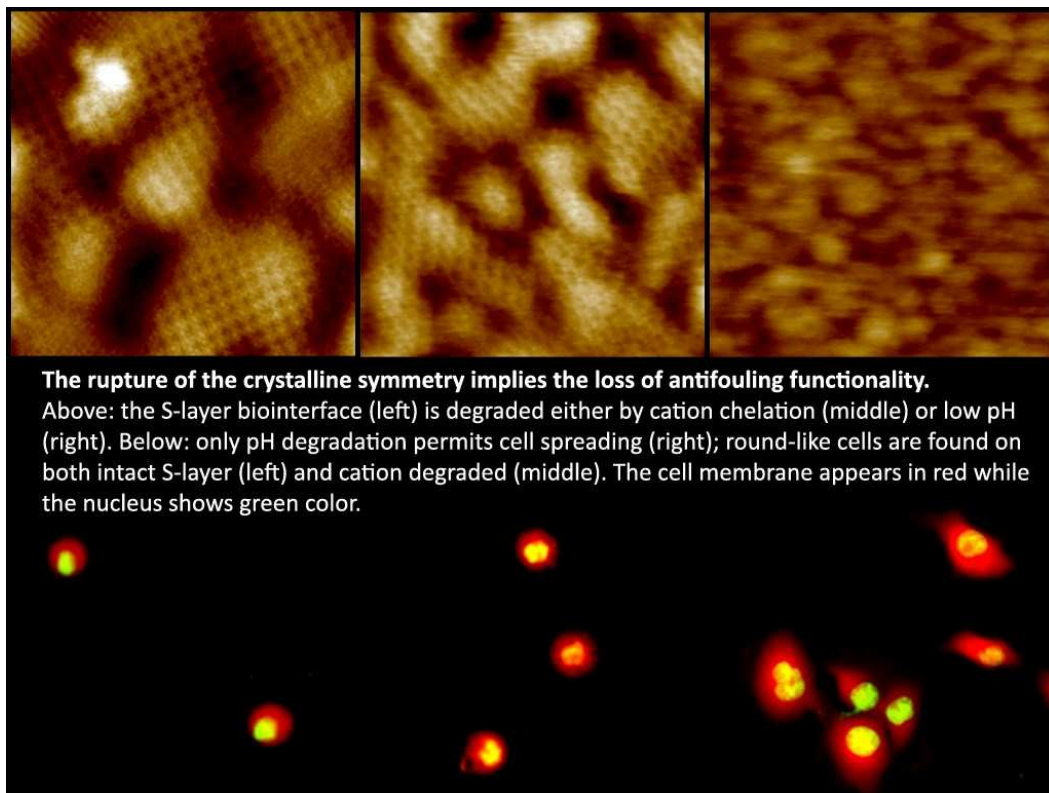
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The SbpA S-layer protein from *Lysinibacillus sphaericus* CCM2177 has been used in this work in order to investigate its loss of anti-fouling activity upon controlled structural degradation processes. This specific protein presents a square (p4) lattice symmetry with a measured pore-to-pore distance of 13 nm (90° angle between adjacent protein subunits)[1].

The crystalline S-layer formation/degradation process, as well as the variation in the properties resulting from the changes in the protein state, have been studied by means of real time QCM-D monitoring and AFM under two distinct procedures: a) Exposure to EDTA, in order to coordinate the Calcium divalent cations which are necessary to achieve the crystalline state; b) pH variations below SbpA isoelectric point ($pI = 4.6$), which influence the preservation of the overall crystal structure. While the former originates the appearance of structural defects and the partial presence of remaining crystalline domains, the latter induces a total switch of the layer properties caused by its denaturation. Thus, three different scenarios are presented -and compared- in terms of antifouling efficiency: non-degraded S-layers (reference), and both EDTA- and pH-degraded S-layers.

Subsequently, their respective interactions with either positive (PEI, PDADMAC) or negative (PSS) charged polyelectrolytes have been studied. In addition, the three type of surfaces produced have been exposed to endothelial HUVEC cells in order to test the respective cell-substrate affinity. The different levels of affinity obtained for the degraded S-layers might be envisaged for the design of functional coatings with an on demand degree of non-fouling efficiency.



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Encapsulation of low-water soluble drugs in yeast-derived beta glucan microparticles by spray drying

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Yeast-derived beta glucan particles (GP) are attractive biotemplates, suitable as drug carriers for macrophage-targeted delivery due to their immunomodulatory activity. In this context, a wide range of water-soluble payloads, including peptides, liposomes, siRNA, and DNA, have been successfully encapsulated in glucan particles. Loading of low-water soluble drugs, such as resveratrol and curcumin, has also been attempted, however, this constitutes an area of study yet to explore.

Low solubility of drugs in water is one of the pharmaceutical industry's major challenges, since about 90% of drugs in the discovery pipeline exhibit low-water solubility and, consequently, a limited bioavailability. The development of amorphous solid dispersions (ASDs) constitutes one of the most promising methodologies for the improvement of drug solubility, and spray drying is a well-established technique that has been successfully used for the production of ASDs. On the other hand, studies regarding the use of glucan particles as potential candidate materials for the amorphization of low-water soluble payloads, have not been found.

In this work, spray drying is used for the encapsulation of low-water soluble drugs, including ibuprofen, curcumin and atorvastatin, in yeast-derived beta glucan particles. Different sets of spray-drying parameters, as well as different drug-to-GPs mass ratios, are evaluated. The influence in encapsulation efficiency and crystallinity microparticles produced is analyzed. The particles obtained were also characterized by SEM, confocal microscopy, among other techniques. Results showed that with an adequate drug-to-GPs mass ratio, completely amorphous composite particles were obtained. In some cases, part of drug was not encapsulated in the GPs, instead it precipitated outside of the particles, which could be related mainly to loading capacity of the GPs and the droplet size generated during the spray-drying process. Finally, higher dissolution rates are obtained for the amorphous drug loaded GPs.

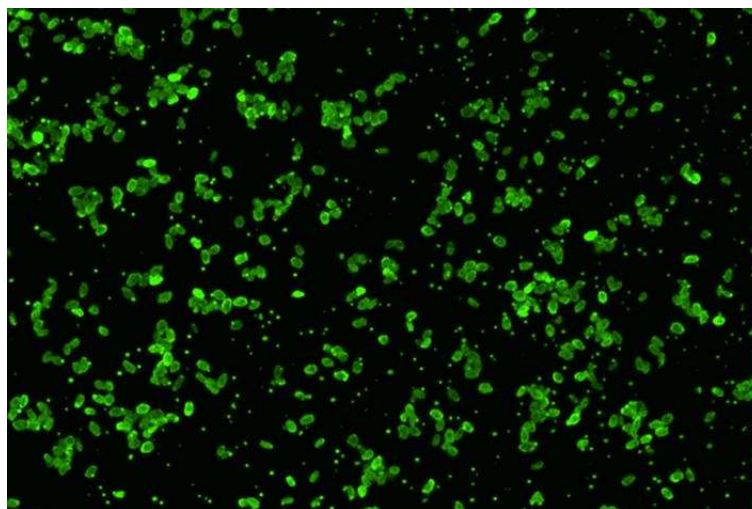


Figure 1. Confocal microscopy image of spray-dried CC/GP particles (CC/GP mass ratio = 5%).

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Preparation and characterization of magnetic microrods and their use in the reinforcement of polymeric materials

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The reinforcement of polymers through the addition of inorganic fillers has been the subject of much technological advancement during the last decades. Nevertheless, many challenges still lay ahead of us, especially when it comes to prepare materials with anisotropic mechanical properties. One solution is to prepare fillers that respond to an external field and can be oriented during the preparation of the composite material. The purpose of this work is twofold: 1) Introduce a novel method to prepare magnetic microrods, with controlled diameter and length through a sol-gel process, and 2) use these rods to reinforce polymeric materials and impart them with anisotropic properties by orienting them in a specific direction through the application of a magnetic field. The first part of the work, i.e., the preparation of the magnetic rods, has been carried out by using a silica sol-gel process developed in our group [1], modified by adding magnetic colloids. These magnetic colloids, with a high affinity for silica, have been used to direct the structure of the silica gel through the application of an external magnetic field. When a static magnetic field is applied, the silica gel structure consists of long parallel rods, loosely bound laterally to one another (Figure 1, left). The diameter of the rods can be controlled by tuning the composition of the sol-gel mixture, from one half to several micrometers. By sonicating these silica gels, single rods can be recovered in large quantities, with precisely controlled diameter (Figure 1, right), and an average length that decreases with increasing the sonication time. The second part of the work consists of first functionalizing the rods with a silane bearing a norbornene moiety, and then disperse the rods in a mixture Cyclooctene, Cyclooctadiene and Norbornene, which can be polymerized via ring opening metathesis polymerization via addition of Grubbs first generation catalyst. The dispersion of the polymer composites so obtained can be controlled by applying a magnetic field during the polymerization process. These rods are randomly oriented in the polymer matrix unless a magnetic field is applied during the polymer same preparation, in which case they are aligned in the field direction. This has been confirmed by electron microscopy and by testing the mechanical properties of the polymer composites, showing clear anisotropy in the case of magnetic rods aligned in the field direction.

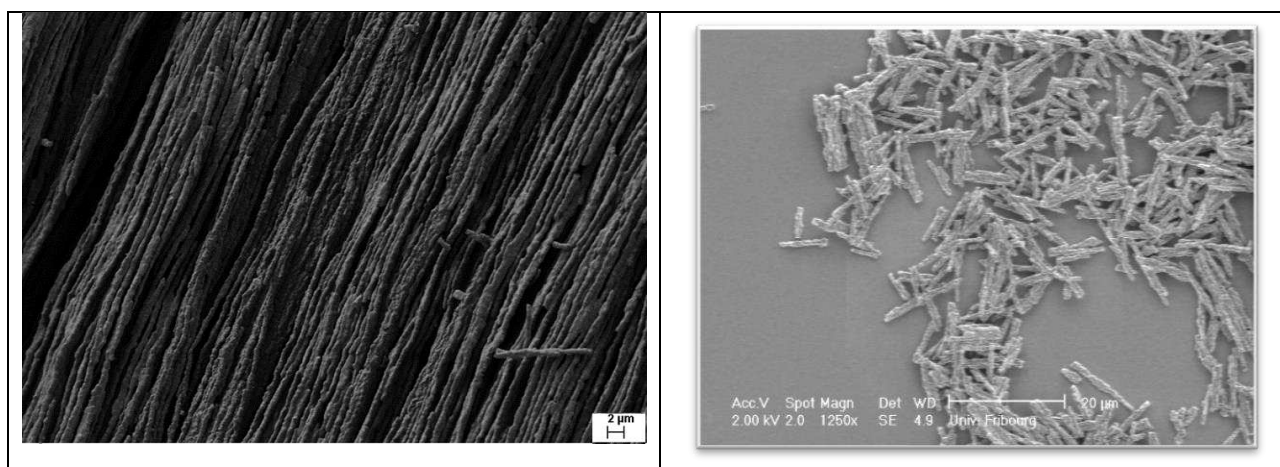


Figure 1. Left: SEM image of a silica gel prepared in the presence of a magnetic field. Right: SEM image of magnetic microrods obtained after sonication of a silica gel.

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A novel scalable method for synthesis of metallic anisotropic particles

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Anisotropic particles are the emerging class of materials where the physical and/or chemical anisotropy of a material not only combine various functionalities in a single body but also may benefit from synergy or the directionality of such properties (Figure 1). The way of the distribution of components in anisotropic particles gives rise to the development of new stimuli-responsive, programmable, synergistic or advanced materials. Janus particles, for instance, exhibit the extreme case of anisotropy, where two components are placed at two opposite sides of the particle (Figure 1a). Synthesis of Janus and other anisotropic structures has been advanced significantly for polymeric materials in last few decades. However, even though the metallic anisotropic structures offer a wider spectrum of properties and application areas, their synthesis is still a challenge as it is complicated and difficult to achieve. The currently available techniques successfully demonstrate the ability of synthesis and immense potential of metallic anisotropic structures in applications; however, they either require very special conditions for synthesis or produce particles with significant defects; therefore, they are far from being scalable. Besides, the examples of material combinations are rather limited.

In this presentation, we will introduce a novel technique for fabrication of metallic anisotropic structures that is simple, robust, scalable and environmentally friendly. The abilities of the technique will be demonstrated on the fabrication of anisotropic Bismuth-Tin (Bi-Sn) and will exemplify its synthesis in various size and forms, including the Janus structure. The particular emphasis will be given to the robustness of the technique as all particles that will be presented are synthesized using the exactly same technique but only with the felicitous control of its synthesis conditions. The topology, chemistry, and crystallographic structure of particles are thoroughly characterized. The chemical distribution in a particle is shown by slicing the particle using focus ion beam technique and show that the anisotropy is not only on the surface (core-shell), but it is throughout the particles (coreless). Therefore, to the best of our knowledge, this technique is the first scalable technique that can produce coreless metallic Janus and other anisotropic structures. In this study, the Bi-Sn system is only considered as a model system, thus the findings can be elaborated on the other systems as the technique allows easy adjustments over other combinations.

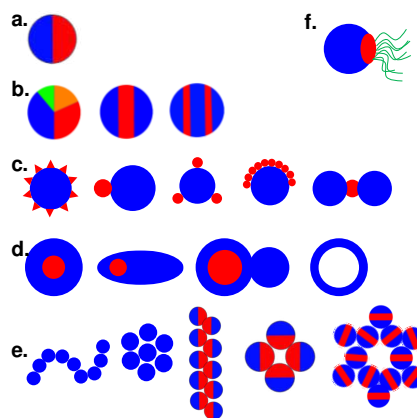


Figure 1. Types of anisotropic particles: a) Janus, b) multi-compartmental, c) Patchy, d) core-shell, e) examples of assembly possibilities. From left to right, complexity increases. f) Functionalized particle. Different colors indicate chemical varieties.

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Optical Characterization of Anisotropic Thiophene-Phenylene Co-oligomer Micro Crystals by Spectroscopic Imaging Ellipsometry

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Here we demonstrate Imaging Ellipsometry as a combination of microscopy and ellipsometry to characterize even micro-sized thin film crystals on plane surface regarding anisotropy, optical properties, crystalline domains and thickness. The semiconducting thiophene phenylene co-oligomer 1,4-bis(5'-hexyl-[2,2'-bithiophen]-5-yl)benzene (dHex-TTPTT) crystals were grown by solvent based self-assembly technique on silicon substrate with 300 nm thermally-grown silicon dioxide (Fig. 1).

The ellipsometric measurements were performed with an Ep4-SE (Accurion). In an ellipsometric high-contrast image of the complete sample we have localized high quality single crystals. After characterization of the biaxial anisotropy of the crystal by using Mueller-Matrix imaging ellipsometry, we performed spectroscopic measurements ($\lambda = 400\text{-}700$ nm in intervals of 5 nm) at the pseudo-isotropic orientations of the sample.

The optical properties were described by using a Lorentz term in the Ep4-Model. After determining the dispersion of the crystals we converted a recorded Delta and Psi-map into a 2D thickness image. Based on a quantitative analysis of the resulting thickness map we have calculated the height of a molecular layer (3.49 nm).

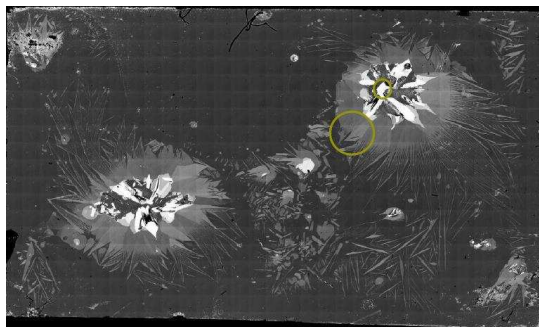


Figure 1. Ellipsometric contrast micrograph of the complete sample with thin thiophene crystals on silicon with SiO₂ (d = 300 nm).

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Preparation of gold nanoclusters, their characterization and application

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Significant development of nanotechnology enabled a preparation of materials with precisely tunable properties on a nano-level usable in many fields, for instance in nano-medicine [1]. Nano-sized aggregates composed of gold nanoparticles (NPs) seem to be a promising cancer treatment. Gold NPs are cyto-compatible, chemically stable and can absorb incoming radiation leading to a temperature increase, what could be used in photothermal therapy or in an analyte detection. Facile surface modification enables a targeting and delivery to a tumour locus in human body or a particular interaction with an analyte.

First, we prepared spherical gold NPs with various sizes from 20 nm to 100 nm and cylindrical gold NPs with various aspect ratios (Fig. 1 upwards) [2-3]. We confirmed unique optical behavior for mentioned shapes of gold NPs. We analyzed them with TEM, UV-VIS spectroscopy and DLS. We self-developed program for shape and size analysis based on DLS measurements. Subsequently, we used spherical gold NPs and prepared spherical gold aggregates sized in units of micrometers via emulsion-templating method (Fig. 1 below) [4]. The best aggregates were obtained with the biggest primary gold NPs and the lowest mass fraction of gold NPs in an initial solution. Then, we prepared fractal aggregates with destabilization of colloidal solution (Fig. 1 below).

In this work, we explored different procedures for preparation of gold nanoparticles and aggregates and new complex analysis of gold NPs via self-developed program.

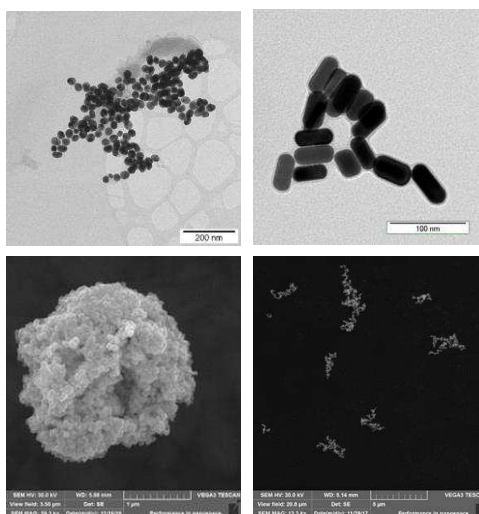


Figure 1. Prepared gold spherical and cylindrical nanoparticles (upwards). Spherical and fractal gold aggregates (below).

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Graphene Oxide/Magnetite Nanocomposites for biomedical application: heterocoagulation vs. heterogenous nucleation

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Potential application of magnetic nanocomposites of graphene oxide (GO) and magnetite (MNP) are a subject of numerous research recently, in the field of medicine as hyperthermic material, diagnostics as MRI contrast agent, molecular biology and environmental technology [1,2].

Among the several synthesis routes for magnetic GO/MNP nanocomposite preparation, such as direct pyrolysis or solvothermal processes, the co-precipitation of magnetic nanoparticles from the mixture of Fe(II) and Fe(III) salt solutions under very alkaline condition is likely the most popular method. In these processes, the in situ crystallization of MNPs takes place on the carbonaceous GO layers (*heterogeneous nucleation*) and usually lead to the simultaneous reduction of GO. We have worked out a one-pot scalable method for the combination of magnetic nanoparticles with graphene oxide nanosheets exploiting the electrostatic interaction between their colloidal particles in aqueous solutions as provided by the development of their opposite surface charge (*heterocoagulation*) [3]. We will present here a comparison of GO/MNP nanocomposites prepared via one-pot scalable method under mild conditions and a low-cost in situ chemical precipitation method. In both processes, the GO/MNP ratio was varied from the low to the high coverage (from 1/5 up to 1/50).

Electrokinetic potentials and Z-average particle diameters of the GO/MNP nanocomposite in aqueous dispersions as a function of the GO/MNP mass ratio, and magnetization measurements and heating curves in AC magnetic fields of nanocomposite dispersions were compared as well. The heat production of nanocomposites with the same magnetite contents (5 mg/ml) was 36 and 46 % higher for 1/5 and 1/50 GO/MNP, respectively, than that of pure MNPs after 5 minutes of AC magnetic field exposure (109.4 kHz, 24.7 mT).

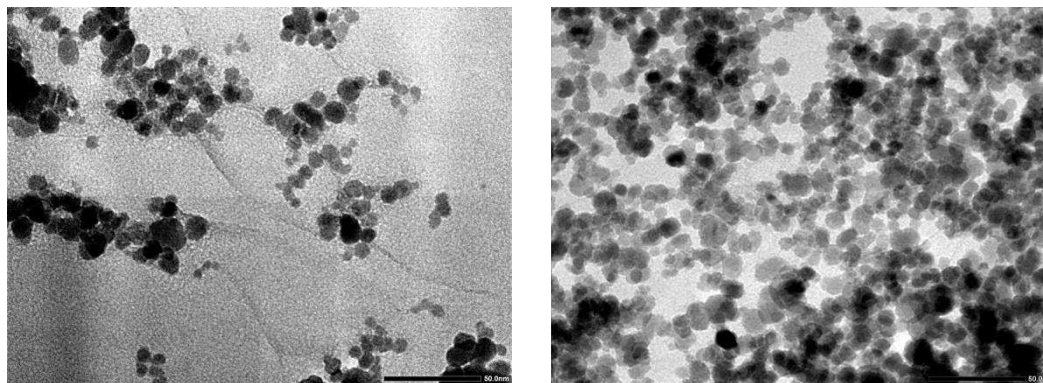


Figure 1. TEM images of composites with GO/MNP mass ratios of (left) 5 to 1 and (right) 1 to 50

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A Study on Film Formation and Fluorescence Enhancement of Silver Nanoparticle Doped Polymer Composites

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In this study, film formation and fluorescence enhancement of silver nanoparticles (AgNPs) doped pyrene (P) labeled polystyrene (PS) composites were investigated depending on annealing temperature and AgNPs content. Nine powder films with different AgNPs content (0-50 wt%) were prepared by using drop casting method. All of powder films were annealed at various temperatures between 100 °C and 250 °C with 10 °C temperature increment, separately. After each annealing step, steady state fluorescence (SSF), fast transient fluorescence (FTRF) and photon transmission (UVV) techniques were used to monitor film formation and enhancement processes. The classical latex film formation was observed in the range of 0-30 wt% of AgNPs content [1]. Above this range, instead of continuous films, partially film formation is seen and transparency of films decreased drastically with increasing AgNPs content. Fluorescence enhancement and reduced lifetime were also observed with increasing AgNPs content due to the interactions between the pyrenes and the electron plasma in nearby silver nanoparticles [2,3]. At 100 °C, it was seen that the presence of AgNPs has almost no effect on fluorescence intensity indicating that no coupling occurs between pyrene and silver nanoparticles at this temperature. However, at 250 °C, the enhancement effect (I_{enc}) was particularly evident above 1 wt% AgNPs, where nearly a 4 fold enhancement is observed for 10 wt% of AgNPs content (Figure 1). In addition, enhancement effect seems to disappear above 20 wt% of AgNPs content indicating that fluorescence quenching [3,4] occurred once pyrenes immediate contact with the AgNPs particles due to interdiffusion of polymer chains.

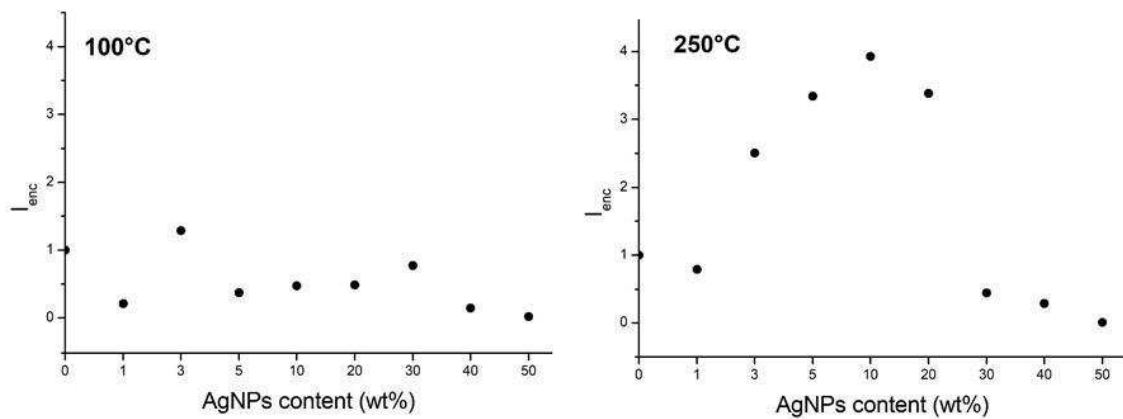


Figure 1. Fluorescence enhancement rate (I_{enc}) versus AgNPs content at 100 °C and 250 °C annealing temperatures, respectively.

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Macroporous polymer-supported ionic liquid like system for enzymatic catalysis

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In this work we report the synthesis and application of polymeric macroporous materials functionalized with ionic liquid-like compounds to serve as a support for enzyme attachment. The method is based on bottom-up approach where polymeric nanoparticles are used as a building blocks.

First, poly(styrene-divinylbenzene) (PS-DVB) core-shell nanoparticles (NPs) containing chloromethyl styrene were synthesized. The macroporous polymeric support was then prepared by salt-induced aggregation of the NPs under static condition followed by reactive gelation of monomer swollen particles [1]. BET isotherm and mercury (Hg) porosimetry were used to characterize main porous properties such as specific surface area and pore size distribution (PSD), respectively. Second, 1-butyl imidazole was introduced into the PS-DVB support to form ionic liquid-like imidazolium, which was consequently used for an enzyme immobilization on the porous surface. To demonstrate enzymatic activity urease catalysing urea conversion into CO₂ and ammonia was used as a model system.

The catalytic activities of the urease were evaluated during the hydrolysis of urea into carbon dioxide and ammonia by measuring changes in pH and by color change of cresol red indicator. The results showed that pH of the urea solution increased over time due to the increasing amount of ammonia as a product of the catalytic reaction. The increase in pH was also confirmed by the color change of cresol red from yellow-orange to purple. Overall, our results indicate that the polymeric supports can combine the advantages of macroporous and IL-like systems for enzymatic catalysis.

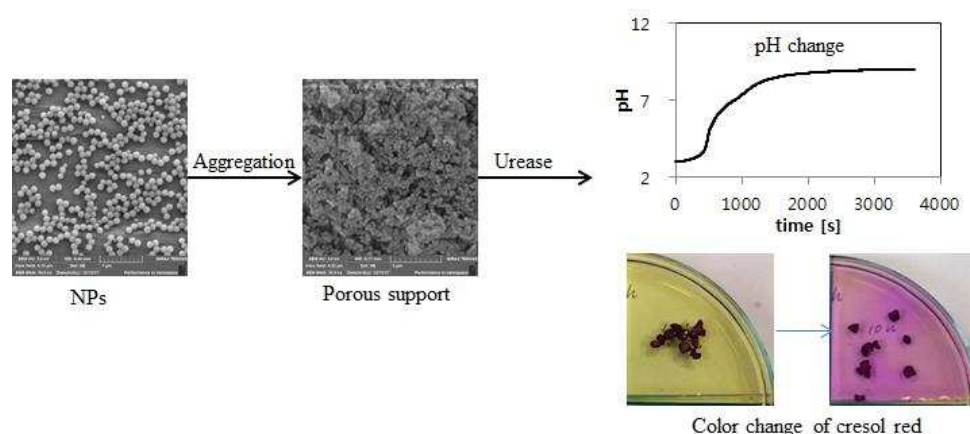


Figure 1. From preparation of porous support to urease catalytic reaction.

Acknowledgements: The financial support of Grant Agency of Czech Republic (Grant No. 16-22997S) is greatly acknowledged.

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Advanced Light Scattering techniques for the characterization of nanostructures

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Static (SLS) and dynamic (DLS) light scattering are powerful optical techniques that are employed to characterize the dynamics and structure of colloidal systems. Accurate characterization using SLS and DLS methods mandates the measurement and analysis of singly scattered light. In turbid samples, the suppression of multiple scattering is therefore required to obtain meaningful results. One powerful technique for achieving this, known as modulated 3D cross-correlation, uses two temporally separated light scattering experiments performed at the same scattering vector in the same sample volume, in order to extract only the single scattering information common to both [1,2].

The performance of this 3D technology can be further enhanced through optical path length reduction. The ability to modify the position of the sample cell by means of a sample goniometer enables the reduction of multiple scattering, thus enhancing the signal quality significantly.

Moreover, if one obtains “clean” single scattered data with no signal contamination by multiple scattering, accurate sample characterization can be greatly enhanced by the theoretical estimation of the detected 3D joint intensity statistics and advanced processing of the measured data.

In this presentation, we will give an overview of the enhanced modulated 3D cross-correlation technology. We will show how it enables us to fully suppress multiple scattering even in very turbid nanoparticle suspension while maintaining a high signal quality. The performances will be evaluated through a SLS study by measuring the structure factor of highly concentrated suspensions.

We will successively present a DLS study of these suspension by estimating their particle size distribution through a novel data treatment procedure based on non-linear weighted integral inversion. We show that this novel procedure outperforms the most widely used classical techniques of CONTIN and CUMULANT analysis. In both cases we will show examples which to our best knowledge have not been correctly measured ever before.

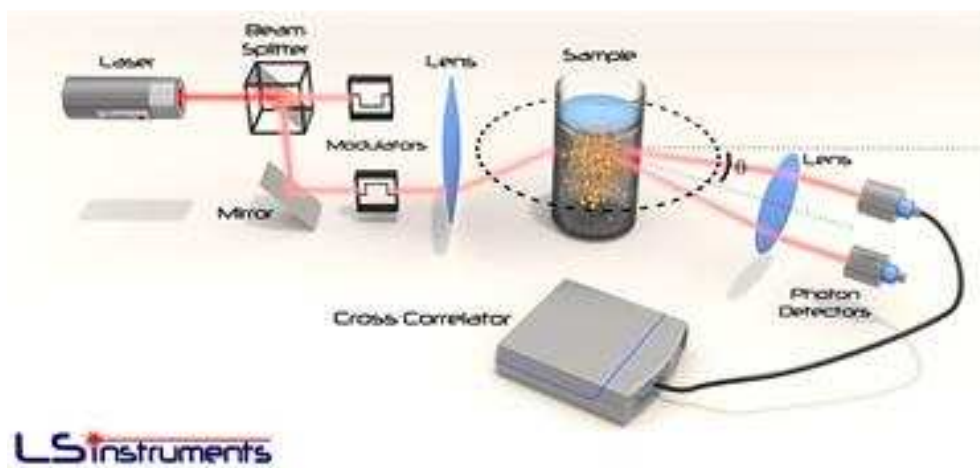


Figure 1. Schematic representation of the modulated 3D cross-correlation set up.

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Interactions of functionalized magnetite nanoparticles with phospholipids in models of biological membrane

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In recent years magnetite nanoparticles (MNP) have attracted great attention of scientist due to their specific properties important for biomedicine such as small size, wide chemical affinity and superparamagnetism resulting in their application potential in magnetic resonance imaging, targeted drug delivery, separation and purification of biomolecules and therapies based on hyperthermia. Functionalization of magnetic nanoparticles surface with bioactive polymers can improve their biocompatibility and dispersity in biological membranes. However, the knowledge on interactions of MNPs with biological systems, especially these functionalized with bioactive polymers, is still limited. This knowledge can be expanded thanks to research on behavior of MNPs in contact with model biological membranes. Model membranes are simplified systems that allow for control many of chemical and physical parameters. Native membranes are generally composed of different lipids as well as functional proteins, whereas the simplified experimental membrane models are mainly formed by phospholipids and controlled number of other components. The great advantage of applying model membrane, e. g. Langmuir monolayer, is their simplicity and possibility of avoiding difficulties during the experiment related to contact with biological fluids and cells.

Here, we present the studies on interactions of MNPs functionalized with starch or chitosan with models of biological membranes, which have been made of different types of phospholipids, such as DPPC, DPPG, POPC, DSPC, etc., using Langmuir technique. We have performed three types of experiments:

- compression of co-spread mixtures of MNPs and phospholipids on the pure water subphase,
- compression of phospholipid monolayers on the water subphase containing different amount of MNPs,
- investigation on kinetics of MNPs adsorption process from water into phospholipid monolayers in different compression states of the monolayer.

During these experiments compression isotherms and Brewster Angle Microscopy (BAM) images were recorded. Subsequently, the films were transferred onto mica substrate for characterization their magnetic properties using magnetic force microscopy (MFM) and superconducting quantum interference magnetometer (SQUID).

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Preparation of hierarchically structured microsieves for filtration processes

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Particle-loaded air and water, like from traffic or industry, and natural sources, such as pollen and bacteria, strain people and disturb industrial processes [1,2]. One possibility to minimize these particles is the filtration [1,2]. Until now mainly fiber filters are used [3]. However, these filters are usually not regenerable and cause high energy costs because of a high pressure drop across the filter [3]. To overcome these disadvantages, microsieves can be used. Microsieves have a uniform pore size and a membrane thickness which is lower than their pore diameter [4]. Moreover, they do not have a branched and complex pore system [4]. This results in a low flow resistance [4].

Microsieves first were outlined by van Rijn with the technique of photolithography [3]. One other technique to produce microsieves is the float-casting process. With this technique, mixtures of hydrophobic colloidal spherical particles and a hydrophobic liquid form wetting layers on a water surface (even though the liquid is non-wetting – therefore, the process is also called particle-assisted wetting) [5]. This approach made it possible to form a hierarchically structured microsieve from three differently sized sieves (see Figure 1). The large-pored microsieve has a pore diameter of about 53 μm , the medium-pored of about 6 μm and the fine-pored sieve, which is the actual filter membrane, of about 325 nm.

Mass flow measurements with water show that these hierarchically microsieves have a much higher permeability coefficient than common cellulose acetate and polymeric netlike membranes with comparable pore sizes. The filtration performance and also the permeability (for comparison with the experiments) can be predicted with the software GeoDict® (see figure 2) [6]. This makes it possible to predict the performance of new pore sizes and combinations of microsieves before the complex manufacturing process.

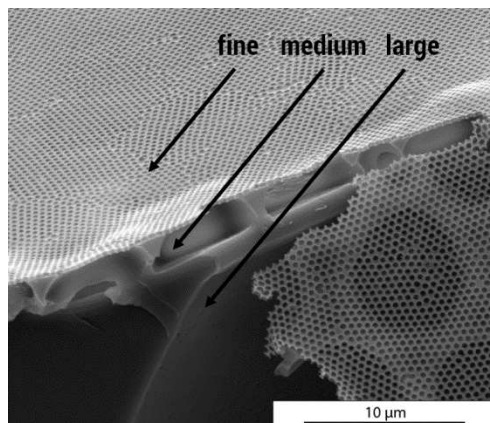


Figure 1. SEM image of the cross section of a microsieve.

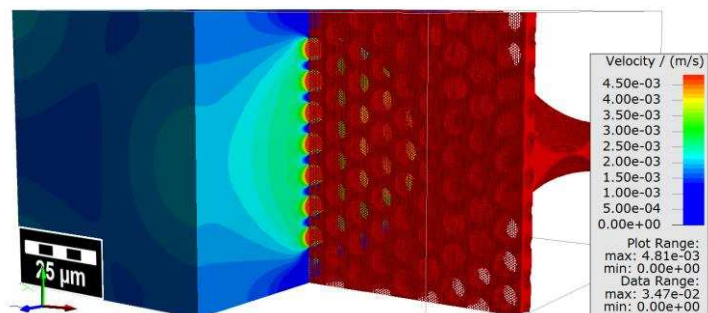


Figure 2. Calculations of the inflow velocity of water of a hierarchically structured microsieve.

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Water Adsorption Induced Forces and Volume Change in Cementitious Materials with Slit-Micropores

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Based on a macroscopic model, molecular simulations, and experimental studies, we discuss the adsorption behavior of differently treated and prepared Portland cement paste on changing relative humidity. Hardened cement paste is of outstanding technical importance, its drying, shrinkage, and swelling due to variation of the relative humidity are important for durability, resilience, and design of concrete members. At low humidity, liquid water is already present in slit-shaped micropores. In several types of concrete compositions, pronounced hysteresis of water vapor sorption and volume change of the solid structure can be observed. Experimental results for water sorption experiments on hardened cement paste revealed a pronounced hysteresis at low humidity, which is linked to the presence of micropores and related to volume-change.

Adsorbed water can exert strong capillary forces changing the volume of pores embedded in elastic solids. Our macroscopic model predicts a pronounced sorption hysteresis for soft materials with slit-shaped micropores. The proposed model can also explain the origin of hysteresis in more rigid materials such as hardened cement pastes with a large fraction of micropores. We have developed a theoretical model that can explain hysteresis and its relation to hysteresis of swelling and shrinkage based on water sorption in micropores and interlayer water [1-3]. The model reproduces important topological features of sorption isotherms in relation to the amount of micropores as well as the different types of isotherms of water and nitrogen sorption for low vapor pressures. Understanding and interpreting experimental sorption diagrams as well as the swelling and shrinkage of hardened cement paste in the whole humidity range requires consideration and improved modeling chemical details of slit-pore walls within C-S-H phases by computer simulations.

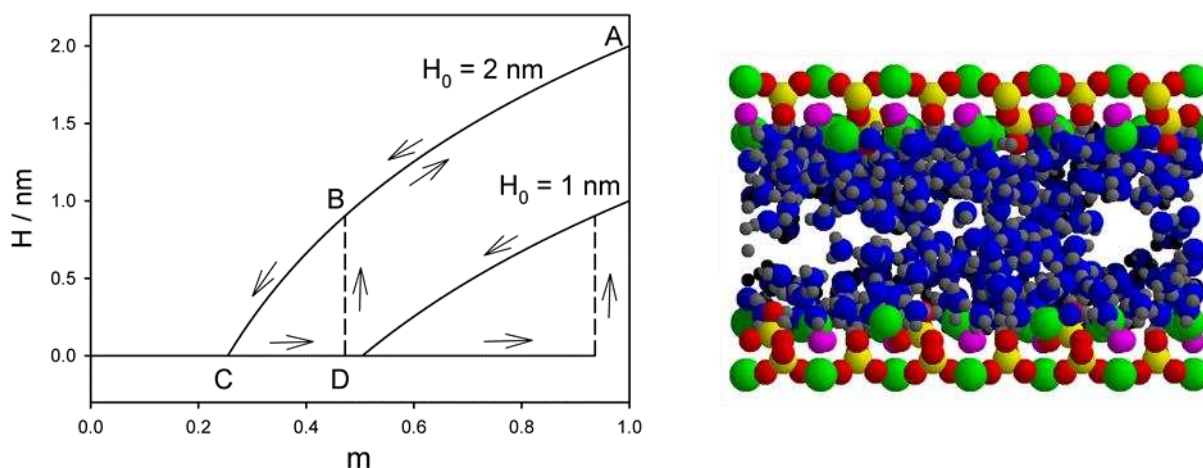


Figure 1. a) Calculated hysteresis of water adsorption in slit-micropores for $H = 2\text{ nm}$ and $H = 1\text{ nm}$, H : width of slit pore, m : humidity, A-B-C: desorption branch, C-D-B: adsorption branch. **b)** Snapshot from Monte-Carlo-simulation: water bridges at humidity 0.9 between slit-walls in a Tobermorite-derived C-S-H model at lamellar repeat distance of 2.4 nm (green: Ca, red: O, Yellow: Si, blue/grey: water).

Acknowledgements: This work has been supported by the German Research Foundation (DFG) through grant DFG MO-600/9-2.

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From delamination to sol-gel synthesis: the role of organic molecules in LDH formation

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Layered double hydroxides (LDHs) represent a diverse class among lamellar materials with ion exchange capacity. Due to their versatile composition, they possess multiple potential applications from catalysis to medicine [1].

In this comprehensive study, we examined the exfoliation, restacking and synthesis of $\text{Mg}_2\text{Al-LDH}$ in the presence of organic liquids. Exfoliation was carried out in amides and alcohols with formamide and 1-octanol as the most effective agent to form stable colloids in the hydrating solution. Aqueous restacking with sodium salts, however, was generally successful, but without the incorporation of the present anions. Furthermore, crystals with unique symmetry were produced from 1-octanol, hence we began to investigate the effects of different alcohols during the common co-precipitation method. It was found that alcohols with medium chain length (6-8 carbon atoms) assist the formation of regular crystals, thus have similar effects that smaller, water-miscible alcohols [2]. Similar observations were made after stirring the material in pure alcohols for $\text{Ca}_2\text{Al-LDH}$, too.

Moreover, a novel-type sol-gel method was developed to obtain $\text{Mg}_2\text{Al-LDH}$ and $\text{Ca}_2\text{Al-LDH}$. In this organic solvent-free process, a mix of two metal alkoxides were added to water or sodium nitrate solution with or without pre-set basic pH. For the synthesis of Mg-containing LDH, the lack of nitrate was advantageous, but $\text{Ca}_2\text{Al-LDH}$ was only purely prepared using NaNO_3 and neutral pH. The morphology of the samples was excellent and they had high purity, as well. In addition, the size of $\text{Ca}_2\text{Al-LDH}$ obtained by alcohol assisted co-precipitation and sol-gel treatment was remarkably high, grains with a diameter of 10-20 microns were observed.

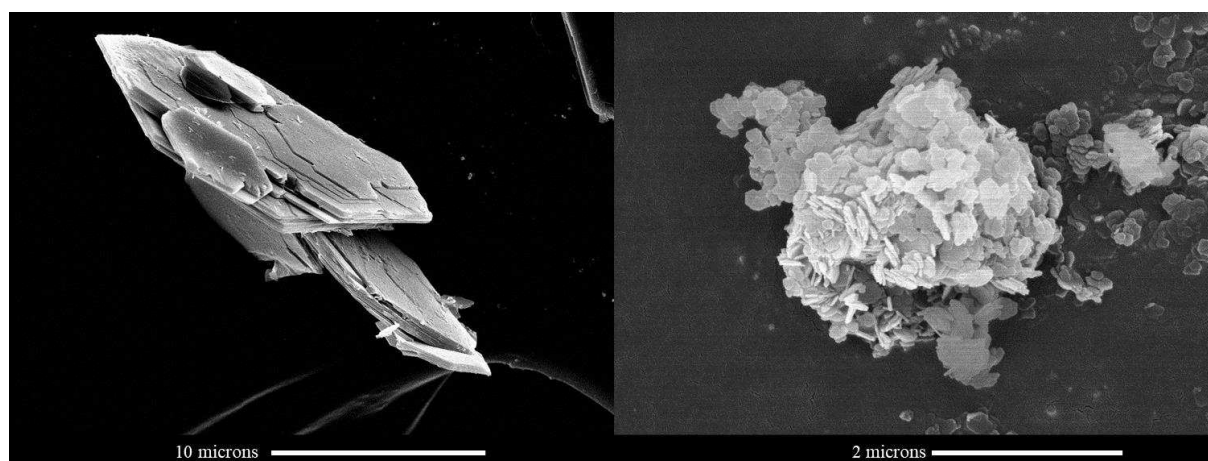


Figure 1. SEM image of $\text{Ca}_2\text{Al-LDH}$ via co-precipitation with 2-ethyl-1-hexanol (left) and $\text{Mg}_2\text{Al-LDH}$ via sol-gel process (right).

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Modification of imogolite with alkylphosphonic acid: a new hybrid lamellar phase

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Imogolite is a natural clay mineral of nano tubular structure with a $\text{Al}_2\text{SiO}_3(\text{OH})_4$ repeating unit. Due to its one dimensional structure and asymmetric nature between internal and external surfaces it features specific properties (liquid-crystal formation, catalysis, etc.) [1]. To enrich their potential applications the surface functionalization of imogolite has been the subject of intense research in the last years. For the external surface, most grafting reactions aim to hydrophobize the naturally hydrophilic external surface in order to disperse the tubes in organic media [2]. Dispersing the tubes can lead to improved matrix properties of polymer composites (i.e. mechanical toughening) [3] or self-assembled membranes [4].

One of the most studied grafting agent families are the alkylphosphonic acids. A strong reactivity between the tubes and the phosphonic acid moiety has been described. The resulting material shows altered properties regarding the unmodified tubes, including the stabilization of Pickering emulsions [4]. However, the integrity of the tubular structure is questionable after modification for most studies.

We revisited the surface modification of imogolite with decylphosphonic acid and investigated on the reaction product by X-ray Scattering, Fourier Transform Infra-Red and Magic-Angle Spinning Nuclear Magnetic Resonance spectroscopy. Our results evidenced the transformation of imogolite into a lamellar phase with unexpected interfacial properties [5].

When the material is dispersed in toluene it stabilizes aqueous droplets at the toluene/water interface. The ability to prevent the coalescence of the droplet with the bulk phase builds over time and is not present when the toluene/water interface is initially formed. The origin of these properties has to be related to the specific structure of the hybrid material.



Figure 1. A water droplet stabilized on the interface between toluene (upper phase) and water (lower phase). Stabilization is achieved by dispersing a lamellar compound in the organic phase.

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Preparation of Heterogeneous Catalyst Containing Palladium Nanoparticles Incorporated in Hydrogel Microparticles

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Palladium (Pd) has valuable catalytic properties and is currently being used as homogeneous and heterogeneous catalysts in the synthesis of many chemicals. However, since palladium is an expensive noble metal, it has a great influence on the manufacturing cost in the production of chemical materials. Therefore, the recovery and reuse of Pd catalyst are very important in catalytic chemical processes using palladium. In recent, as the production of metal nanoparticles has progressed actively, many researchers also study palladium nanoparticles (PdNPs) as catalysts for the production of various chemicals. In addition, heterogenization or immobilization of PdNPs is one of the most important research topics for easy recovery and reuse.

Here, we report the heterogenization of PdNPs on hydrogel microparticles. In order to maximize the advantages of the excellent heterogeneous catalyst, a hydrogel, which is a porous material having a low diffusion resistance, was used as a catalyst support and catalysts were formed into a micrometer size that was easy to recover. Further, the enhancement of stable immobilization of PdNPs on hydrogel polymer network was induced by using hydrogen-bondable polymer linking material between hydrogel polymer chains and PdNPs stabilizer. The PdNPs were synthesized by microwave-assisted polyol process with polyvinylpyrrolidone (PVP) and water-soluble Pd precursor. The prepared PVP-stabilized PdNPs were introduced into the hydrogel microparticles through the micromolding method, which can provide the uniform size and shape hydrogel microparticles, using a photocurable hydrogel precursor (polyethylene glycol diacrylate: PEGDA) and a hydroxyl group-containing polymer (polyethylene glycol: PEG). The prepared PdNPs-containing hydrogel microparticles were washed out with ethanol to remove unreacted materials and residual PEG and PdNPs. The catalytic activity of the prepared catalyst was confirmed by the hydrogenation of 4-nitrophenol to 4-aminophenol.

The prepared PdNPs-containing hydrogel microparticles catalysts showed uniform micrometer sized and the recovery of the catalyst was very easy by a simple method such as filtration or centrifugation from the reaction mixture. PdNPs immobilized on the polymer network of the hydrogel exhibited excellent stability to maintain immobilization stability even after being left in the solvent for a long time. Finally, the heterogenized PdNPs containing hydrogel microparticle catalysts exhibited excellent catalytic activity and were stable even after reuse of storing in the solvent. These indicate that the polymer doped noble metal nanoparticles can be applied to this method and will be useful for various liquid phase chemical reaction.

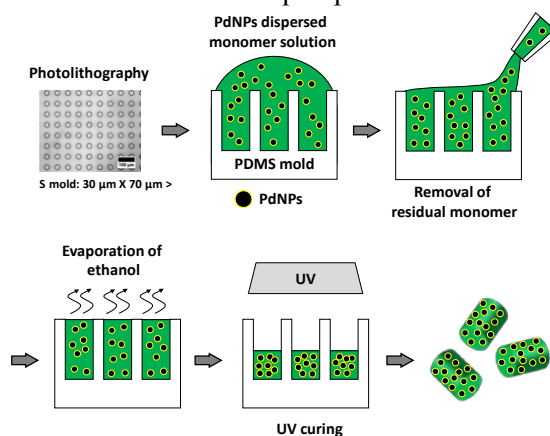


Figure 1. Preparation of hydrogel microparticle catalysts containing PdNPs of uniform size using micromolding method.

CNT/Pd Nanocolloids/Poly(vinyl chloride) Hybrid Thermoelectric Materials for Energy Conversion

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Fundamental materials for nanoscience and nanotechnology are expected to be provided by organic-inorganic hybrid complexes. Most of the remarkable properties of metal nanocolloids are based on high surface area and quantum size effect. Metal nanocolloids have been applied to various fields. They are used as catalysts in solution for various organic reactions such as hydrogenation, hydrosilylation, hydrogen generation, hydration, oxidation, C-C bond formation, dehalogenation, and so on. Other applications include hydrogen storage, sensor, optical devices, electric circuit, magnet, drug, and so on. From the viewpoint of global problems for human beings, improvement of information technology and energy conversion is very important. Our group has been interested in organic-inorganic hybrid systems consisting of a polymer and metal nanocolloids [1,2]. In a previous study, we found that the thermoelectric power factor of polyaniline thin films could be increased by dozens of times by hybridization with Bi₂Te₃ nanocolloids. In a recent study, we reported a hybrid system composed of PEDOT-PSS and spherical Au nanocolloids. We used several kinds of Au nanocolloids with different protecting ligands and found that some of the Au nanocolloids were effective as additives to improve the thermoelectric properties, especially the electrical conductivity, of the PEDOT-PSS hybrid films. In this study, we focus on another hybrid system consisting of carbon nanotubes (CNTs), Pd nanocolloids and poly (vinyl chloride) (PVC).

Pd nanocolloids protected by dimethylformamide were prepared by a refluxing method in aqueous of palladium(II) acetate and CNTs. Contaminants like ions in the dispersions were removed by washing the dispersions three times with ethanol by using a membrane filter. Complete removal of the solvent and volatile byproducts by vacuum evaporation gave CNT/Pd nanocolloids hybrids. The CNT/Pd nanocolloids/PVC hybrid films were prepared by a conventional drop-casting method from the mixed dispersion of CNTs, Pd-colloids and PVC in NMP at the designed ratios on a polyimide substrate. Seebeck coefficient and electric conductivity of hybrid films were measured with a thermoelectric evaluation system (ZEM-3M8) at 330-380 K under vacuum with helium gas at least three times.

Figure 1 shows transmission electron micrograph of the obtained CNT/ Pd nanocolloids. The most Pd nanocolloids have the average diameter of 1.9 nm and relatively small standard deviation. The power factor of CNT/ Pd nanocolloids /PVC hybrid films was 1.4 times higher than that of the CNT/PVC. The hybrid films have high thermoelectric performance due to the effective dispersion of Pd nanocolloids and the enhancement of the carrier transport between CNT/PVC and Pd nanocolloids.

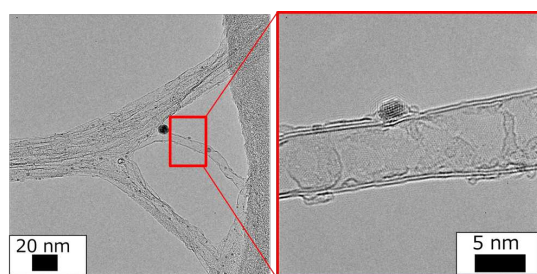


Figure 1. Transmission electron micrograph of CNT/Pd-colloid hybrids.

Acknowledgements: This work was supported by MEXT, NEDO and ZEON Corporation, Japan project on “Development of high-density energy devices using nano carbon materials”.

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Hierarchical multiphase magnetically separable Ru-based nanocomposites for the catalytic hydrogenation/hydro-deoxygenation of eugenol

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The synthesis of valuable chemicals from biomass using a simple and energy-efficient process is a global challenge. Noble metal nanoparticles such as ruthenium (Ru) are especially efficient catalysts for the hydrogenation and transfer hydrogenation reactions involved in converting biomass or CO to important chemicals [1,2]. Because they are expensive it is desirable to fabricate easily separable support. Magnetically separable support is one of such. Among other factors, such as the catalyst particles' morphology and size, the nature of the support can have a significant influence on the catalyst's activity and selectivity. Many studies revealed that carbonaceous materials are a suitable support due to their non-reducibility and the electronic interactions between the support and the catalyst [3,4].

Magnetic carbon based supports were synthesized by hydrothermal carbonization of sucrose dissolved in aqueous colloidal suspension of magnetic iron oxide nanoparticles followed by annealing in an atmosphere of Ar at 300 °C, 500 °C, 600 °C and 750 °C. Powders were dispersed in isopropanol by milling and Ru nanoparticles were deposited on the magnetic support by solvothermal reduction of Ru(acac)₃. Prepared catalysts were tested for simultaneous hydrogenation and deoxygenation of eugenol- a lignin monomer model compound.

The temperature of annealing had a strong impact on surface properties, composition and morphology of magnetic support. Non-annealed support was rich with surface O functional groups, which content significantly decreased when annealed above 500 °C. Carbonaceous matrix gradually transformed from amorphous sp³ hybridized C to graphitic nanocrystalline C. Magnetic phase remained as iron oxide till 500 °C, at 600 °C a small amount of non-magnetic wustite formed and at 750 °C all of the iron oxide was transformed to Fe and Fe₃C, strongly increasing the magnetization. Deposition of Ru was influenced by the temperature of annealing (Figure 1). Practically no Ru deposited on non-annealed support and only a small amount of non-uniformly dispersed Ru nanoparticles on support annealed at 300 °C. At higher temperatures the dispersion was uniform and average size of Ru nanoparticles decreased from 2.7 nm (support annealed at 500 °C) to 1.5 nm (support annealed at 750 °C). Prepared nano-catalysts showed remarkably different catalytic activity.

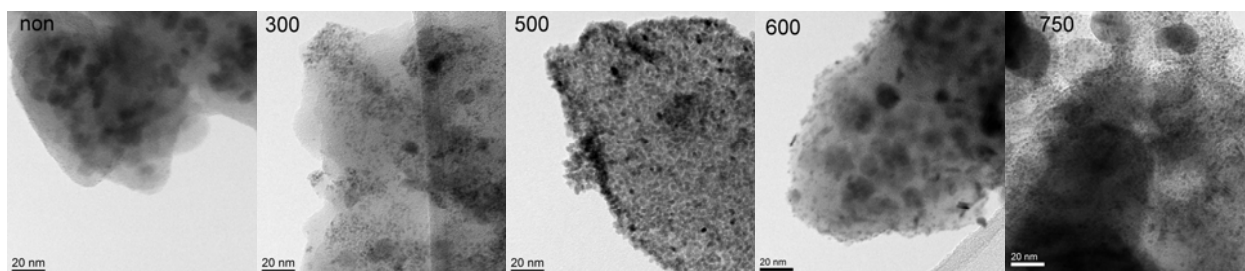


Figure 1. TEM images of catalysts prepared by annealing magnetic support at different temperatures.

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Rattle-type colloidal crystals incorporating a movable silica/titania core developed for switchable materials

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Colloidal crystals, composed of monodisperse particles, should be one of promising optical materials because of their angle-dependent colour following the Bragg's law. Rearrangement of the particles is commonly required for varying the optical property of colloidal crystals. We have focused on rattle-type particles, which are hollow particles incorporating a core, to be employed as building blocks of the colloidal crystal with a switchable optical property. The optical property of the rattle-type particles could be controlled reversibly by switching the location of inner cores via external stimuli such as a magnetic and/or an electric field. A previous work reported by our group demonstrated that micron-sized, magneto-responsive cores incorporated into hollow particles were attracted each other in the 2D colloidal crystal of the particles by the application of a magnetic field [1]. For submicron-sized cores in the crystal, the core motion was also tuned by the application of an external electric field [2]. Since the optical property of colloidal crystals depends on the refractive index of the building blocks comprising colloidal crystals, employment of highly refractive cores such as titania cores could be a useful approach to improve their optical properties. In the present work, we firstly synthesized two types of rattle-type particles incorporating silica (SiO_2) cores and SiO_2 cores coated with titania ($\text{SiO}_2@\text{TiO}_2$), respectively. Secondly, 3D colloidal crystals of the two rattle-type particles were fabricated to be measured for their reflection spectra. Thirdly, the motions of inner SiO_2 and $\text{SiO}_2@\text{TiO}_2$ cores were compared under the application of an external AC electric field.

Figure 1(a) shows the TEM image of $\text{SiO}_2@\text{TiO}_2$ rattle-type particles. The size of rattle-type particles and $\text{SiO}_2@\text{TiO}_2$ cores were approximately 810 nm and 310 nm, respectively. The element mapping of Si and Ti showed that the SiO_2 particles were coated with a thin TiO_2 shell. According to the reflection spectra shown in Figure 1(b), the angle-dependent peaks were measured by the 3D colloidal crystal of $\text{SiO}_2@\text{TiO}_2$ rattle-type particles, suggesting the assembly of the particles were highly ordered. Compared to the spectra acquired from the crystal of SiO_2 rattle-type particles, the peaks were slightly red-shifted. The motions of these cores under the electric field were observed with an optical microscope. The $\text{SiO}_2@\text{TiO}_2$ cores moved parallelly to the direction of applied electric field, whereas the SiO_2 cores exhibited perpendicular motion to the direction inside the hollow sphere. The difference in core motions was probably caused by high permittivity of titania components. The result indicated that employment of building blocks with different dielectric constants could vary the field-induced motion of inner cores in the colloidal crystals.

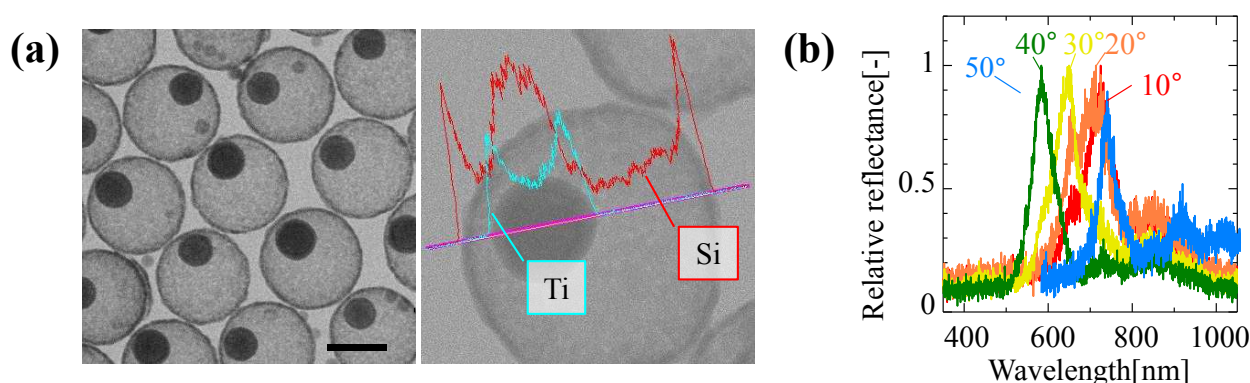


Figure 1. The TEM image and EDX mapping of $\text{SiO}_2@\text{TiO}_2$ rattle-type particles (a) and the reflection spectra measured in 3D colloidal crystal of $\text{SiO}_2@\text{TiO}_2$ rattle-type particles (b).

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Electron-beam induced growth of organic 3D nanodendrites on the meteorite surface

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In [1], the use of decomposition of a precursor (a metal-containing gas) for the growth of thin metal lines in an electron microscope was first reported. Works similar to [2] are aimed at developing this method in the practice of industrial use.

Amino acids and their precursors exist in interstellar clouds, comets and on a surface of meteorites. Possibly at the origin of the organic matter in space, this material may be considered as a potential source for prebiotic chemistry on planets. In this work the influence of a stream of electrons on the organic substances which are on a surface of meteorites is studied at low temperatures and high vacuum.

The experimental system is a transmission electron microscope (base pressure 10^{-7} Torr) equipped with a variable temperature in microscope (90-300 K). For a substrate a polished thin plate (50 μm), with several holes, made of an iron meteorite "Sikhote Alin" has been used. Growth 3D nanodendrites (NDs) from paraffin, stearic acid triglyceride, and 20 essential amino acids on a substrate from a meteorite have been studied (Fig.1). The analysis shows that the relation between the length and the diameter of structural elements of NDs can vary to a large extent from 1:1 to 50:1 and depends on many factors. The speed of growth of NDs can vary to a large extent to 10 nm/s. The mechanism of growth of NDs, including initial lasting inductive period, forming a leader with the diameter of 2 nm and length to 10 nm and further periodic growth of NDs, consisting of short intermediate periods, with thickening of the leader was suggested. In our option this researched electron beam induced growth of NDs on the surface of polymeric systems can be related to electrokinetic phenomena.

This phenomenon can be interesting for the origin of life theory and radio biology, and also allows creating industrial manufacturing techniques of materials with the developed nanostructured surfaces.

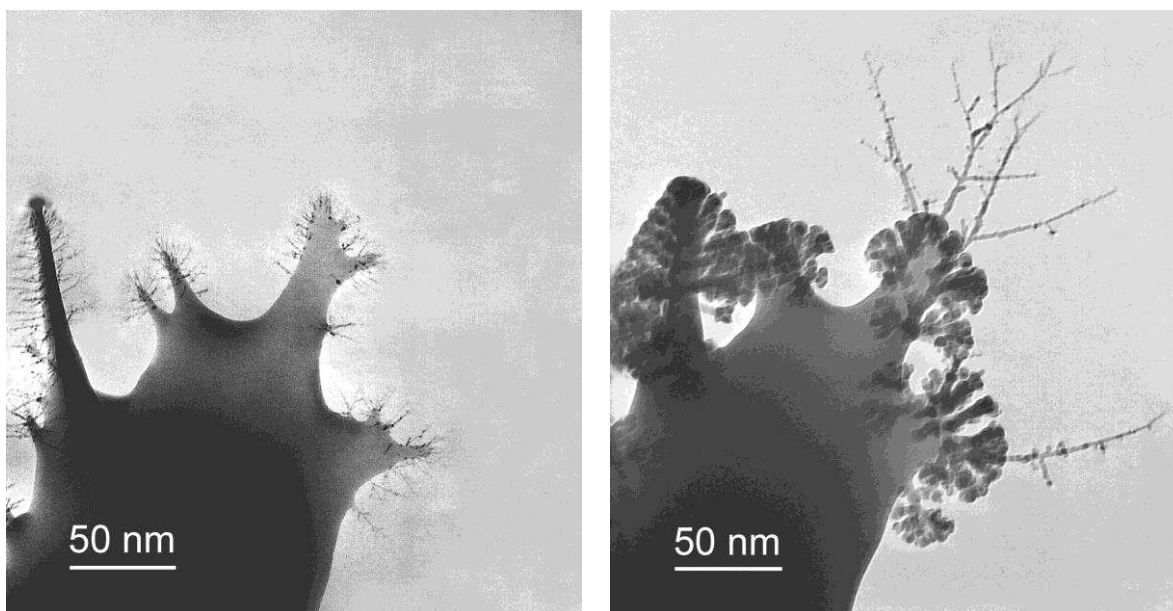


Figure 1. Primary and secondary growth the 3D nanodendrites from D-L-valine on a substrate from a surface of meteorite "Sikhote Alin" (95 K, 10^{-7} Torr)

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Fluorescent nanoparticles coated with mesoporous silica shell with tunable shell thickness and pore size distribution

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Up-converting nanoparticles (UCNPs) doped with rare-earth ions which can emit visible light after excitation by near-infrared light are attracting appreciable attention due to their unique optical properties such as long fluorescence lifetimes and narrow emission peaks. Thanks to these properties UCNPs exhibit great potential in many fields such as medicine, biotechnology or electronics [1, 2]. UCNPs produced by the various methods have good optical properties and narrow size distributions, but are capped by hydrophobic ligands [1, 2]. As a consequence, the surface of such UCNPs has to be modified to ensure excitation by near-infrared light are attracting appreciable attention due to their unique optical properties such as long fluorescence lifetimes and narrow emission peaks. Thanks to these properties UCNPs exhibit great potential in many fields such as medicine, biotechnology or electronics [1, 2]. UCNPs produced by the various methods have good optical properties and narrow size distributions, but are capped by hydrophobic ligands [1, 2]. As a consequence, the surface of such UCNPs has to be modified to ensure water solubility. One of the most used methods of surface modification is coating UCNPs with amorphous silica shell. The ability to obtain the mesoporous silica layer with specified porosity degree is very important for biological applications, because concentration of drug molecules is directly correlated to particle size, surface area, and pore geometry.

Our team has developed a novel, versatile and universal procedure for direct coating of up-converting nanoparticles with a uniform mesoporous silica layer via a facile two-phase system [3, 4]. The coating is carried out in a biphasic system in which silica precursor is delivered heterogeneously from a top organic layer to the bottom aqueous layer containing a base catalyst and UCNPs stabilized by surfactant. The proposed procedure allows to easily control the morphology and the properties of the silica shell by performing the interfacial polymerization of the silane monomers under different synthesis parameters (catalyst, solvent, hydrophobic chain length of surfactant).

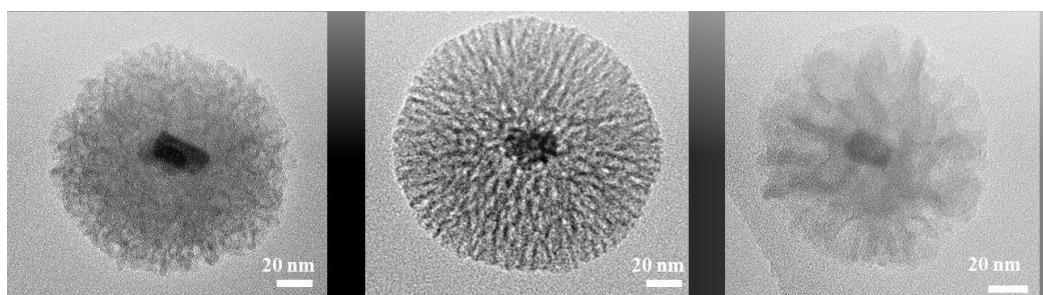


Figure 1. TEM images of UCNp@SiO₂ synthesized with various surfactants.

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Effective Bone Tissue Engineering Using Silk Fibroin Nanofiber/PGA Hybrid Scaffolds Fabricated by Electrospinning and 3D Printing Techniques

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Bone tissue engineering aims regeneration of defected biological bones by combining cells, scaffolds, and growth factors. However, growth rate of bone tissue components are slower than adjacent soft tissues. Therefore, defected bone tissues are required a barrier membrane and a scaffold in consideration of guiding ability, biomechanical property, dimensional restoration of a target tissue. Here, we prepared and demonstrated patient-customizable guided bone regeneration (GBR) membrane/guided tissue regeneration (GTR) hybrid scaffolds for precise bone tissue restoration without dimensional collapse.

Poly(glycolic acid) (PGA) scaffolds (100 - 800 μm in pore diameter) were fabricated by 3D printing method. Silk fibroin nanofiber membranes were prepared by electrospinning method. Dimension of a disc shape scaffold was set as 7.5 mm in diameter and 1 mm in thickness. The microstructure of silk fibroin nanofiber and PGA scaffolds was observed by SEM. In vitro cell attachment and proliferation evaluated using preosteoblasts by MTT assay on day 1, 3, and 7. Animal tests with Rabbit (230-280 g, 8 weeks old) were used as the experimental model to evaluate the ability of the regeneration of calvarial defect (8 mm in diameters) as guided bone tissue regeneration for 4 and 8 weeks of the breeding period.

Silk fibroin nanofiber mats were fabricated by adjusting electrospinning parameters for use as a GBR membrane. The average diameter of the nanofibers at 4 wt% was 639 ± 150 nm. To guide bone regeneration, we fabricated a porous PGA scaffold using a 3D printer. Porous PGA scaffolds with a strand diameter of 207 ± 11 μm and pore size of 353 ± 7 μm . In vivo animal experiments of rabbit calvarial defect model showed that samples with the silk fibroin nanofiber-PGA hybrid scaffold group promoted bone formation. Micro-CT images (Figure 1) showed that the silk fibroin-PGA hybrid scaffold group promotes bone formation.

Silk fibroin-PGA scaffold groups showed significant regeneration of bone compared to control groups in rabbit calvarial defect model. Masson-Trichrome staining of regenerated tissue with silk fibroin-PGA hybrid scaffolds showed thick and dense bone formation in 8 weeks. Silk fibroin nanofiber-PGA scaffold construct will be a prospective approach for regeneration of bone defect.

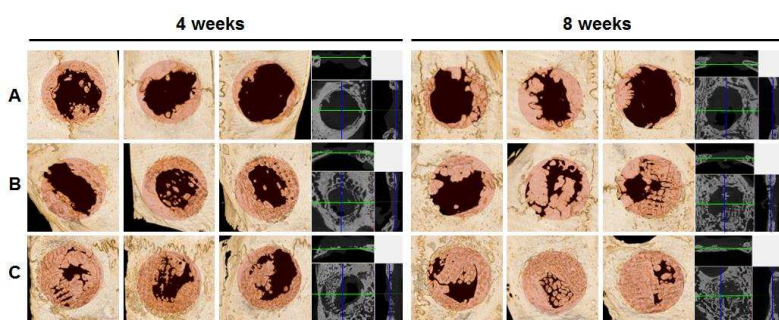


Figure 1. Micro-CT images of the control (A), PGA scaffold (B) and PGA-silk fibroin nanofiber scaffold (C) groups after 4 and 8 weeks of surgery.

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Preparation of edible, barrier films from zein nanoparticle dispersions in water

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Zein is a storage protein from corn. It is edible and thus suitable for use in food, pharmaceutical and cosmetic industry as encapsulating material, carrier, or coating and film forming material [1, 2]. Zein, being a prolamine, is insoluble in water, and soluble in aqueous ethanol and other organic solvents. Therefore, zein films and coatings are usually prepared by spraying or casting its aqueous ethanol solutions [3, 4]. The use of ethanol in many applications related to preparation of edible barrier films and coatings is unwanted.

In this work, zein films were prepared by coalescing zein nanoparticles from aqueous zein dispersions i.e. zein latexes. Zein latexes were prepared by antisolvent precipitation, where 10% zein solution in 90% aqueous ethanol was drop-wise added to water to obtain dispersions of zein nanoparticles in water. The remaining ethanol was evaporated to obtain 4% m/m zein latexes. Thereafter, zein films were prepared by casting the latexes in silicone molds and air-drying at 50°C. The obtained films were characterized for morphology, surface roughness, water vapor permeability, opacity and color, and were benchmarked against zein films obtained by casting its aqueous ethanol solutions. Effect of plasticizer (30% propylene glycol on zein mass) on the film properties of the latex films was also investigated.

It was found that continuous zein films can be prepared out of zein latexes, with and without use of the plasticizer. SEM and AFM analysis showed that coalescence of zein nanoparticles took place during the film formation process. Water barrier properties of the latex films were found to be comparable to the films obtained from zein ethanol solutions. Surface roughness is higher for the latex films compared to the solution films, but is decreased when the plasticizer is added. Latex films with plasticizer added had smaller contribution of yellow color and lower opacity, than films without plasticizer and films obtained from zein solution.

Acknowledgements: This work was financed by Ministry of Education, Science and Technological Development of Republic of Serbia, Grant No. III 46010/3, and APV Grant No. 142-451-3680/2017-01/01.

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Nanomaterials in the environment: application and nanosafety

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Engineered nanomaterials (NMs) have been commercially produced even prior to the development of nanotechnology as it is known today. The small size of the materials is a reason for their special characteristics. Although a broad definition, nanomaterials are defined as having at least one external dimension between 1 and 100 nm. NMs that have one dimension in the nanoscale are layers, such as a thin films or surface coatings. Materials that are nanoscale in two dimensions include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids, quantum dots (tiny particles of semiconductor materials) nanocrystalline materials, made up of nanometre-sized grains and many others.

NMs have a large surface area to volume ratio giving them unique characteristics that differ from bulk material of the same chemical composition. Their surface adsorption, dissolution, and photocatalytic activity are among the most important characteristics governing their beneficial use and also their safety.

Surface adsorption is the primary force directing nanomaterial aggregation, molecular corona formation, and other complex interactions of nanomaterials in the environment and with biological systems. In fact, the adsorbed biomolecules and their dynamic exchange determine the biological identity of nanosized materials [1]. This nanomaterial characteristic is responsible for nanomaterial-biological interactions ranging from harmless effect (Figure 1.) to nanotoxicity.

On the other side, surface adsorption and photocatalytic activity of nanomaterials can be beneficiary exploited in many environmental applications. Nanomaterials could effectively remove contaminants from the environment. The challenges of future applications of nanomaterials have to address technical hurdles, high costs, and potential environmental and human risks. To overcome these barriers and avoid unintended consequences, collaboration between research institutions, industry, and governments is necessary.

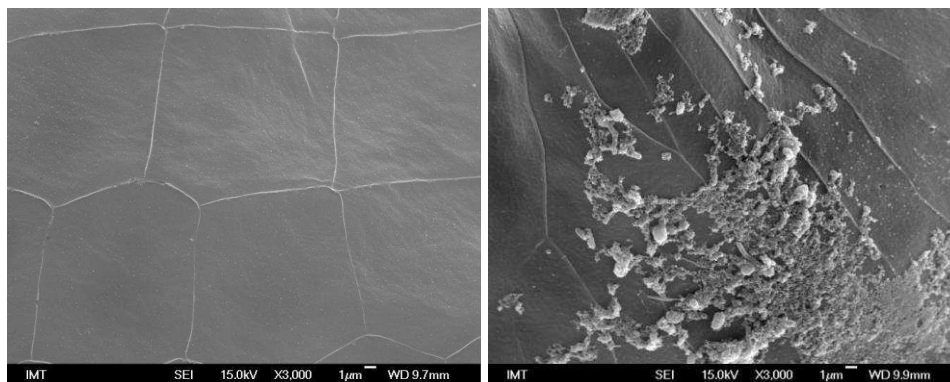


Figure 1 a, b. SEM image of a part of the *D. magna* cuticle with adsorbed material after 24 h exposure to 100 mg TiO₂ NPs/L [2]

Acknowledgements: The research was cofounded by NanoFASE (EC H2020 grant agreement No 646002) and by SLO-KIT/17-18-06 collaboration.

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Fluorescent silver nanoclusters as optical sensors for heavy metal ions in water

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Environmental pollution such as the poisoning of drinking water by heavy metal ions is a huge issue for human and planet health. In order to detect metal ions many analytical techniques are being used namely atomic absorption spectroscopy, atomic fluorescence spectroscopy, etc., but these are expensive, bulky, time consuming and require a well-trained analyst. Optical devices are very cheap, easy to prepare and they have a fast response; those based on nanomaterials have already been used with success to detect heavy metal ions such as Ni^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} and As(III) [2,3].

Metal nanocluster (MNCs) are small aggregates of metal atoms with a mean diameter up to 2 nm, which show a quantum behaviour. Typically, few tens of metal atoms build NCs and their electronic structure presents discrete energy levels with quantum confinement of electrons. This characteristic makes colloidal suspensions of MNCs luminescent [3].

We synthesized silver NCs capped with poly (methacrylic acid), PMAA, through UV irradiation. The synthesis is carried out in presence of N_2 gas flow to prevent silver NCs oxidation. In a typical synthesis, AgNO_3 and PMAA are solved in deionized water. The solution of PMAA is stirred and the silver nitrate is dripped inside the capping solution adjusting the pH value with nitric acid (HNO_3). Subsequently, the solution was irradiated by UV light for 6 minutes in presence of N_2 gas. In figure 1(a), the black curve represents the optical absorption of AgNO_3 /PMAA solution after the UV irradiation, the peak at around 420 nm confirms the presence of silver NCs; the red curve shows the normalized photoluminescence (PL) of the same solution excited at 365 nm. Figure 1 (b) and (c) show pictures of the solution under daylight and UV light. In the latter, a pronounced red colour due the luminescence of the nanoclusters is evident. By transmission electron microscopy (TEM) we found that NCs are well dispersed in solution with a high monodispersion level presenting an average dimension of 1.6 ± 0.3 nm. We tested this system as optical sensor for different metal ions in water. In particular, we found that our AgNCs are very sensible to the presence of Pb^{2+} showing an enhancement of the luminescence as a function of the contaminant ion concentration. A tentative model of interaction AgNCs/ion is proposed.

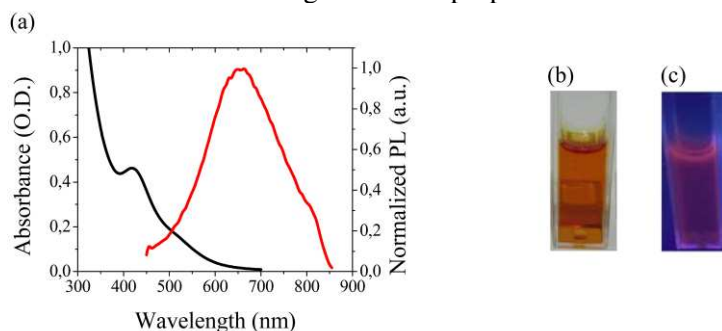


Figure 1. (a) Absorption (black line) and emission (red line) spectra of AgNCs colloidal solution after 6 min. of UV irradiation; Photographs of AgNCs solutions under daylight (b) and UV light (c).

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On the role of surface active substances in atmospheric aerosols

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Ambient (sub)micrometre particulate matter (PM) is one of the major air pollutants and has detrimental impacts on the ecosystem, the climate and human health. When considered together with the atmospheric gaseous phase in which PM is dispersed, atmospheric aerosol is addressed. Besides its inorganic constituents, PM consists of a plethora of organic compounds, the majority of which is still unknown. It is believed that, among others, the constituting surface active substances (SAS) could importantly influence the cloud condensation nuclei (CCN) activity of PM, i.e., its cloud-forming efficiency [1]. This has indirect implications in climate forcing because clouds importantly alter Earth's radiative balance.

The ability of an aerosol particle to act as CCN and to become cloud droplet is described by the Köhler theory, which also considers the surface tension (σ) of hydrated particle [2]. The theory results in size and composition dependent growth curves of hydrated particles/droplets in humid air and only a fraction of hygroscopic particles competing for the available water vapour in the surrounding can grow beyond their critical sizes and become droplets at a given supersaturation. Due to sensitivity limitations, we determined for the first time how surface active size-segregated PM is and studied the influence of SAS size distribution within PM on the cloud-forming efficiency of ambient aerosol. We show that size-segregated SAS-induced σ depression during cloud activation can increase droplet number for about 10%, especially in spring and summer when a distinct fraction of small particles is enriched with SAS as presented in Figure 1 by a surfactant activity factor (SAF). The observed droplet number increase could trigger the precipitation at clean atmospheric conditions of pristine environments.

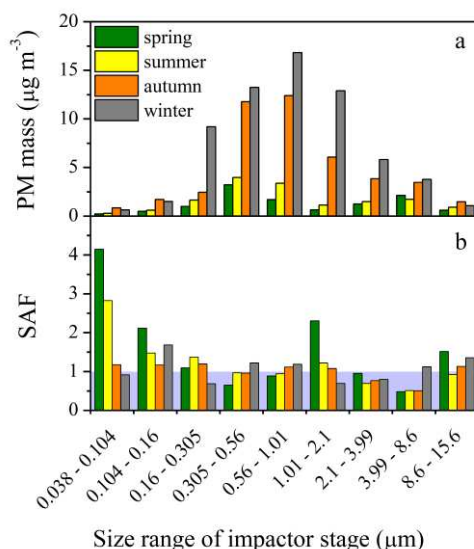


Figure 1. Size-segregated a) PM mass concentration in ambient air and b) surfactant activity factor (SAF) corresponding to the surfactant enrichment within particular particle population.

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Fungi as regulators of colloidal soil organic matter

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Soil organic matter (SOM) is the largest reservoir of carbon in terrestrial ecosystems. The stability of SOM in relation to microbial decomposition is controlled by biological and physicochemical factors. The molecules co-assemble into supramolecular aggregates that are stabilized by hydrophobic interactions and/or by interactions with mineral particles [1]. Ectomycorrhizal fungi are thought to have a key role in mobilizing nutrients (such as nitrogen) trapped in soil organic matter (SOM). However, the extent to which ectomycorrhizal fungi decompose SOM and the mechanism by which they do so in order to gain access to those nutrients remain unclear [2].

The colloidal nature of SOM is hypothesized to influence the extent and kinetics of degradation, and studying the structure of these aggregates, at various stages of SOM degradation, is therefore of great interest. Hereby using small angle X-ray scattering (SAXS), static and dynamic light scattering (SLS and DLS) along with standard chemical composition analysis we highlight the SOM decomposition as a function of time for a wood decaying, saprotrophic species of the genus *Gleophyllum*, and the ectomycorrhizal fungus *Paxillus involutus*. Figure 1 shows SAXS profiles of the dissolved organic matter (DOM) and the metabolized DOM after 1, 3, 7 or 11 days of incubation with *Gleophyllum*. It appears that there is a considerable effect not only in the absolute intensity, but also in the scattering profile at low q . On the other hand, scattering profiles of DOM after incubation with *Paxillus involutus* did not show any changes. This information provides insights both into the effect of fungal metabolism on soil organic matter and also in the colloidal nature of the latter.

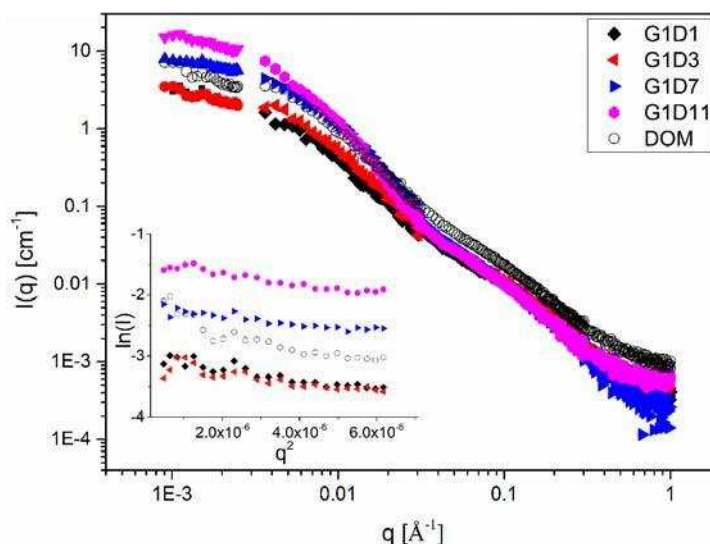


Figure 1. Scattering profile of the dissolved organic matter extracted from boreal soil and the same solution after 1, 3, 7 and 11 days of fungal growth. The scattering profiles were made by joining SLS and SAXS. SLS were scaled with an empirical factor.

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Aggregation of nanoparticles in presence of organic molecules and ions – experiment and simulation

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The small size of nanoparticles results in high surface-to-volume ratio as well as in good colloidal stability that prevents them from sedimentation. Most of colloidal systems are stable as a result of repulsive electrostatic forces arising between particles bearing the same surface charge, e.g., silica, latex or titania nanoparticles.

Aggregation of nanoparticles is usually an unwanted process which leads to drastic decrease of surface area and ultimately causes destabilisation of the suspension and sedimentation. In case of the suspensions stabilized by the electrostatic forces, the most common source of aggregation is the presence of oppositely charged ions and organic molecules (macromolecules). The oppositely charged ions/molecules adsorb on the surface of nanoparticles and neutralize/screen their surface charge which reduces the repulsion forces and results in the aggregation [1]. Since nanoparticles are so commonly used nowadays and are believed to be toxic, it is of great importance to gain better understanding of the aggregation from the perspective of colloidal and also environmental sciences.

In this work we present a study regarding aggregation of titania and silica nanoparticles in the presence of ions and organic molecules such as fulvic acid and different derivatives of benzoic acid. The aggregation was followed by dynamic light scattering, zeta potential and adsorption measurements. Investigation of the colloidal stability of the systems allowed us to understand relationship between different parameters (pH, concentration of organic molecules and ions) and evaluate their contribution to the formation of the aggregates. Trends seen in experimental data were rationalized by performing the molecular dynamic simulation of organic molecules behaviour in water as well as their adsorption on the surface of nanoparticle. Molecular dynamics simulations captured correctly the interactions of organic molecules in solution as well as the nature of their interaction with the charged silica surface.

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Medium-assisted dispersion forces

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Dispersion forces, such as van der Waals forces between two neutral, but polarisable particles, Casimir forces between two dielectric bodies, or Casimir-Polder forces between a polarisable object and a dielectric body, are caused by the ground-state fluctuations of the electromagnetic fields. They are the weakest forces on small scales which can lead to the binding of particles. These forces have been studied in a large number of experiments and theories. However, all these investigations were restricted to laboratory conditions, where the objects were located in vacuum. Due to the importance of these interactions in natural systems, such as particles immersed in solvent medium, the physical impact of an environment is of interest for recent investigations.

By applying methods from macroscopic quantum electrodynamics to the ground-state fluctuations, the dispersion forces separate into the response function of the material and the photon propagator expressed by the scattering Green's function. Thus, the estimation of a dispersion force simplifies to the determination of a classical scattering process. Following this description, the environment influences dispersion forces by a change of the scattering and by a modification of the atomic states caused by the additional boundary conditions. We concentrate on the scattering effects and present a model which includes the influence of an environment effectively.

A microscopic consideration of a particle embedded in a medium shows that in a vacuum bubble forms around the particle, which is caused by the balance of attractive dispersion forces and a short-range Pauli repulsion. Such cavities can be assumed to be fixed to the particles and move along with it. This leads us to consider the particle + bubble system as an effective object. Hence, the optical paths which have to be considered for the determination of the dispersion forces have to pass the boundary between the environmental medium and the vacuum bubble before they can interact with the particle leading to the effective polarisability models [1,2].

We present the theory of an effective modification a particle's properties when embedded in media based on the excess polarisabilities [1,2]. In order to illustrate our results, we apply this method to greenhouse gases solved in water and determine their behaviour at the water-air interface [3].

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The studies on the possibility of the application of the hops essential oil as ecological pesticide.

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A large group of compounds produced by plants (so-called phytochemicals) possesses confirmed antimicrobial, antioxidant, anti-inflammatory or even anticancer activity. Therefore, the possibility of the application of these substances in various areas of medicine, pharmacy or biotechnology is intensively investigated. To the group of these substances belong for example the essential oils, which due to their antimicrobial potency are treated as excellent candidates for the application as natural antimicrobial agents in food industry, cosmetics or agriculture. As far as the latter area is considered the intention is to eliminate the use of synthetic plant protection compounds, which have negative impact both on the environment and humans health [1]. The plant derived extracts including the essential oils are ecological alternative for toxic chemicals characterized by antimicrobial properties, selective phytotoxicity and relatively short time of biodegradation. Unfortunately environmentally safe substance are still uncommonly used in agriculture and they constitute only 1% to 3% of value of the global plant protection products markets [2]. In our experiments the essential oil from *Humulus Lupulus* (hop cones) was extracted and then the potential of this raw material to be used as a natural pesticide was investigated. Although it is known that the mechanism of antimicrobial activity of phytochemicals is the combination of different effects, a direct influence on lipid membrane organisation is postulated as the most important step from the point of view of phytochemicals activity [3,4]. Therefore, in our studies the influence of the hops essential oil on artificial bacteria membrane was investigated to verify the ability of this substance to incorporate into membrane and change its organization. As model systems ternary monolayers and bilayers composed of characteristic bacterial lipids – phosphatidylglycerole (POPG), phosphatidylethanolamine (POPE) and cardiolipin (TOCL) were used, however, the experiments for one component lipid systems were also performed. All the collected results confirmed that the hops essential oil components are able to incorporate into the lipid monolayer and bilayer and change their condensation. However, the magnitude of this effect is determined by the system composition, its condensation and the oil concentration. Highly important finding was that at a given dose the effect of the essential oil on membrane stabilizes and further increase of the oil content does not cause additional modifications in membrane organisation. It can be concluded that the hops essential oil alters the properties of lipid bacteria membrane and probably it could be used in agriculture as the natural pesticide.

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The influence of PAH molecules on model *Bacillus subtilis* bacteria membrane

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Polycyclic Aromatic Hydrocarbons (PAHs) belong to the group of Persistent Organic Pollutants (POPs). These compounds are of strong toxicity to the living organisms, they are able to persist in various parts of environment for a long time and to be easily transported over long distances and they are capable of bioaccumulation [1,2]. PAHs can be easily deposited in soil and sediments; they are released into the atmosphere, they can leach from soil into water as well as be introduced into the food chain. Thus, the living organisms are systematically exposed to PAH influence [3, 4]. Therefore, the reduction of the emission of these pollutants and their elimination from the environment is of great importance. From the point of view of degradation of organic contamination the activity of microorganisms seems to be the most important. Namely, bacteria and other microorganisms treat these organic compounds as a source of carbon and energy and in the presence of enzymes, responsible for PAH metabolism, they cause mineralization of these pollutants [5]. Highly essential problem concerning both bioremediation of PAHs and in general their presence in the environment is the toxicity of these compounds to cells [6]. The harmful effect of these lipophilic substances is connected with their direct incorporation into cellular membrane. It was evidenced that this structure is the first site of action for PAH molecules, which undergoes structural, compositional and functional modifications in the presence of these compounds [6,7]. Thus, PAH molecules, in the presence of required enzymes, can be decomposed or, if there is lack of enzymes, they accumulate in membranes. However, the exact effect of these compounds on membrane organisation is under elucidation.

The aim of performed experiments was to verify the effect of PAH molecules on the organisation of bacteria membrane in model lipid system. For these investigations pyrene, tetracene and Naphtho[1,2,3,4-def]chrysene (chrysene) were chosen and their effect on ternary lipid monolayers imitating gram(+) *Bacillus subtilis* soil bacteria was studied. The experiments involved the surface pressure-area measurements, Brewster Angle Microscopy studies and the analysis of the relaxation of the monolayers. It was found that PAH molecules tend to be excluded from the monolayer, however, they change morphology of the film and cause strong destabilization of model membrane. The monolayer material desorbs from the interface in time, however, the mechanism of this process depends on the kind of PAH molecule added into the model system. It was found that pyrene interacts with membrane lipids at its low level in membrane, while in the case of the remaining PAHs the interactions occur mainly at their higher content in the system. Based on the collected results it can be summarized that the effect of PAH directly on membrane organisation is an important step in the mechanism of toxicity of these compounds.

Acknowledgements: This project was financed by the National Science Centre (No 2016/21/B/ST5/00245).

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Versatile applications of X-ray Photoelectron Spectroscopy (XPS) in the fields of Geology and Environmental Sciences

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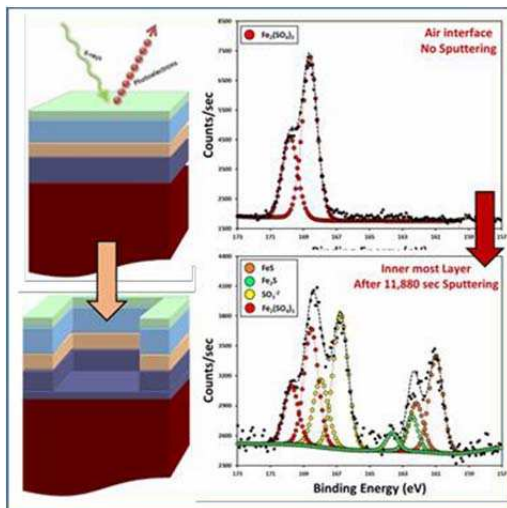
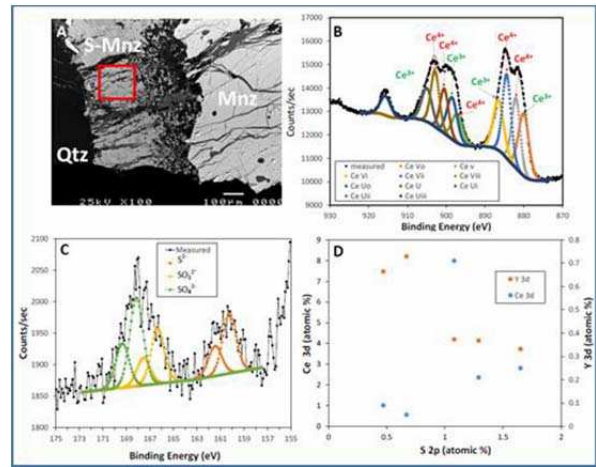
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X-ray Photoelectron Spectroscopy (XPS) has numerous applications in the fields of surface analysis. However, there are not many examples of direct applications of XPS in the geological and environmental fields available in the literature. In this poster, we will show three case studies of successful applications of XPS in the geological and environmental studies.

Case Study I. Role of sulphate in ree mineralization: sulphatian monazite, Eureka carbonatite, Namibia

Figure 1. (A) Backscattered electron image of monazite overgrown by sulphatian monazite from Eureka. (B) Narrow scan of the Ce 3d binding energy peak from the area shown in (a). The Un and Vn notation refers to the multiple metastable electron configurations possible in Ce 2p, 3d and 3f orbitals following photoelectron emission. Characteristic peaks for both Ce(III) and Ce(IV) are observed, indicating the presence of highly oxidising conditions during secondary monazite precipitation and alteration. (C) Narrow scan of the S 2p binding energy peak indicating sulphur present as sulphide inclusions (probably chalcocite), and sulphate and sulphide structurally bound in monazite. (D) Quantification of the binding energy spectra from 5 analysis areas showing a negative correlation between Ce and S, and a positive correlation between Y and S.



Case Study II. Accelerated low water corrosion: the microbial Sulphur cycle in microcosm

Accelerated low water corrosion is a form of microbially influenced marine steel corrosion characterised by sulphate reduction at the steel surface, protected from the atmosphere and oxic water column by a layer of oxyhydroxides and oxysulphates. Corrosion rates are up to 5 times higher than normal marine corrosion (NMC). The formation of the marine corrosion blisters can be related to sulphate reducing bacterial activity at the steel surface, and subsequent bacterial iron and sulphur oxidation, encapsulating most of the mineralogical sulphur cycle, on the outer surface blisters.

Figure 2. Depth profiling of the corroded sample reveals the variation in sulphur oxidation states.

Third example would be from the degradation study of phosphate-labelled poly(lactic acid) (PLA) blended with cotton fiber (FA) in a simulated soil to investigate the effects of phosphate delivery from PLA composites applied as a soil amendment.

Following the layer-by-layer polyelectrolyte coating of bacterial cells using STED microscopy

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Coating bacterial cells with polyelectrolytes on the basis of the electrostatic interaction between oppositely charged entities, named layer-by-layer (LBL) deposition method, was described and usually performed on solid particles or dead cells. Details of such coating of viable bacteria were never sufficiently described and there is a lack of understanding of the primary interactions between living cells and charged polymers as well as their localization on or within living cells [1].

Here, we utilised super-resolution stimulated emission depletion microscopy (STED), which can bypass the diffraction limit of light microscopy to increase the resolution down to 20 nm, thus enabling new insight and understanding of what is happening with the nanometer-thick coating on the micrometer-sized cells. The main challenge was to label the cell membranes and polyelectrolytes with STED dyes without disrupting their behaviour. For the labelling of bacterial membranes, a new dye based on nile blue scaffold (PAG-19, Fig. 1c) was synthesised, which provided bright signal and excellent photostability. Its amphiphilic structure enabled its incorporation into bacterial cell membrane (Fig. 1). For the first layer of polyelectrolyte coating, polyethylenimine (PEI) of two different molecular masses (25 000 and 600 000 Da) were used [2]. Labelling of the positively charged polyelectrolytes was done with commercially available dye (Atto 594) in a form of N-hydroxysuccinimide ester that was covalently bound to amine groups of PEI. The protocols for both, labelling the cell membrane as well as the polyelectrolytes, were developed and thorough optimisation is still needed. In order to observe these two structures simultaneously, the chosen labels were spectrally separated with minimum interference, which was further reduced by adjusting the gating, lifetime, line accumulation and other imaging parameters.

The use of STED microscopy enables the localisation of polyelectrolyte adhesion to the bacterial surfaces and its connection to the polymer's molecular weight, the determination of its interaction with the bacterial membrane and the reasons for potential toxicity effects of the polymer coating.

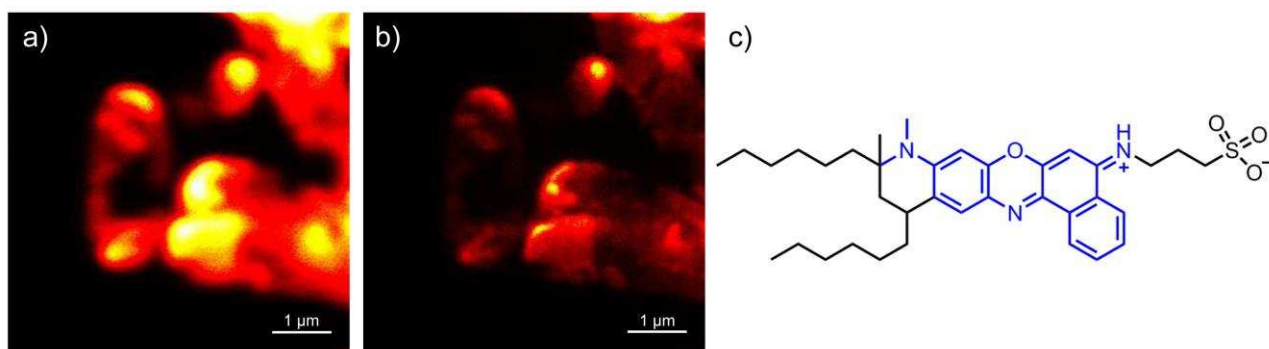


Figure 1. Images of bacterial cells (*Bacillus* sp.) with membrane, labeled by synthesized amphiphilic probe PAG-19, obtained with confocal (a) and STED microscopy (b). The molecular formula of the PAG-19 with its nile blue scaffold marked blue is shown on (c).

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Interaction of perfluorotelomer alcohol and fluorocarbons with model decomposer membranes

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In recent years a group of emerging hazardous chemical, perfluorinated compounds, was added to the list of persistent organic pollutants (POP). Initially, because of their unique physicochemical properties like thermal stability (presence of the carbon-fluorine bond), oxidative resistance, perfluorinated pollutants (PFPs) were used in several industrial application. Moreover because of their excellent surface activity they were used as surfactants in different advanced technologies [1,2].

Unfortunately, PFPs have not only the beneficial properties, but they are also persistent in the natural environment, bioaccumulative, and have a toxic potential towards humans and wildlife [2]. What is more concerning about PFPs is that long chain compounds and perfluorooctanesulfonate have a much longer elimination half-lives from natural environment in comparison with shorter chain homologues and perfluorononanoic acid [1-3].

So far there is little available information on these chemical pollutants. Since the better knowledge on the topic could lead to a more appropriate use of soil bacteria and prevent from decomposers community depletion, we tried to shed some light on matter.

In this research we focused our attention to long chain PFP that are insoluble in water that is: perfluorotelomer alcohol (perfluorotetradecanol) and two structurally different perfluorinated hydrocarbons (perfluorotetradecane, perfluorobiphenyl). Langmuir monolayers formed by different phospholipids typical to bacterial membranes were applied as model biomembranes. The monolayers were characterized by surface pressure (π)- mean molecular area (A) isotherms registration and visualized upon the compression by Brewster Angle Microscopy (BAM). The structure of the monolayers at molecular level was studied with the application of the Grazing Incidence X-ray Diffraction (GIXD) technique at SOLEIL synchrotron.

The results showed that the presence of the PFPs profoundly affected the phospholipid monolayers. In particular perfluorotetradecanol miscibility with the phospholipid is determined by the size and charge of the polar headgroup. Moreover BAM pictures proved that the presence of perfluorinated molecules changes profoundly the monolayer texture. Analysing the results from BAM and GIXD and other cases described in scientific literature we hypothesized that perfluorinated hydrocarbons form an additional monolayer anchored on top of the phospholipid film. Also this study proved that polar and non-polar perfluorinated pollutants can be toxic to decomposer organisms and that their toxicity is strictly correlated with the phospholipid composition of the cellular membrane.



Figure 1. Representatives Brewster Angle Microscopy pictures for DMPE monolayer with the addition of perfluorotetradecanol (PFTol) of mole fraction equal 0,1. The numbers on the picture indicates the value of surface pressure.

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Studies of the interactions between polychlorinated pesticides and model decomposers membranes

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In the past decades one of the most widely employed class of organic pesticides were the polychlorinated derivatives of cyclic alkanes. Nowadays these substances are banned in most countries due to proven toxicity on humans and negative effects on the environment (high persistence, bioaccumulation) [1]. They were added to the list of Persistent Organic Pollutants (POPs) of the Stockholm Convention, and despite the fact that their usage was forbidden, they can be still detected in the different types of environmental samples (air, water and especially soil) [2].

Considering their persistence, hydrophobic nature and low water solubility, polychlorinated pesticides (PCPs) are mainly absorbed on particulate matter and accumulate in sediments and soils [3]. Unfortunately not every soil bacteria is capable to break down those substance, the cause lies in the possible absence of a proper enzymatic apparatus. In the case the biodegradation is possible a low concentration can be insufficient to induce an enzymatic activity or promote the growth of microorganism. Although a too high concentration can become toxic to bacteria [1].

The main aim of this study was to assess the interaction between the PCPs and phospholipid Langmuir monolayers applied as decomposer membrane models. Among the PCPs five of them were chosen: hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), endrin (END), octachloronaphthalene (OCN), and mirex (MX). The mechanical properties of the monolayers were characterized by the surface pressure (π) – mean molecular area (A) isotherms registration and stability tests. Their textures were studied with the application of the Brewster Angle Microscopy (BAM) whereas the monolayer structure at molecular level was monitored by Grazing Incidence X-ray Diffraction (GIXD).

All the obtained results point to the existence of a relationship between the PCPs structure and their ability to interact with the model membranes. Specifically MX and OCN form aggregates and stay separated from the phospholipids monolayer. As for the other tested PCPs, endrin was the one compound that influenced the most the model membranes, which means that it is also the most toxic for real biological systems. GIXD results led to the conclusion that at a molecular level endrin and other PCPs do not affect the organization of TMCL molecule in crystalline domains but significantly change the organization of the double-chain anionic phospholipid DMPG.

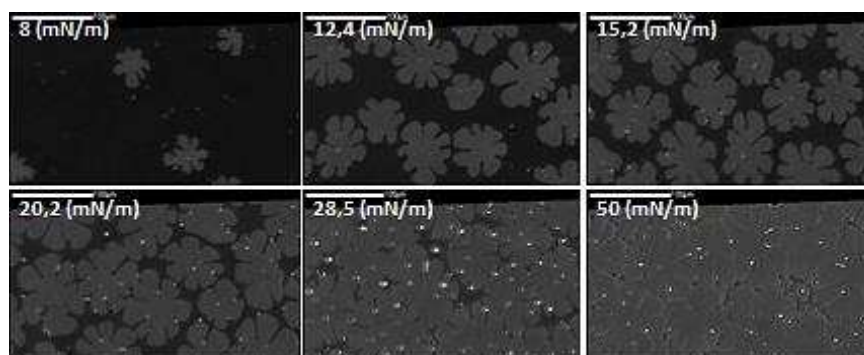


Figure 1. Representatives Brewster Angle Microscopy pictures for TMCL monolayer with the addition of endrin of mole fraction equal 0.3. The numbers on the picture indicates the value of surface pressure.

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Investigation on the influence of polycyclic aromatic hydrocarbons incorporation into model biological membranes on phospholipase A2 activity

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Polycyclic aromatic hydrocarbons are ubiquitous pollutants listed as Persistent Organic Pollutants under the Stockholm Convention. These compounds are emitted into the environment mainly through anthropogenic sources. Those sources are: industrial processes, coal and wood combustion, car fumes and also oil products spills that contains PAHs [1].

PAHs are characterized by significant chemical and physical stability as well as limited biodegradation. Moreover, because they are strongly attached to soil particles they usually accumulate in soil and sediments which function as reservoirs of these compounds [2]. Similarly to other POPs, polycyclic aromatic hydrocarbons have great toxic potential towards all living organism which means that not every bacteria or fungi are capable of PAHs degradation [3-4]. The situation that occurs in most cases is that PAHs built into bacterial cell membranes but are not further transported or metabolized. This leads to the accumulation of PAHs in the cell membranes and changes in the membrane structure. Those membrane structural changes can cause an excessive activation of the phospholipase A2 (PLA2) enzyme that breaks down membrane phospholipids. As a consequence the cell membranes might be destroyed leading to the cell death, which in global terms means a significant impoverishment of the microbial biocenosis in a given area[5].

The aim of the study was to examine the effect of selected PAH on the activity of phospholipase A2 in model bacterial membranes. Langmuir monolayers formed by anionic phospholipids typical to bacterial membranes: cardiolipin and phosphatidylglycerol were used as model membranes. Brewster Angle Microscopy (BAM) was applied to evaluate changes in the model membranes before and after the injection of the enzyme.

The obtained data showed that only small additions of PAHs (about 10%) to the model membranes lead to an increased PLA2 activity, while the higher amount of PAHs are able to lower the enzyme activity or even inhibit its actions. Additionally the results exposed the existence of a strong correlation between PAHs structure and their ability to incorporate into the model membranes. In fact, the angular cluster molecule (benzo[a]pyrene) is incorporated easier than a linear molecule (pentacene) into the model membranes. However, pentacene separates from phospholipid monolayer and forms multilayer aggregates that lead to an even increased activity of PLA2.

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Molecularly imprinted polymers for specific adsorption of Patulin toxin

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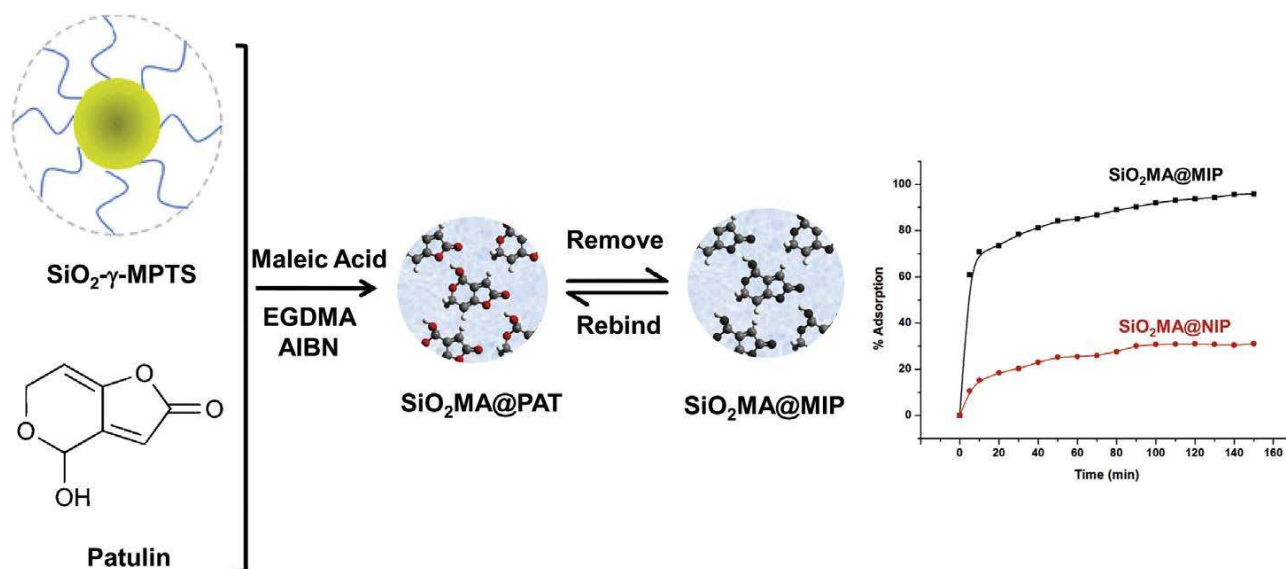
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A molecularly imprinted polymer material (MIP) was developed as thin films of polymer attached on the surface of a solid support. MIPs are made of strongly cross-linking functional polymer materials having "functional cavities" of the shape of the invited molecule. Such molecular imprints are created by radical polymerization of the functional monomer mixed with a high ratio of cross-linking agent in the presence of the invited molecule strongly interacting with the functional monomer. Washing off the invited molecules from the polymer material leaves "molecular imprints" at the surface. Designing the MIP material as thin film bound to the surface of a solid support increases much the specificity of the molecular recognition by the molecular imprints.

Such materials were made of Stöber silica particles chemically modified with methacryloyl groups, to which poly(methacrylic acid) or copolymers of methacrylic and maleic acids were grafted during their radical polymerization [1]. The polymerization was carried out in the presence of the Patulin mycotoxin and the resulting materials were used as a matrix for separation of Patulin.

The syntheses of the MIPs and the corresponding non-imprinted materials (NIP) were characterized by means of FT-IR, ¹³C NMR and elemental analysis. Evidence of the specific molecular recognition by molecular imprints has been given by comparison of adsorption behavior to the MIP and NIP materials. The uptake capacity of Patulin by the MIPs was 1.55 $\mu\text{mol}\cdot\text{g}^{-1}$, four times higher than the corresponding NIP. The adsorption of Patulin on the MIP reached a steady state in only 20 min whereas full adsorption on the NIP took 120 min under the same conditions [1]. Solid Phase Extraction (SPE) devices have been developed for preconcentration of Patulin by extraction from apple juice samples [2]. Such analysis device allows increasing the sensitivity of the detection of the Patulin toxin in apple beverages.



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The adsorbent based on the wastes of the heat power plants for concentration of heavy metal ions and phenol from industrial wastewaters

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The creation of resource-saving technologies in the field of recycling secondary waste (domestic, industrial) is one of the main tasks of green chemistry and environmental chemistry. The problem of decontamination of ash waste from thermal power plants (TPPs) is a major environmental problem. According to statistics, the utilization of ash and slag wastes in the CIS countries does not exceed 10%, whereas this index, on the average, is 60% in the developed countries. Technogenic ash dumps cause great ecological economic and social damage to the population of the region, which requires a rational and immediate solution.

The purpose of this research is to evaluate the effectiveness of chemically modified sorbents based on fly ash to remove heavy metals and phenol from industrial wastewater.

The sorbents have been obtained by modifying the fly ash of urban thermal power plants by citric acid, tannin followed by low-temperature thermal treatment with water vapor.

Materials have been characterized by X-ray phase and fluorescence analysis, FT-IR spectroscopy, DTA/TGA, electron microscopy, potentiometry and spectrophotometry, etc.

The specific surface area of the sorbents has been determined by the BET method. The investigations of adsorption capacity of the sorbents with respect to iodine, MB, phenol and heavy metal ions have been carried out under the static conditions. The thermodynamic and kinetic parameters describing the adsorption processes in the systems have been calculated.

In addition, the adsorbent has been used in the purification of industrial wastewater from the galvanic plant manufactories. On the basis of the studies, the conditions leading to the maximum degree of wastewater purification from metal ions (on the example of real objects) and recommendations have been prepared.

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Gd³⁺ adsorption over a mesoporous silica foam functionalized with poly(amidoamine) dendrimer

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The separation and recovery of rare earth elements (REEs) are critical to meet the ever-increasing demand for REEs extensively used in many high technology devices [1]. For their efficient separation via adsorption, a stable adsorbent with a high adsorption capacity and fast adsorption kinetics is required. The poly(amidoamine) dendrimer (PAMAM) with a three-dimensional tree-like architecture possessing a large number of functional nitrogen and amino groups [2] can serve as a chelating agent toward metal ions including REE ions. Herein, the second generation PAMAM dendrimer-grafted mesoporous silica foam structure (G2/PAMAM-MSF) with sufficient textural properties (surface area: 210 m²·g⁻¹, pore volume: 0.73 cm³·g⁻¹, and pore size: 15.2 nm) was prepared and applied as an adsorbent for the recovery of gadolinium ion (Gd³⁺) from the aqueous medium.

The G2/PAMAM-MSF was characterized by XRD, N₂ adsorption-desorption isotherms, FT-IR, ICP, SEM/TEM EDX-mapping, and elemental analysis to confirm the successful introduction of the functional groups. The adsorption of Gd³⁺ ion on the G2/PAMAM-MSF was examined in detail as a function of solution pH, initial concentration of Gd³⁺, and contact time. The adsorption equilibrium data correlated well with the Langmuir model, and the maximum adsorption capacity of G2/PAMAM-MSF toward Gd³⁺ ion was estimated to be 132.4 mg/g at the optimal pH of 6.5, which is higher than that by the other currently reported materials. Adsorption equilibrium was reached within 20 min and the data were fitted well by the pseudo-second order kinetics model. G2/PAMAM-MSF could be reused for a minimum of five cycles with only a slight loss of the adsorption capacity. Gd³⁺ adsorption in the presence of competitive transition metal ions was carried out, indicating high selectivity. Finally, recycle runs were conducted, which demonstrated the structural stability of G2/PAMAM-MSF in five adsorption-regeneration cycles.

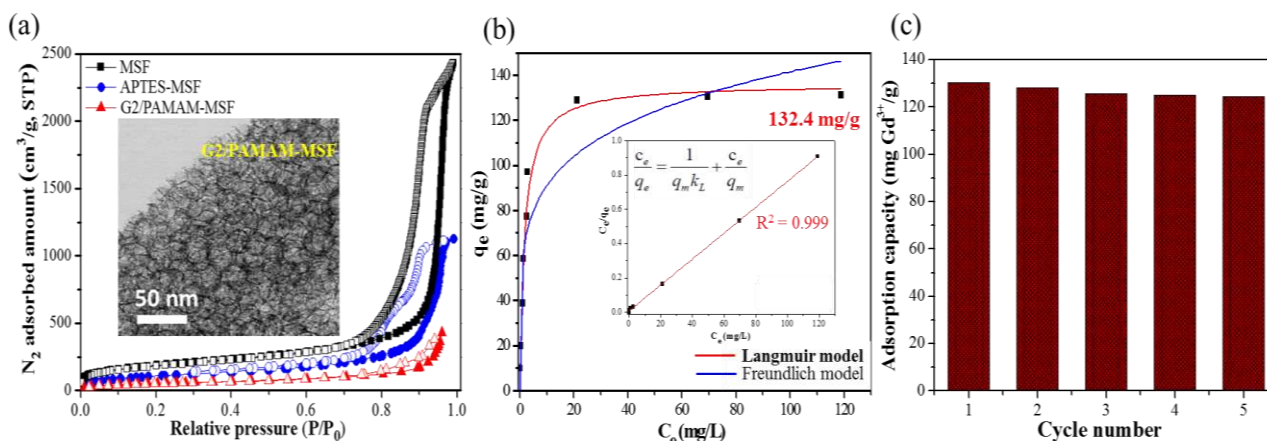


Figure 1. (a) N₂ adsorption-desorption isotherms of the samples (insert: TEM image of G2/PAMAM-MSF), (b) adsorption isotherm of Gd³⁺ on G2/PAMAM-MSF fitting to Langmuir model, and (c) reusability.

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Specific monovalent anion effects on aggregation of allophane nanoparticles

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An understanding of dispersion and flocculation behaviour of soil colloid is important when considering environmental problems such as transport of pollutants in soil, soil erosion, and water quality conservation. Allophane and imogolite are typical clay particles in volcanic-ash soil widely distributed in Japan. Allophane is an amorphous hollow spherical particle with a size of 3-5 nm [1]. It is known that the aggregation of allophane occurs around its isoelectric point [2]. Furthermore, specific anion effects on colloidal properties of allophane particles and suspension have been studied by measuring electrophoretic mobility (EPM) and viscosity [3, 4]. So far, however, systematic measurements on the influence of anion species on the aggregation behaviour of allophane are lacking. Therefore, to unveil the anion specific effect on the allophane aggregation, we studied the stability ratio of allophane nanoparticles by dynamic light scattering (DLS). We used the purified allophane sampled from Iwate, Japan. The electrolyte solutions used were NaF, NaCl, NaBr, NaI, NaBrO₃ and NaIO₃. Our results showed a slight difference in critical coagulation concentration (CCC) for each electrolyte solution. We presume that the difference in hydration radius of each ion affected the CCC. For NaF solution, much lower CCC and charge inversion detected by EPM were confirmed. These results demonstrate that fluoride ion has strong specific interaction with allophane.

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Bioencapsulation as a sustainable targeted agricultural delivery of bioactive agents in the conventional cultivation of *Lactuca sativa* L.

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The simultaneous encapsulation of biologically active agents such as fungi and agrochemicals is a useful way of nutrient delivery for an ecological and sustainable plant production. The benefits of encapsulation of bioactive agents are: slow and controlled release, more efficient use of agrochemicals with better safety and environmental protection. Encapsulation of single bioactive agents is a standard method used in agriculture.

Successful delivery of active agents at the right place and the right time is an attainable and desirable characteristic for all bioactive agent delivery systems. In order to obtain the required microparticles, effective for simultaneous encapsulation of multiple controlled release bioactive agents, it is important to optimize the parameters during the preparation of the microcapsule/microspheres.

Since numerous microorganisms, especially those associated with roots, have the ability to increase plant growth and productivity, *Trichoderma viride* (STP) was used in this research. *Trichoderma* species are among the most prevalent culturable fungi in soils, based upon the frequency of isolation on suitable media. The dual roles of antagonistic activity against plant pathogens and promotion of soil fertility make *Trichoderma* species as a promising alternative to standard plant protection and nutrition technologies.

Recently, microparticles containing both biological and chemical agents were investigated in terms of physicochemical properties, microparticle morphology, and release kinetics. The effects of different cations (calcium and copper ions), microparticle size, the presence of outer chitosan layer on the release of the cations as well as the release of *Trichoderma viride* (STP) spores from alginate-based microcapsules were investigated [1,2]. Optimization was performed with the intention to produce microparticles with delivering active agents to the plants at the rate that closely approximates plant demands over an extended period. The investigation pointed out that proper selection of agroformulation variables helps in designing microcapsules/microspheres with the desirable release of *Trichoderma viride* (STP) spores and copper/calcium ions for plant nutrition.

After the optimization, microparticles containing different combinations of $\text{Ca}^{2+}/\text{Cu}^{2+}$ ions, *T. viride*, alginate and chitosan were applied to the soil in the conventional planting of lettuce (*Lactuca sativa* L.). The application was performed just before planting. After the lettuce harvest, fresh samples were used for the preparation of extracts. Extracts were analyzed in terms of biological activity, with regards to the total polyphenols, antioxidant activity, chlorophyll, total sugars as well as the $\text{Ca}^{2+}/\text{Cu}^{2+}$ ions content. Principal component analysis and agglomerative hierarchical clustering were performed to see the significant differences between the treatments.

Results revealed significant differences when comparing the treated lettuce against the control (untreated) with regards to almost all of the measured parameters, i.e. the obtained biomass yield, rosette diameter and height as well as the content of bioactive compounds and antioxidant activity.

Bioencapsulation alongside the presence of chemical agents revealed a promising, sustainable, environmentally friendly, rapid, convenient, economical and efficient delivery of biological and chemical agents for plant nutrition.

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Evolution of the surface of silica nanoconfined media

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The prediction of the evolution of silica nanoporous materials in aqueous solutions is of great interest in environmental sciences. Such long time prediction requires the use of geochemical modelling which is generally not adapted to pores of few nanometers since the thermodynamic models and rate laws used are commonly obtained from diluted media [1]. Indeed, in a nanopore, the strong interactions between the water molecules and the silica surface leads to a decrease of water activity. The activity can be also modified by ions sorption with the silica surface. And, since in nanopore the average distance between ions are about the same order than the surface curvature, the structure and the motions of water molecules in the interfacial layer of nanopores are strongly modified [2]. Such phenomenon is of primary importance since it is known that on a planar surface, for which the radius of curvature is infinite, the water structure into the interfacial layer drives the hydrolysis rate of materials [3]. Nevertheless, the impact of the surface curvature on the hydrolysis rate of the nanopore wall in presence of ions has not been assessed yet.

Based on our recent methodology using nanoporous model materials [4], we characterized the evolution of hexagonal mesoporous silica having 6 nm pore size (SBA15 type) at 50°C in water and in 1 M XCl_2 electrolytes solutions containing cations having more or less kosmotrope properties ($\text{X} = \text{Mg}, \text{Ca}, \text{Ba}$) by in-situ Small Angle X-ray Scattering. Fitting these SAXS patterns with the model of Cambedouzou et al. [5] including a layer of altered silica in the vicinity of the pores edge, we determined the hydrolysis rate of silica nanopore wall and apparent water diffusion through the microporosity of the pore wall. The results show that the hydrolysis rates of the nanopore wall are related to the water structure and transport which is driven by the size of the hydrated cations and their surface excess in the interfacial layer. Comparing with others materials having dense pore wall, it appeared that the water diffusion through the silica nanopore wall delays the recondensation of the dissolved silica at the pore surface even if the hydrolyzed silica concentration into the pores is 3 orders of magnitude higher than the hydrolyzed silica concentration at the equilibrium in bulk solution. This highlights the modification of the silica dissolution process in nanopores.

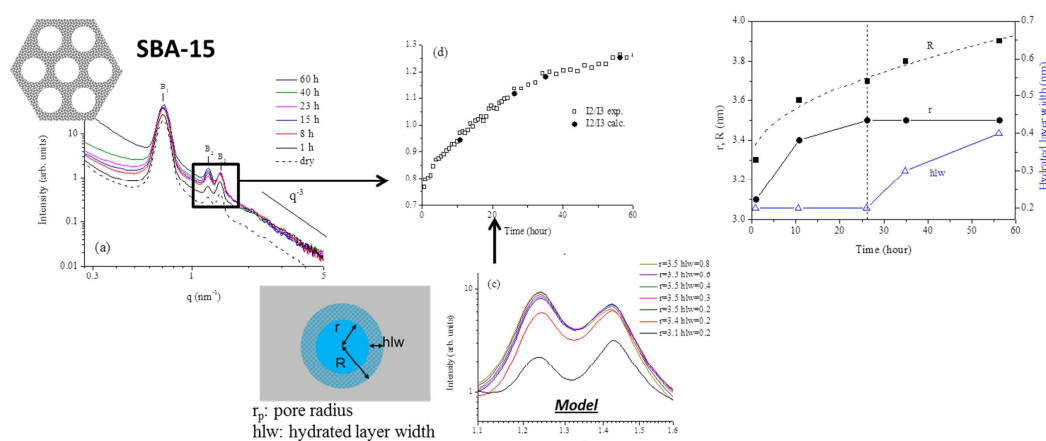


Figure 1: Schematic view of the method used to determine the dissolution of silica nanopore wall.

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Effects of doping on photocatalytic activity of titania thin films

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Clean water (i.e., water that is free of toxic chemicals and pathogens) is essential to human health. As the available supplies of fresh water are decreasing due to competing demands from various users, population growth, more stringent health-based regulations and extended droughts, we are facing a formidable challenge of meeting rising demands for clean water. [1] In recent years, advanced oxidation processes (AOP, i.e. photocatalysis with TiO_2) have emerged as a potential alternative for purification of waste waters because they are able to completely mineralize adsorbed organic pollutants to CO_2 and H_2O . [2,3] The main drawback of using titanium dioxide as a photocatalyst is its relatively large band gap (3.2 eV), which means it can only be activated upon irradiation with UV light ($\lambda < 380$ nm). Because the solar spectrum consists of 4-5 % of UV light and approximately 40 % of visible light, efforts have been made to increase the photocatalytic activity of titanium dioxide under visible light via nonmetal and metal doping. [4]

Titanium dioxide thin films and corresponding powders were prepared by a particulate sol-gel synthesis, with titanium tetrachloride (TiCl_4) as a precursor (inorganic route). Various acids, which increase the rate of precursor dissolution, and dopants (urea, tiourea, ammonium nitrate, chloroplatinic acid) were added during the synthesis. The resulting sols were then deposited onto object glasses by dip-coating technique and thermally treated in a muffle furnace to promote crystallization.

Thin films and corresponding powders were characterized using thermal analysis (TG-DSC-MS), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-Ray photoelectron spectroscopy (XPS), band-gap and specific surface area measurements. Photocatalytic activity of the prepared thin films (under visible light illumination) was determined by observing the decoloration rate of Plasmocorinth B (PB, an organic pigment, extensively used in textile industry) with UV-Vis spectroscopy. The results of characterization methods have shown that the characteristics of thin films and powders depend on the type of acid and dopant used. Results have also shown high photocatalytic efficiency of nonmetal and metal codoped titania thin films under visible light illumination. Figure 1 shows the kinetic results for PB degradation of an undoped sample (REF) and sample doped with S, N and Pt (S3_N0.5+2%Pt). A kinetic model for adsorption (zero order rate constant k_0) and subsequent degradation (first order rate constant k_1) was used to fit the experimental data. We observed a significant increase in photocatalytic activity under visible light illumination of samples, doped with S, N and Pt, compared to undoped samples.

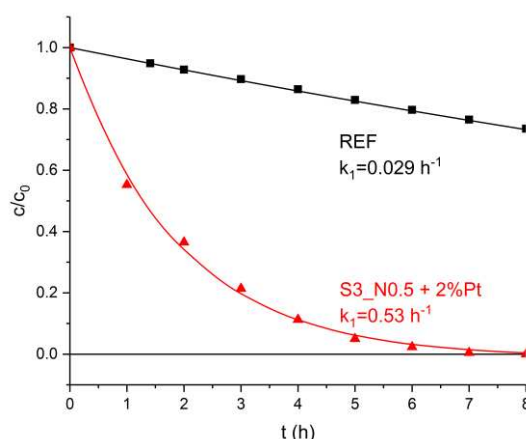


Figure 1: Photocatalytic activity of selected samples.

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Sorption of phytopharmaceutical compounds by chitosan-based blend materials

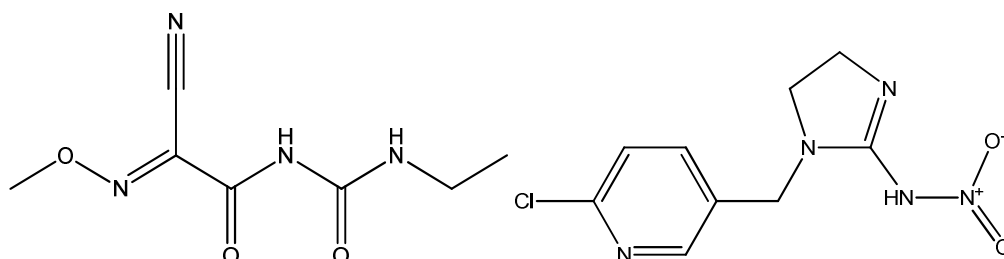
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In Agriculture, a large quantity of pesticides (over 2 million tons per year) is used worldwide [1], and their presence in surface water bodies is reaching alarming concentration values. The use of low cost and environmentally friendly sorbents in the remediation of contaminated environments, especially those consisting of natural polymers, have been receiving significant interest in the last decades. Chitosan (CS) is a polycationic polysaccharide obtained by deacetylation of natural chitin which can be found naturally in the shellfish exoskeleton and crustaceans. Chitosan is the most commonly used cationic biopolymer (positively charged at pH <6.5). The CS is non-toxic, biocompatible, is able to form films and therefore it has found many applications in food industry, cosmetic fabrication, among others. In this communication, we report the synthesis and characterization of blend gels of chitosan and pectin (either in the native state or modified with β -CD) for the removal of two different phytopharmaceutical compounds: Cymoxanil and Imidacloprid (scheme 1).

Both hydrogels were evaluated using nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The hydrogels were further characterized in terms of thermogravimetric analysis (TGA) and swelling kinetics. The interaction between the hydrogel and phytopharmaceutical aqueous solutions has been evaluated through sorption isotherms and kinetics. The gels were then subjected to sorption/desorption cycles to have an assessment of the capability of the adsorbents for re-use. The mechanism of sorption interaction and the selectivity of the adsorbents towards different compounds will be discussed.



Scheme 1. Molecular structure of (1) Cymoxanil and (2) Imidacloprid.

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Remove surfactants by adding porous colloids at the interface

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We have explored a new strategy for cleaning the surface of water contaminated by surfactants. We have studied porous colloidal particles as cleaning agents able to adsorb on their pores ionic surfactants accumulated at the air-water interface: some “micron- vacuum cleaner” [1]. For this purpose we evaluated the decontamination efficiency and the adsorption kinetics, investigating also the interfacial motion of micron sized mesoporous silica particles. We have used two model contaminants: CTA^+OH^- and CTA^+Br^- surfactants, and mesoporous silica with pore size of 2, 4 and 7 nm. Two main factors control the decontamination efficiency: the pore size and the particle surface charge induced by adsorption. The adsorption of surfactants and counter-ions is efficient only if surfactants can access the inner structure of the mesoporous silica. Hence, surfactant adsorption on porous silica particles is fundamentally different from the adsorption on planar silica surfaces. In fact, adsorption can be hindered by clogging of the pores and by electrostatics. In this context, we have measured by ellipsometry and surface tension that both CTA^+OH^- and CTA^+Br^- surfactants adsorbed on planar silica surfaces, but only CTA^+OH^- adsorb efficiently on porous silica particles. Surface tension experiments were used to quantify the surfactant removal [2] by porous silica, which points to high surface concentration Γ in agreement with the formation of surface self-assembled structures in the pores (Figure 1). Zeta potential experiments on mesoporous colloids in presence of surfactants show net changes depending on the particle pore size, surfactant concentration and the nature of the counter-ions. We have also proven that the particle deposition method has a considerable influence on the adsorption kinetics. Since the surfactants at the interface are in equilibrium with the bulk, even at concentrations much ahead from the cmc, we have investigated the adsorption kinetics when mesoporous colloids are trapped at the interface or added in the volume. A clear difference in the surfactant adsorption kinetics was observed, which suggests the importance of studying porous colloids at the interface for the removal of soluble and insoluble contaminants.

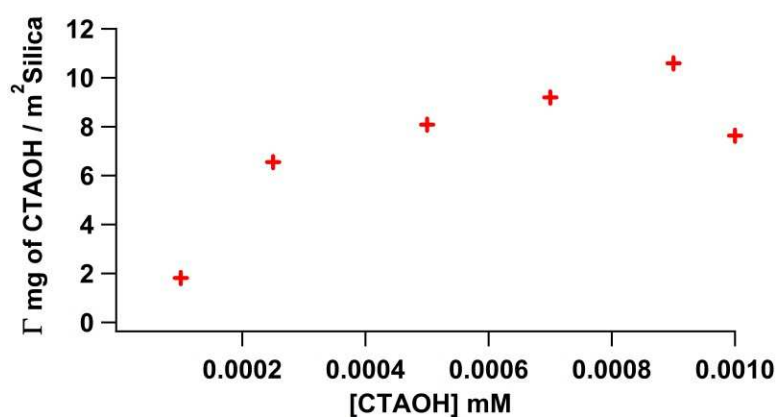


Figure 1. Adsorption of CTAOH onto porous silica colloids with 7nm pore size

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Brownian dynamics simulations on sedimentation behaviour of a dispersion composed of spherical and rod-like particles

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There are a variety of potential methods for improving the water quality of small lakes and ponds. For instance, there are a self-cleansing method by means of the aeration, an adsorption method using porous media such as active carbons and zeolites, a filtering method, and a flocculation method using a flocculant. Among these methods, the flocculation and the adsorption methods may be potentially available for improving the visibility of water in small lakes and ponds. From this background, in the previous study [1], we have treated turbidity-causing (TC) particles and the adsorption agents or particles with a spherical shape in order to elucidate the adsorption performance of the agents in the gravitational field by means of Brownian dynamics simulations. This technique for the adsorption is based on the use of the translational Brownian motion of the adsorption particles. If non-spherical particles are used instead of spherical ones as adsorption agents, then the rotational Brownian motion is also expected to make a significant contribution to the adsorption performance. This is a motivation of the present study for elucidating the behaviour of a suspension composed of spherical and rod-like particles. In the present study, we have employed the modelling of adsorption particles as large spherocylinder particles and TC particles as small spherical particles with a sub-micron size in order to perform Brownian dynamics simulations of an adsorption and sedimentation problem of these model particles in a gravitational field. We here show the characteristics of the adsorption performance under the same condition of the volumetric fraction of adsorption agents. For the case of a small aspect ratio $r_p=3$ of the adsorption particles, the adsorption rate is not significantly improved and is better only by several percent in comparison with the spherical case. This implies that the rotational Brownian motion hardly contributes to the adsorption process in the case of the particles with this aspect ratio. In contrast, for the case of a large aspect ratio $r_p=15$, the adsorption rate is much better than spherical particles by 25% improvement, and therefore it is seen that the rotational Brownian motion of the rod-like particle gives rise to a much more significant adsorption performance in this aspect ratio. This is mainly because the opportunity for the agent particles contacting with TC particles increases more significantly due to the influence of the rotational Brownian motion with increasing aspect ratio. From these results, we understand that the use of rod-like particles with a large aspect ratio as adsorption agents can adsorb TC substances much more efficiently in comparison with spherical particles.

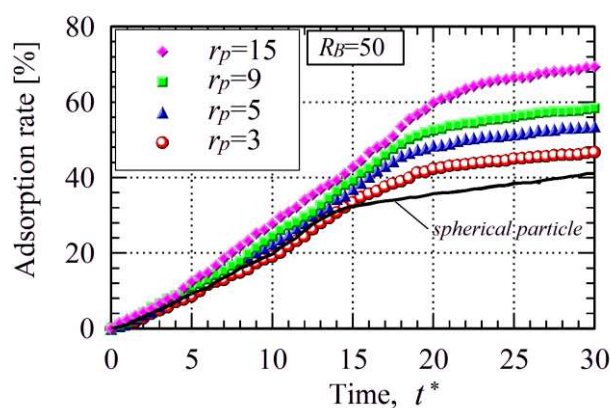


Figure 1. Time variation in the adsorption rate for $R_B=50$

Preparation of pore-filled composite-type cation and anion exchange membranes and their electrodialysis properties for water purification

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The contamination of low concentration (~1000ppm) of various cations and anions in seawater, brackish water and especially, in groundwater has become a serious problem in production of drinking water in the world. Several technologies can be adopted: nanofiltration, adsorption, biodegradation etc. Electro-dialysis process with cation and anion exchange membranes can be cost-effectively applied to this water purification application.

Novel composite-type anion- or cation- exchange membranes were prepared as follows; first, pore-filling of monomer mixtures - styrene/divinylbenzene (DVB), vinylbenzylchloride (VBC/DVB)) and an initiator (α,α -azobis(isobutyronitrile)(AIBN)) were impregnated in commercial PTFE porous films, respectively. Thermal polymerization was followed in high temperature oven for the formation of precursor membranes. Finally, post-sulfonation was done with chlorosulfonic acid in acetone to give sulfonated group for the preparation of cation exchange membranes. Post-amination was performed in trimethylamine (TMA) in acetone to give aminated group for the preparation of anion exchange membranes. SEM analysis confirmed these membranes were successfully prepared. The composite membranes showed excellent electrochemical properties – electric resistance, water uptake and IEC value - depending on the monomer dope compositions (styrene/DVB ratio and VBC/DVB ratio). These membranes showed lower electric resistance, higher IEC, but comparable or lower water uptake than commercial membranes due to thin PTFE supports. These results showed our membranes could be applied to the electro-dialysis process for the drinking water production from seawater, groundwater or brackish water.

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Understanding of Icing Phenomena on Particle-based Heterogeneous Surfaces

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Icing is a common phenomenon in nature and technology that influences our daily lives. In most cases, icing causes severe problems such as, for example, increase in the energy consumption of transport vehicles (aircraft, cars), or alternative energy sources (wind turbines), which eventually leads to increased maintenance costs or failures.

Therefore, the development of surfaces with reduced icing or easy de-icing is of paramount importance [1]. To invent effective coatings it is of crucial importance to get a deeper understanding of the icing phenomena. In general, strategies to prevent ice can be divided into anti-icing and de-icing mechanisms. To investigate the anti-icing ability of the surfaces it is necessary to completely consider the whole process of nucleation starting from the nucleation which happens during the condensation from air humidity and the freezing process afterwards. In addition, the phenomenon of freezing rain can be simulated by looking at the impact of one single supercooled water drop on top of a cooled substrate to get a comprehension of the processes which happen during the freezing of a drop depending on the substrate topography and chemistry. The de-icing ability can be investigated by various adhesion strength methods, which use the principle of centrifugal, shear or vibrational force.

In the end, the combination of the both anti-icing and de-icing properties in one material is very challenging task and requires the controlling of several parameters such as ice nucleation, growth and ice adhesion [2].

We report two approaches for the design of heterogeneous surfaces with anti-icing and de-icing capabilities. These surfaces are based on different polymer-modified hybrid core-shell systems. First, we use a mixture of different types of particles with controlled and tuneable chemical composition and size in various ratios to form heterogeneous surfaces. Second, we fundamentally investigate their wettability, ice nucleation behaviour during condensation and the drop impact of a super cooled water droplet as well as the ice adhesion properties using different experimental setups [2, 3, 4].

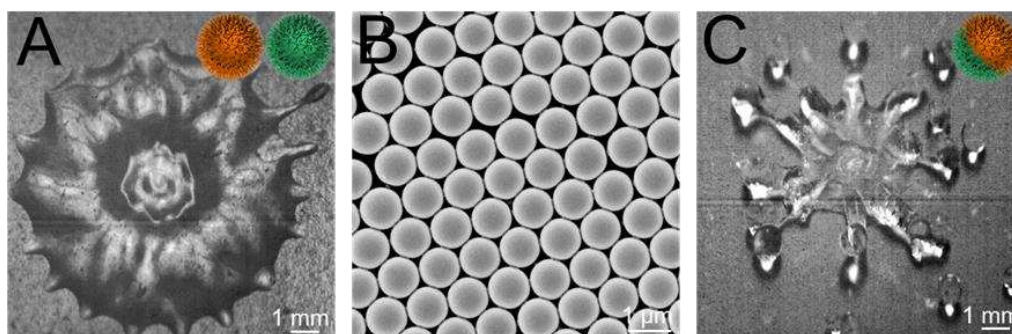


Figure 1. A) Representative optical image of the impact of a super cooled water drop on a particle mixture-based surface, B) SEM image of a particle-based surface, C) representative optical image of the impact of a super cooled water drop on a Janus particle-based surface.

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Understanding the Immobilization of Nanocatalysts onto Hybrid Isotropic and Janus Particles for Catalysis at Interfaces

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The design of colloidal particles with advanced architectures and controlled chemical functionalities is highly demanding for discovering of responsive and adaptive multifunctional materials. Combining two materials with different properties in the same particle leads to the development of structured hybrid core-shell systems with unique functionalities that can be used as carriers for catalytically active species. Immobilization of nanocatalysts, such as enzymes and metal nanoparticles, onto well-designed polymer interfaces provides an excellent base for their exploitation by enhancing their stability in different environmental conditions, and facilitating their recovery. Herein, we report on the targeted synthesis of hybrid hairy particles with controllable size, grafting density, chemical functionality, and heterogeneity (Fig. 1a), and show their loading with nanocatalysts. We propose the application of both isotropic and Janus particles for (interfacial) catalysis that benefits from the unique properties and architecture of these carrier materials.

In the first approach, we discuss the correlation between the controlled design of polymeric interface on substrates and its impact on immobilization of laccase from *Trametes versicolor*. To get a better understanding of the immobilization process, we vary particle size, polymer grafting density and chain length of polymer brushes using a “grafting from” approach. We also show how immobilization of laccase via physical adsorption affects the properties of the final polymer-enzyme layer [1,2].

In the second approach, we exploit the superior interfacial activity of Janus particles (Fig. 1c) and apply them for interfacial catalysis through selective modification of one of their sides with catalytically active species. This way, functional active interfaces loaded with hybrid hairy Janus particles are created resulting in successfully catalyzed reactions and the subsequent easy recovery of the hybrid catalyst [2,3].

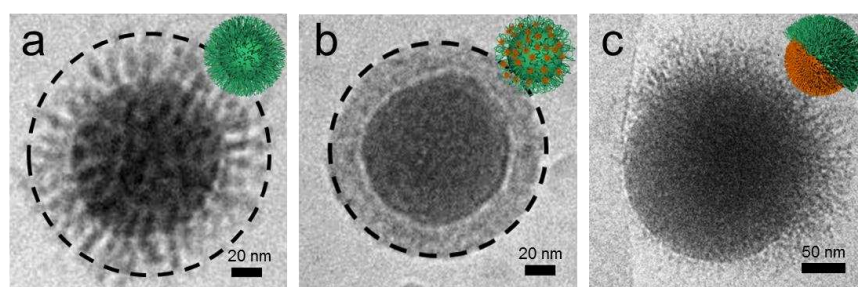


Figure 1. Representative cryo-TEM images of (a) an isotropic hybrid hairy particle without any catalytic species, and (b) an isotropic hybrid hairy particle with immobilized laccase from *Trametes versicolor*, and (c) a hybrid hairy Janus particle. Insets show schematic illustrations.

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Cellulose Self-Assembly

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Cellulose is our most abundant biopolymer, and hence an important renewable raw material for many materials. It is (semi-)crystalline with a high melting point, and chemically decomposes far before melting can be reached. Processing of cellulose thus require dissolution of the cellulose pulp. Dissolving cellulose, however, has turned out to be a challenge. Cellulose happens to be fascinatingly insoluble in all classical polar and non-polar solvents, because of its stable crystalline state. Solubility may, however, be obtained for example in certain ionic liquids and also (partly) in a strong base, the latter being the basis for the production of viscose fabrics. There are two major polymorphs of cellulose, native (wood) Cellulose I and the more stable Cellulose II. Dissolving cellulose pulp (Cellulose I), may therefore result in a supersaturated solution with respect to Cellulose II, and the association of cellulose in solution [1-5]. In this talk we will discuss cellulose dissolution and association in solution, with the potential application of textile fiber spinning [6].

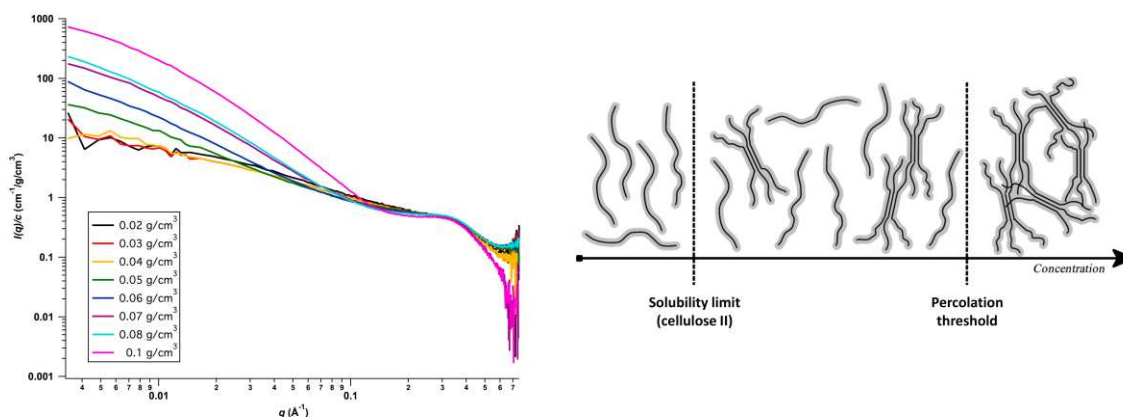


Figure 1. (Left) Small angle X-ray scattering patterns, normalized by the concentration, obtained from cellulose dissolved in 40 wt.% (1.3 M) tetrabutyl ammonium hydroxide (aq) in the concentration range 0.02 to 0.10 g/cm³ [5]. (Right) Illustrating the association of cellulose in solution, as precipitation of Cellulose II, and the potential percolation and gelation [4].

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Mixed complex formation in thermoresponsive block copolymer-bile salt systems

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Mixtures of polyelectrolytes and oppositely charged surfactants give rise to complexes with highly ordered structures and functionality that are important for both biological and technological applications [1-5]. When block copolymers with temperature-sensitive blocks are used as components in these complexes [6] they can provide smart systems for inclusion and release of active molecules.

Thermoresponsive diblock copolymers presenting a positively charged block have been shown to interact strongly with oppositely charged bile salt surfactants [7]. In this work, the effect of temperature on the self-assembly behavior in aqueous mixtures of cationic poly(N-isopropyl acrylamide) (PNIPAAM) diblock copolymers of different block lengths and various bile salts was investigated in a range of molar charge fractions using static- and dynamic light scattering, differential scanning calorimetry (DSC), cryo-transmission electron microscopy (cryo-TEM), small angle X-ray scattering and electrophoretic mobility measurements.

The phase behavior was found to be highly dependent on the lower critical solution temperature of PNIPAAM as revealed by a sharp increase in turbidity of the solutions around 35 °C. On the same time, the DSC thermograms presented endothermic transition peaks indicative of PNIPAAM dehydration. At temperatures below the cloud point, the intermolecular interactions are predominately of electrostatic origin and very interesting hierarchical supramolecular structures formed via electrostatically driven co-assembly as demonstrated by cryo-TEM. In one case, both globular-like objects of well-defined size and long tape-like structures was found to co-exist at 25 °C (Figure 1).

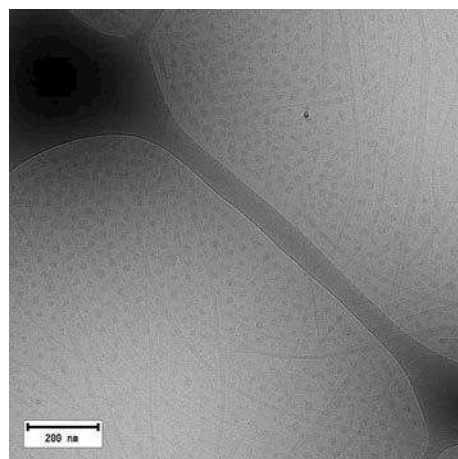


Figure 1. Examples of supramolecular structures in mixed PNIPAAM diblock copolymer-bile salt systems.

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Self-assembly of core/shell colloids at air/water interfaces

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The encapsulation of rigid nanoparticles by linear or cross-linked polymers yields core/shell particles that spontaneously self-assemble at air/water interfaces. In contrast to purely polymeric microgels that do not feature a hard core, long-range attraction between core/shell particles leads to cluster formation already at low packing fractions at such soft interfaces [1]. Transfer of the monolayer from the interface to macroscopic solid supports allows for the fabrication of hexagonally ordered superstructures with large single crystalline domains [2]. Depending on the length/thickness of the polymer coating of the building blocks such structures possess inter-core distances from a few up to several hundred nm. Due to an imbalance in interfacial tension between monolayer covered and monolayer-free areas, freely floating monolayers show a time dependent extension with increasing inter-particle distances with increasing time [2]. Multiple depositions on one substrate [3] or deposition on substrates with different contact angles gives access to a broad range of complex superstructures including honeycomb, Moire and square lattices (see figure 1).

In this contribution we will demonstrate the structural diversity that is accessible by interface-mediated self-assembly of hard/soft core/shell particles. We will shine light on the monolayer extension behavior by addressing the role of shell softness and surface activity. Furthermore, we will show how assembly of particles with plasmonic cores can lead to superstructures that show collective optical responses that differ strongly from the single particle behavior. The observed diffractive/plasmonic coupling can be reversibly tuned by addressing the refractive index environment through changing the swelling state of a responsive hydrogel matrix [4]. This way fully reversible resonance tuning becomes possible by either solvent exchange or temperature.

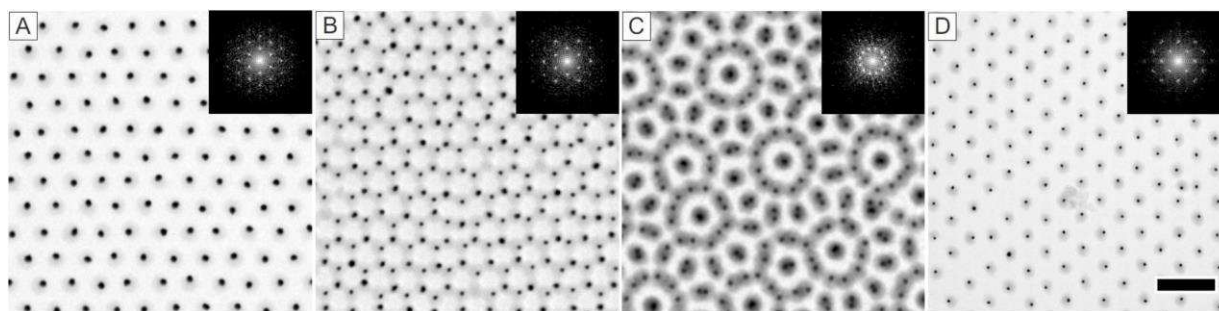


Figure 1. Structural diversity of monolayers prepared from interface-mediated self-assembly of core/shell microgels. A: Hexagonal lattice, B: Honeycomb lattice, C: Moire lattice, and D: Square lattice.

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Nanoreactors from electrostatically bridged like-charged surfactants and polyelectrolytes

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Association colloids such as micelles, vesicles or aggregates of surfactants with synthetic- or bio-polymers play an important role in modern technologies including pharmaceuticals and cosmetic, food, laundry and home care.

We report a complex multicomponent system, containing ethoxylated anionic surfactants, anionic polyelectrolytes and enzymes, which possesses a high efficiency to solubilize poorly water-soluble immobilized proteins (Figure 1A). By considering separate combinations of the system components at varied concentration regimes we addressed competitive interfacial and intermolecular interactions on different time- and length-scales. Using a set of methods such as dynamic tensiometry, solubilisation assay, molecular dynamic simulations we disclosed unexpected attractive interactions of fully neutralized polyacrylic acid (PAA) with like-charged surfactants in the presence of multivalent cations. A key contribution to the understanding and characterization of the macroscopic effect of enhanced solubilisation performance was gained by the analysis of dynamic processes at interfaces and of competitive binding interactions with Ca^{2+} ions in the multicomponent system (Figure 1B-C). In a narrow compositional range, the proposed bridging interactions via complexation with Ca^{2+} provide self-assembly of multicompartament dynamic soft nanoreactors with the solubilisation capacity exceeding that of conventional micelles [1].

Incorporation of a protease into such dynamic nanoreactors results in a synergistically enhanced cleaning performance. Apart from direct impact of these findings on the sustainability of laundry technology, revealing novel electrostatic association mechanisms and understanding interactions of hydrophobic species with biocompatible assemblies, like reported here compartmentalized surfactant/polymer/enzyme carriers, may give rise to new design approaches of delivery systems with possible biomedical applications.

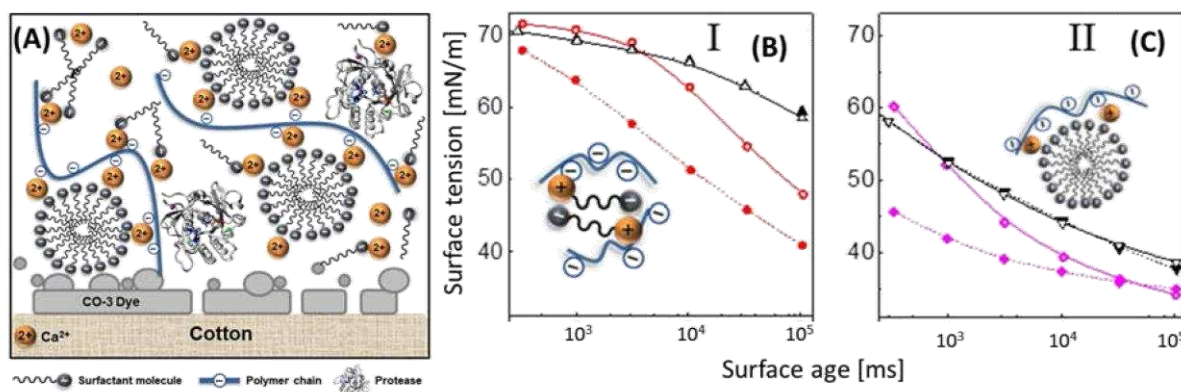


Figure 1. (A) Schematic of a multicomponent system highlighting individual and associated species formed between protease, SLES surfactant, polymer PAA and immobilized hydrophobic protein. (B,C) Kinetic curves of the surface tension of SLES solutions I (below CMC) and II (above CMC) in soft water (black triangles) and in the presence of Ca^{2+} ions (empty circles and diamonds) and PAA/ Ca^{2+} (filled symbols).

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Hydrogel Formed by Organogelator - Surfactant-Mediated Gelation

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Low molecular weight gelators (LMGs) can easily form a gel through a simple dissolution and cooling process in a solvent. The resulting gels can be used for various applications such as drug delivery [1], environmental pollutant recovery [2], and chemical sensors [3]. In such gels, the LMG molecules form self-assembled fibrillar networks (SAFiNs) which arrest the solvent. An example of an LMG is the organogelator 12-hydroxyoctadecanoic acid (12-HOA) which gels various organic solvents but not water. However, it is anticipated that hydrogels can be produced by dissolving 12-HOA in an aqueous surfactant solution due to the solubilization capacity of surfactant self-assemblies, i.e. micelles (surfactant-mediated gelation, SMG). It is reported that microemulsions [4] and liquid crystals [5] formed in a three-component water-oil-surfactant system can be gelled with 12-HOA. However, hydrogel formation in oil-free water-surfactant systems with 12-HOA is also possible. This contribution deals with the formulation of gelled micellar [6] and gelled lamellar liquid crystalline [7] phases and we show that both surfactant self-assemblies and SAFiNs coexist in an orthogonal self-assembled way [8].

A clear transparent solution was obtained when 0.1 mol L⁻¹ of 12-hydroxyoctadecanoic acid (12-HOA) was added to an aqueous micellar solution (0.15 mol L⁻¹) of cetyltrimethylammonium bromide (CTAB) and heated to 80°C. Then the sample was gradually cooled to room temperature and a gel was obtained. 12-HOA was also added to a lamellar liquid crystal formed by didodecyltrimethylammonium bromide (DDAB) and the same treatment was carried out to obtain a gel. Small- and wide-angle X-ray scattering (SWAXS) measurement on the gels revealed a coexistence of the gelator fibers of 12-HOA and the surfactant aggregates. Transmission electron microscopy (TEM) images support the coexistence of lamellar liquid crystals and gelator fibers in the gelled lamellar phase. Dynamic viscoelasticity measurements showed that the gelled samples have a higher storage modulus (G') and loss modulus (G'') than the non-gelled samples, indicating that SAFiNs of 12-HOA improve the mechanical properties of the sample.

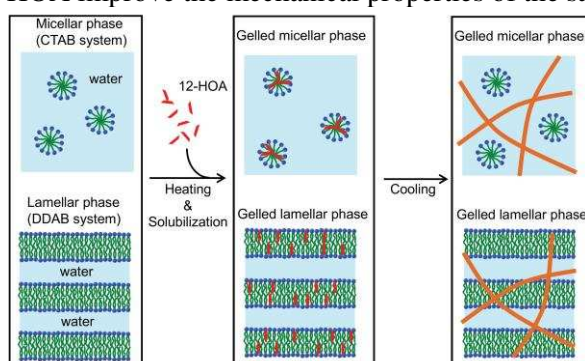


Figure 1. Hydrogelation with an organogelator through surfactant-mediated gelation (SMG)

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Unique aqueous self-assembly behavior of a new thermoresponsive diblock copolymer

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We describe the synthesis of a new amphiphilic diblock copolymer *via* a one-pot RAFT-mediated polymerization-induced self-assembly (PISA) protocol and investigate its unique thermoresponsive behavior. More specifically, dimethylacrylamide (DMAC) was polymerized at 80 % w/w solids in aqueous solution at 30 °C in the presence of a carboxylic acid-functionalized RAFT agent. ¹H NMR spectroscopy confirmed full monomer conversion and GPC analysis indicated good batch-to-batch reproducibility for the synthesis of this water-soluble precursor block. Subsequently, this PDMAC macro-CTA was chain-extended with a water-miscible monomer, 4-hydroxybutyl acrylate (HBA), under aqueous dispersion polymerization conditions at 30

°C to produce diblock copolymer nano-objects at 20 % w/w solids in mildly acidic solution (pH 3).

On cooling to ambient temperature, a viscous fluid was obtained, indicating the formation of block copolymer worms. Oscillatory rheology studies indicated that a significant reduction in viscosity occurred on cooling the 20 % w/w diblock copolymer dispersion from 20 °C to 5 °C. This phase transition is fully reversible: the viscosity increases on returning to ambient temperature. Shear-induced polarized light imaging (SIPLI) studies performed at 18 °C confirm the appearance of a characteristic Maltese cross motif: this indicates birefringence resulting from the *in situ* alignment of the anisotropic worms. Heating this aqueous copolymer dispersion up to 23 °C resulted in disappearance of the Maltese cross and a concomitant reduction in solution viscosity. An intense Maltese cross motif was again observed at around 50 °C and was accompanied by an increase in solution viscosity. DLS and SAXS studies conducted on a 1 % w/w diblock copolymer dispersion suggest that these changes in physical properties are the result of thermally-induced morphological transitions from spheres (5 °C) to worms (6 °C) to vesicles (20 °C) to lamellae (50 °C). Moreover, these thermal transitions occur rapidly and are fully reversible.

Variable temperature ¹H NMR spectroscopy was used to probe this remarkable self-assembly behavior: this technique provided direct evidence for a continuously varying degree of hydration for the weakly hydrophobic block over the temperature range of interest, which accounts for the evolution in diblock copolymer morphology.

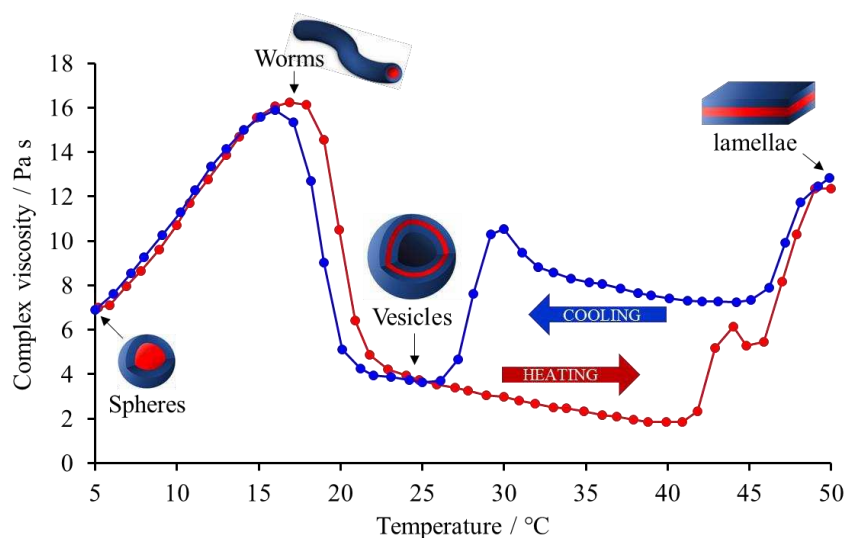


Figure 1. Temperature dependence of the complex viscosity observed for a 20 w/w% aqueous dispersion of PDMAC₅₄–PHBA₂₆₉. Conditions: frequency = 1.0 rad s⁻¹ at an applied strain of 1.0% and a heating/cooling rate of 1 °C min⁻¹.

Programming hierarchical self-assembly of patchy particles into colloidal crystals via colloidal molecules

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The scope for tuning the interactions between colloidal particles offers enormous opportunity to program their self-assembly [1]. In particular, hierarchical self-assembly of colloidal particles, which is currently at an early stage of exploration [2,3], offers a bottom-up route to an increased level of structural complexity. However, programming hierarchical self-assembly faces a major challenge in bridging hierarchies of multiple length- and time-scales associated with structure and dynamics, respectively, along the self-assembly pathways.

In this presentation, we will demonstrate how a hierarchy of interaction strengths realized with triblock patchy colloidal particles can be exploited to address this multiscale design problem [4]. Our designer patchy particles are spherical in shape, having two asymmetric, attractive patches, A and B, at the poles across a charged band in the middle. Such triblock spherical particles were recently synthesized at the micrometer scale and shown to undergo staged assembly triggered by stepwise change of the ionic strength of the medium [5]. However, the assembly at the first stage produced a distribution of cluster sizes, including tetramers and hexamers, posing serious limitations to the formation of colloidal crystals in the next stage [5].

We employed a variety of computer simulation techniques to show hierarchical self-assembly of our designer triblock patchy particles into colloidal crystals via small colloidal clusters, i.e. the so-called colloidal molecules, of uniform size and shape, as illustrated schematically in Figure 1 [4]. In particular, we demonstrate the hierarchical self-assembly of triblock patchy particles into a cubic diamond lattice *via* tetrahedral clusters, thus underpinning a novel strategy for its experimental realization. This route relaxes the stringent requirement on the fidelity of particle synthesis associated with the fabrication of precisely tetrahedral patches [6]. Additionally, for a wider patch width and a longer patch–patch interaction range, we show that these triblock patchy particles self-assemble into a body-centered cubic crystal with a two-level structural hierarchy *via* octahedral clusters, thus lending generality to this design principle. We also characterized dynamical pathways for crystallization, revealing that the crystals with a two-level structural hierarchy are indeed assembled stagewise *via* colloidal molecules [4].

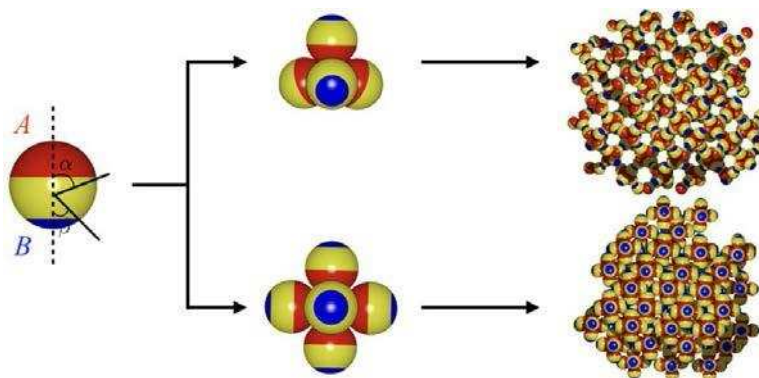


Figure 1. A schematic representation of hierarchical self-assembly of triblock patchy particles into colloidal crystals via colloidal molecules.

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Characterization of Self-Assembled Surface Active CO₂/EO Compounds in Aqueous Solution

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Using CO₂ as a raw material in the production of materials is a viable alternative to the conventional, petroleum-based raw materials and therefore offers great potential for sustainable chemistry. Surfactants containing CO₂ in their head groups show characteristic molecular self-assembly behavior in aqueous solution, just as normally observed for nonionic surfactants. These novel compounds are yielding nanoscale structures

i. e., micelles, of different shapes, and are relevant for practical applications as they are similar to alkylethoxylates that have been “working horses” in detergency for a long time but also in a large number of other applications [1].

In this study we present the characterization of these CO₂ containing surface active compounds with respect to their colloidal properties, surface activity, and their self-assembly behavior, and this as a function of temperature. Compounds with different CO₂ content and alkyl chains are compared here in a systematic fashion also to their commercial alkylethoxylate counterparts. The surface-active behavior is characterized via surface tension measurements, which also allows to determine the critical micellar concentration (CMC). In addition, the HLB values are determined to give a detailed information about the application potential in solubilization and to compare the CO₂ surfactant with conventional commercial EO surfactants.

Finally, the micellar structure was characterized by dynamic (DLS; Fig. 1 B) and static (SLS) light scattering as well as by small angle neutron scattering (SANS), where the data gives detailed insights into the mesoscopic organization. From the scattering data a consistent picture of the micellar structure as a function of concentration as well as of the temperature can be obtained (Fig. 1 A). This structure is in general depending on the length of the EO chain and the CO₂ content and therefore the understanding and comparison of the shape and structure is crucial to understand the influence of the CO₂ unit [2].

As a result we can conclude that the CO₂ containing surface active compounds are interesting amphiphilic molecules with a high degree of versatility towards applications and are in particularly appealing as they are associated to a more sustainable chemistry production than conventional amphiphiles.

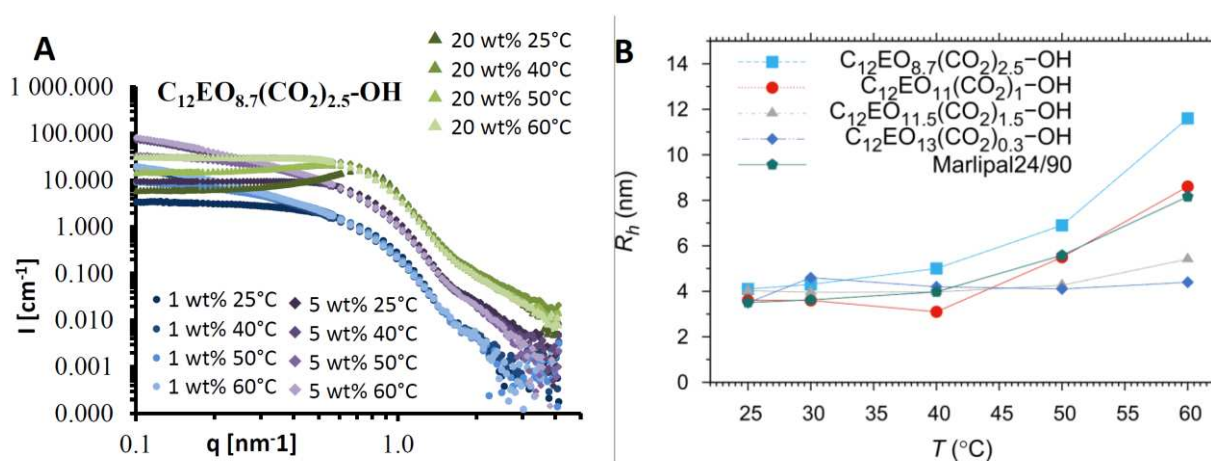


Figure 1. A: SANS spectra of temperature dependent measurements of the surfactant $\text{C}_{12}\text{EO}_{8.7}(\text{CO}_2)_{2.5}\text{-OH}$ (1wt% (blue), 5wt% (violet) and 20wt% (green)) at 25°C, 40°C, 50°C and 60°C. B: Temperature dependent hydrodynamic radii of the C12 EO/CO₂ surfactants calculated via DLS measurements.

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Nanoxerography Assisted by Convective Surface Assembly

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Nanoxerography relies on electrostatic interactions to assemble nanoparticles on predefined patterns efficiently with possibly sub-micron resolution [1]. Solvent removal during the drying of the substrate is however delicate since the assembly may be altered by capillary interactions (see [2] and references therein), especially for micron-sized particles. This is a major issue limiting the range of particles that can be effectively assembled by nanoxerography and which could serve as active or sensing elements in applications (e.g. photonics).

To remove this restriction, we present here an adaptation of the nanoxerography process using a blade coating method to control solvent evaporation and induce an auxiliary convective surface assembly phenomenon. It permits to increase the density of (large) particles deposited on charged patterns while preserving the remarkable selectivity of nanoxerography. The assembly is reproducible and robust even for micron-sized particles [3].

Complementary particle-field Brownian dynamics (PF-BD) simulations and experiments are also reported (see Fig. 1). They shed some light on the kinetics and on the limiting factors of this electrostatically and hydrodynamically driven assembly.

Concerning kinetics, we demonstrate that the density of assembled particles increases with time in a two-step process. The first fast regime is dominated by the pattern-particle electrostatic interactions, and the second slower regime is mainly determined by diffusion and particle-particle interactions. Both of these regimes have been modelled on a continuous level with a transport equation accounting for long-range pattern- particle and particle-particle interactions adequately through an effective diffusion coefficient depending on the osmotic pressure of the suspension. The model predictions agree very well with the PF-BD simulations without fitting parameters, and the long-time scaling predicted by the model is indeed observed experimentally. The limiting factors of the selective assembly are revealed by the model, the simulations, and the experiments. In particular, the model explains the captured density dependence with time, volume fraction, and interaction range and intensity. The inefficiency of regular nanoxerography for particles approaching the size of the pattern details is explained by particle-field BD simulations. Finally, for the coupled nanoxerography / blade coating process, the dependence of the captured particle density with blade velocity is determined experimentally and explained by simulations.

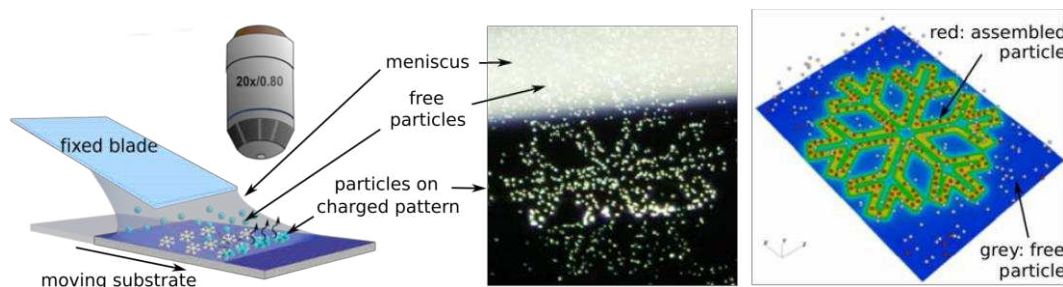


Figure 1. Experimental setup (left), corresponding microscope image (middle), and simulation (right) showing the assembly of 1 μm latex particles on a charged snowflake pattern. The colour field on the simulation image is the electrostatic potential field close to the substrate.

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Self-assembly of gapped DNA duplexes

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Liquid crystalline phases of double-stranded DNA in aqueous solutions have been studied comprehensively in the past [1-4]. However, so far no smectic phase was observed in DNA duplexes. Here, we show that introducing a flexible single-stranded region into double-stranded DNA can lead to smectic ordering. This finding is indeed surprising, since it's known that flexibility destabilizes layer-like ordering in lyotropic systems. Gapped DNA duplexes- two double-stranded DNA fragments connected with a single-stranded flexible DNA spacer- were found to form an unconventional folded type of smectic mesophase. The smectic layers form due to folding of flexible parts in duplexes and end-to-end stacking interactions between their blunt ends. The folding scenario was backed up by Monte Carlo simulations which highlight that folded smectic phase is thermodynamically stabilized both from entropic and enthalpic point of view [4]. Furthermore, preliminary results demonstrating the impact of suppressed blunt-end attractive interactions on formation of smectic phase will be shown. These results unveil the DNA as a molecular tool which offers numerous possibilities for engineering of lyotropic liquid crystals.

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Assembly in mixtures of bile salt derivatives

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Three-dimensional structures with nanoscopic dimensions, yielded by self-assembly of lipids and surfactants, are particularly interesting for their applications in nanoscience. In these applications the possibility of controlling and modifying the particle features like structure and charge allows the regulation of fundamental aspects such as their ability to load molecules (drugs, DNA, proteins, etc.), to aggregate and to penetrate membranes. Due to a rigid and unconventional amphiphilic structure, anionic obtained by chemical modifications of the steroidal surfactant bile salts (BS) and cationic derivatives have proven to provide uncommon ordered supramolecular structures [1-3]. They also allowed for a fine tune of the aggregate charge and structure by changing the mixture composition.

In this context this contribution finds its relevance by reporting about the co-assembly of new BS based derivatives bearing hydrophobic rigid groups on the steroid rigid skeleton. Results demonstrate that aggregates with different morphologies and charge can be prepared by properly choosing the derivatives and tuning the mixture stoichiometry (Figure 1), thus promoting these mixtures to versatile systems for preparations of supramolecular nanostructures.

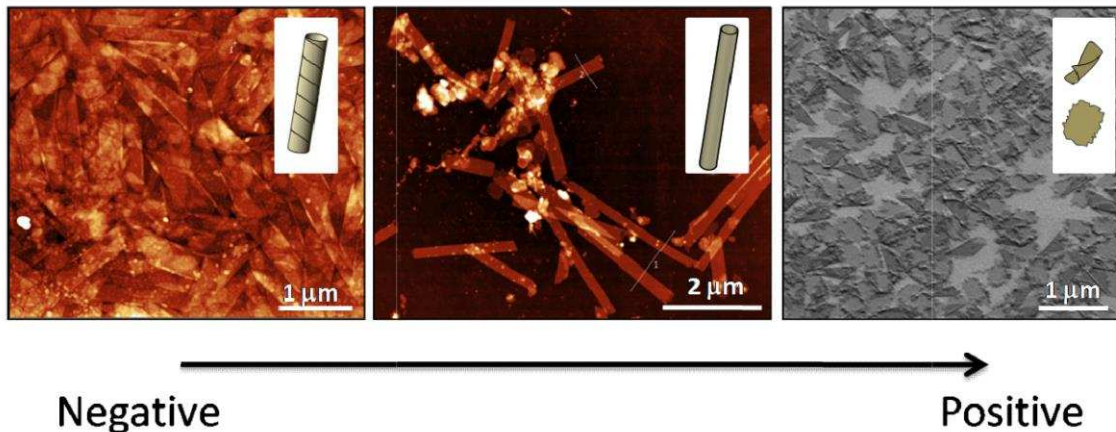


Figure 1. Charge and morphology evolution in supramolecular BS catanionic nanostructures.

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Solubilization of solvophobic polymer chains in interpolyelectrolyte complex cores of non-stoichiometric co-assembled nanoparticles

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We studied the electrostatic co-assembly of double hydrophilic copolymers containing a polyelectrolyte (PE) block and a neutral water-soluble block with the oppositely charged PE homopolymers and the solubilization of solvophobic polymer chains in cores of associates by dissipative particle dynamics (DPD) computer simulations. DPD is a coarse-grained simulation technique which employs three types of forces: (i) conservative force (soft repulsion and other forces that come into account in different systems), (ii) dissipative force (emulating friction) and (iii) random fluctuating force (emulating thermal motion) [1]. If PE systems are studied, electrostatic interactions have to be included into the simulation scheme as a second conservative force. There exist alternative approaches, e.g., the "ion-free" approach [2] which do not take electrostatics into consideration. We use DPD with explicit electrostatics [3,4] because we are of the opinion that the entropy of counterions and electrostatic correlation effects are properly described and accounted for only if the used DPD variant employs explicit electrostatics.

In the first part of our presentation, we will shortly outline the principles of DPD and problems connected with the implementation of electrostatics. In the second part of the presentation, we will present results of our recent simulations on the solubilization of solvophobic compounds in co-assembled nanoparticles. Results of simulations indicate that solvophobic oligomers and polymers can be easily solubilized in interpolyelectrolyte complex (IPC) cores, which allows for tuning the core properties without hindering the co-assembly or destabilizing the dispersions.

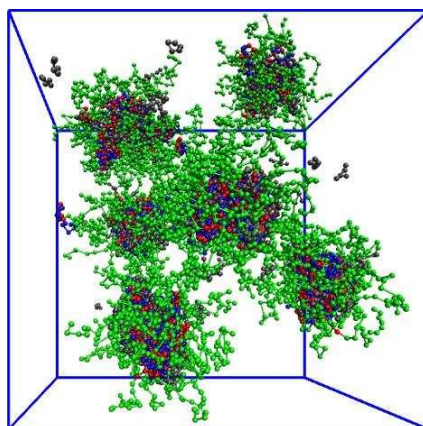


Figure 1. A typical snapshot of the simulation box showing the co-assembled nanoparticles with polymer chains (black) solubilized in interpolyelectrolyte cores (red and blue); shell-forming chains – green.

Acknowledgements: The study was supported by the Czech Science Foundation (Grant 16–12291S).

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Molecular Mechanisms for Self-Assembly in Hydrogen-Bonding Rich Non-Aqueous Solvents

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Self-assembly of surface-active molecules is not well understood in *polar* non-aqueous solvents, such as glycerol and ethylene glycol. Such an understanding is not only important on a fundamental level, but also vital to product formulations. An emerging class of polar non-aqueous solvents is *deep eutectic solvents* (DES), which are a mixture of two solvents at the eutectic molar ratio, so-called due to their ionic nature [1] and their depressed freezing point compared to the constituent parts. DES can be made from renewable and sustainable sources, such as choline chloride (ChCl) and glycerol (known as *glyceline*) [1].

In the theoretical framework of Israelachvili [2], hydrogen bonding capacity underpins the driving force for self-assembly in water. Several key physical parameters can be compared, such as the boiling point and the viscosity, which show a dependence on the *hydrogen bond number per molecule* ($n = 4, 9$, and 9 for water, glycerol, and glyceline respectively), whereas the surface tensions are related more closely to the hydrogen bond density [3,4]. However, a large difference in hydrogen bond density (75.6 nm^{-3} vs 19.8 nm^{-3} for glycerol and glyceline respectively) does not explain a small difference in their surface tensions (64.0 mN m^{-1} vs 63.5 mN m^{-1} , respectively). We postulate that the molecular shape and volume play an important role in the self-assembly process, which has not been fully accounted for in the established theoretical models.

Experimentally, we have investigated self-assembly behaviour of surfactants at interfaces and in the bulk solution. Surface tension data revealed that the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) (an anionic surfactant) increased in the following trend: glyceline (5.6 mM), water (8.1 mM), and glycerol (10.8 mM), suggesting that the solvophobic effect is strongest in the DES. X-Ray reflectivity was used to characterize interfacial structure of dodecyltrimethylammonium bromide (a cationic surfactant) at the mica-liquid interface, with mild Kiessig fringes observed, indicating its interfacial activity. In addition, we have observed gelation behaviour of SDS in glycerol and glyceline at concentrations ranging from 50 mM to 220 mM of SDS, suggesting the formation of elongated SDS micelles as gelators, not previously observed. The self-assembled structure in solution and gel was probed by small-angle neutron and X-ray scattering techniques, and results will be discussed in light of the observation by polarised light microscopy (**Figure 1**), which also suggests worm-like aggregate formation. Our results are valuable to the fundamental understanding of molecular self-assembly within hydrogen-bonding rich non-aqueous solvents with potential for future green industrial formations.

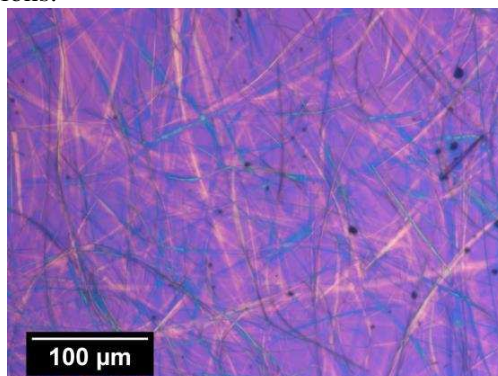


Figure 1 Polarised light microscope image of 220 mM SDS in glycerol (taken using a 530 nm waveplate).

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Aggregation of soft-patchy colloids

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The hierarchical self-assembly of triblock terpolymers (ABC) in selective solvents is a bottom-up approach for constructing decorated (or patchy) colloidal aggregates with multiple morphologies [1,2]. Importantly, these aggregates exhibit transitions in their shape and decorating patterns as a response to changes in the system conditions. These assemblies have potential medical applications as nanocarriers for drug delivery and as prototypes for biological structures such as organelles, cells, and viruses. Due to the multiscale nature of the colloidal-assembly process the understanding of the thermodynamic and kinetic balance leading to a variety of decorating patterns remains elusive. Here, we use the dissipative particle dynamics method [3] (DPD) to investigate how the volume fractions of the polymer blocks, the polymer-solvent interactions, and solubilization methodology determine the shape and number of patches [4]. The control of the size and patch distribution allows the fabrication of a variety of anisotropic colloids. We find that multistage assembly schemes offer robust control over the morphology of the aggregates. Our computational simulations demonstrate that patchy colloids form larger structures via fusion and stacking. Additionally, we observe that the interfacial energy between the polymeric blocks determines the morphological evolution of the patches upon the colloids aggregation. We construct the phase diagram for patchy colloids formation providing new insights into the complex mechanisms driving their morphology. Finally, we propose the theoretical description of the assembly process in terms of the free energy of the system. Our results are consistent with experimentally reported structures [1,2], and explain the multiplicity of these structures for different entropic and enthalpic conditions. Future work includes the study of larger aggregates such as vesicles or multicompartament microscopic structures.

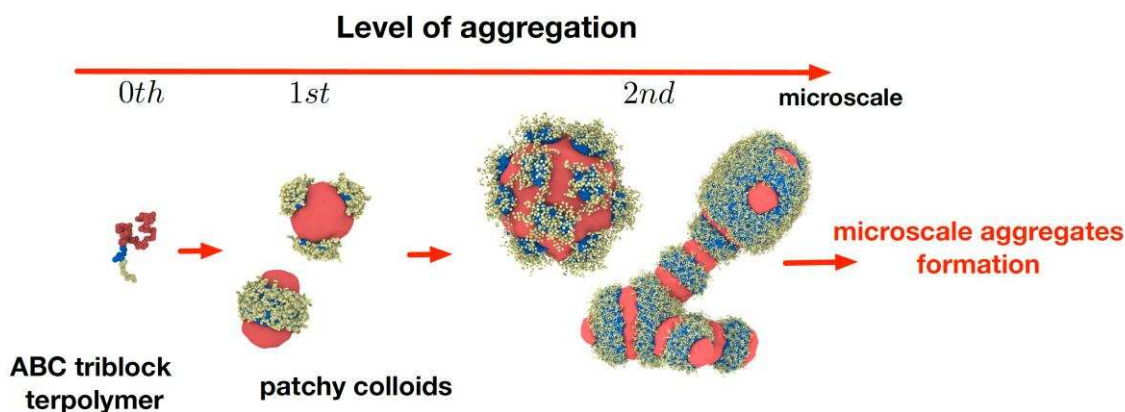


Figure 1. Schematic representation of the hierarchical assembly of triblock terpolymers

Acknowledgements: The authors acknowledge the Okinawa Institute of Science and Technology for funding this project.

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Molecular self-assembly at solid-liquid interfaces under electrochemical control

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In recent experiments [1] the spontaneous and reversible transition between two- and three-dimensional self-assembly scenarios of a supramolecular system (PQPClO₄) at a solid-liquid interface under electrochemical conditions [Au (111) in 0.1 M HClO₄] has been demonstrated. By a simple variation of the interfacial potential, it was possible to selectively organize the target molecules (i) in an open porous pattern, (ii) to fill these pores to form an auto-host-guest structure or (iii) to stack the building blocks in a stratified bilayer.

In our complementary theoretical investigations effort is dedicated to rationalize these experimental observations. To this end the molecules are modeled as rigid entities composed of atomistic constituents. Based on *ab initio* calculations we take into account long-range electrostatic- and short-range Lennard Jones-potentials for intermolecular interactions, describe the solid-liquid interface in terms of a slab-geometry with a lower perfectly conducting soft wall and allow for an external electrostatic field.

The self-assembly scenarios of these molecular models at an interface is studied and identified via optimization tools that are based on evolutionary algorithms. The complexity of the problem forces us to use advanced techniques of these optimization tools, including a basin hopping memetic approach combining the heuristic nature of evolutionary strategies with deterministic local gradient descent algorithms. The gradient descent method – relying on LAMMPS potentials and gradients – deterministically evaluates every basin's local minimum with high accuracy while the evolutionary search gradually adapts its population to the energetically most favorable solution, exploring the search space for the global optimum.

Our theoretical results allow predicting, on the basis of the model above, the experimental conditions under which the various self-assembly scenarios can be observed. Moreover, our algorithm does not only apply to the PQPClO₄ system but we implemented a framework which can cope with arbitrary (rigid) molecules in any kind of periodic or non periodic system. We demonstrate that we are able to make reliable predictions for the ground state for a variety of combinations of cations (PQP⁺, PQPC₆⁺) and anions (ClO₄⁻, AQDSA²⁻, BS⁻) at a solid-liquid interface under electrochemical control [1, 2]. In addition, our findings indicate the location of the ClO₄⁻ anion relative to the cation, an information which is – due to the anion's high mobility – not, or only very limited [2], accessible experimentally.

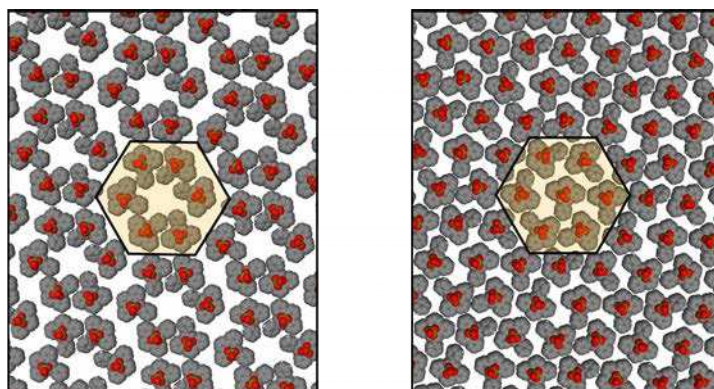


Figure 1. Prediction for the ground state configuration of the porous- (left) and the auto-host-guest-PQPClO₄ system (right).

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Properties of Fluorocarbon surfactants in Fire-fighting foam formulations

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The known theory underpinning the use of fire-fighting foams is basic and empirical; few attempts have been made to model or investigate the behaviour of foam formulations from a chemical perspective [1-3]. This being due to the formulations containing complex mixtures of both environmentally hazardous fluorocarbon (FC) surfactants and benign hydrocarbon (HC) surfactants. Partially fluorinated surfactants are used predominantly to give the formulation its desired properties, however it is not really known how the HC surfactants interact with the FC surfactants when they are mixed in the formulations. Therefore, by gaining an understanding of how these surfactants behave in the formulations, both individually and as mixed systems in mimics of the real formulations (F/F mixtures and F/H mixtures), will allow insight into important structure-property relationships between surfactant mixtures in fire-fighting foam formulations.

This work will present new advances and understanding about the surface and bulk properties of FC surfactants in fire-fighting foam formulations. The formulation was broken down into its constituent parts so that the individual FC surfactants could be well characterised in terms of their surface and bulk properties. Interestingly, common force tensiometry techniques could not be used to accurately characterise the adsorption behaviour, this being due to the commercial nature of the surfactants. For this reason, both small-angle neutron scattering (SANS) and neutron reflection (NR) were employed to learn how these surfactants behave both at the air-water interface and in bulk solutions. Figure 1 shows the SANS profiles for the three FC surfactants in this study, different bulk behaviours are observed in each case. Finally, initial characterisation of the FC/HC mixed systems using SANS and NR will be discussed.

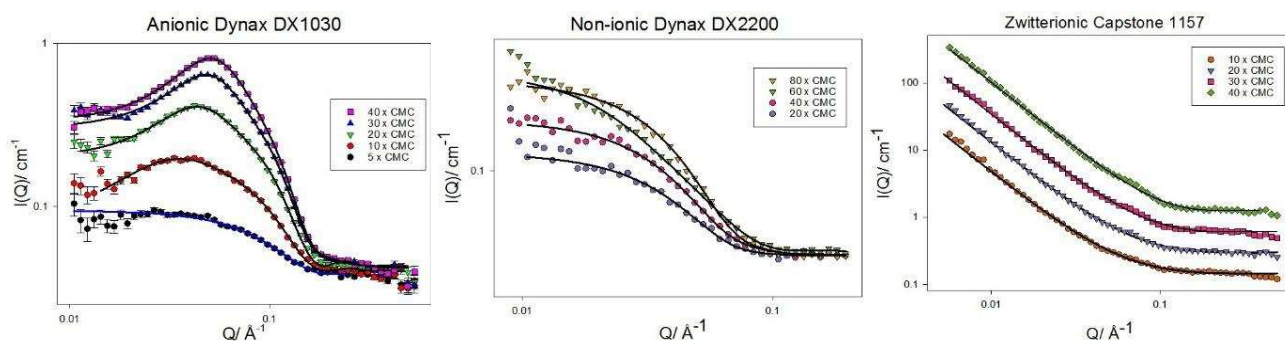


Figure 1: Showing neutron scattering profiles for the three FC surfactants.

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Constant width ribbons, in the A₁₀K model peptide system

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Self-assembled protein fibers are a key ingredient in life as we know it, making up a large part of the human cell [1]. However, under certain circumstances the formation of fibrillar structures can be just as disruptive, e.g. in diseases such as Alzheimer's and Huntington's, where fully functional proteins reassemble into fiber structures, eventually leading to an irreversible degradation of the brain. The neurotoxicity of such structures has been found to correlate with the specific one-dimensional geometry [2], rendering a need of fundamental understanding of governing factors behind the geometrical restriction in protein fibers.

The synthetic peptide model system A₁₀K has been shown to self-assemble into ribbon-like structures consisting of $2n+1$ laminated β -sheets, exhibiting a constant width of approximately 7 nm. In this work we present experimental data from X-ray scattering techniques as well as electron microscopy confirming the ribbon structure. Furthermore we present a thermodynamic model that predicts a constant width of the ribbons using an adaptation of a thermodynamic model for such geometrically restricted aggregates [3]. In the model we consider two contributions to the free energy. Firstly an interfacial free energy associated with the hydrophobic alanine chains, favoring large n . Secondly, an energy penalty arising from the stretching of the chiral β -sheet to fully accommodate their lamination, which increases with increasing n . Summing up the two contributions we find a minimum in the free energy per molecule for a given finite value of n (Figure 1). The model will be discussed in the light of experimental data.

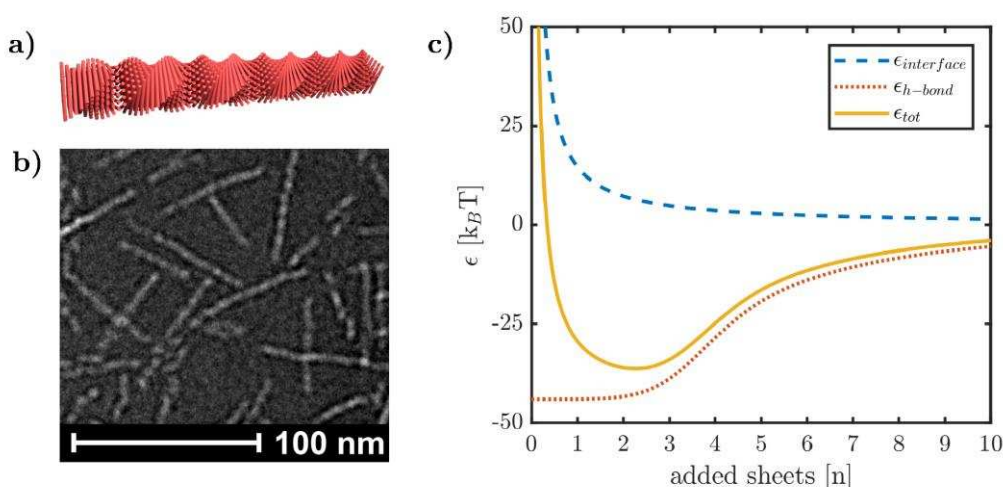


Figure 1. a) An idealized model of the A₁₀K aggregates, visualized by negatively stained EM in b). c) A total energy minimum of the ribbon structure in the A₁₀K system for a finite amount of laminated β -sheets is shown. The model considers interfacial free energy, associated with hydrophobic residues, and an energy penalty due to the stretch of hydrogen bonds within the beta sheets.

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Dancing performance of multiple organic droplets in aqueous solutions

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The emergence of complex behaviour in systems consisting of interacting agents is an interesting phenomenon that is intensively studied in a variety of scientific areas, such as animal and cell swarming in biology, the behaviour of social groups, or particle interactions in chemistry and physics. Here the interesting interactions of organic droplets are described. We have observed that droplets consisting of a mixture of ethyl salicylate (ES) and paraffin liquid floating on the surface of aqueous sodium dodecyl sulphate solution (SDS) in a Petri dish (covered by a lid) exhibit collective-like behaviour that can be divided into four stages (Figure A): the random motion state (stage I), the ring structure state (stage II), the cluster oscillation state (stage III), and the final static state (stage IV) [1, 2]. Other system consisting of decanol droplets floating on sodium decanoate solution [3, 4] on microscopic slides (system open to the environment) have shown qualitatively similar behaviour. Moreover because of water evaporation from the system we can observe two more stages, namely (V) disintegration of the cluster and separation of droplets and (VI) shape changes of droplets (Figure B) [5, 6]. Although the systems differ in several parameters, we think that the phenomena observed should be based on the same principles. Present work aims to compare the behaviour during whole the experiments in both systems, namely the fascinating oscillating behaviour of droplets in a cluster.

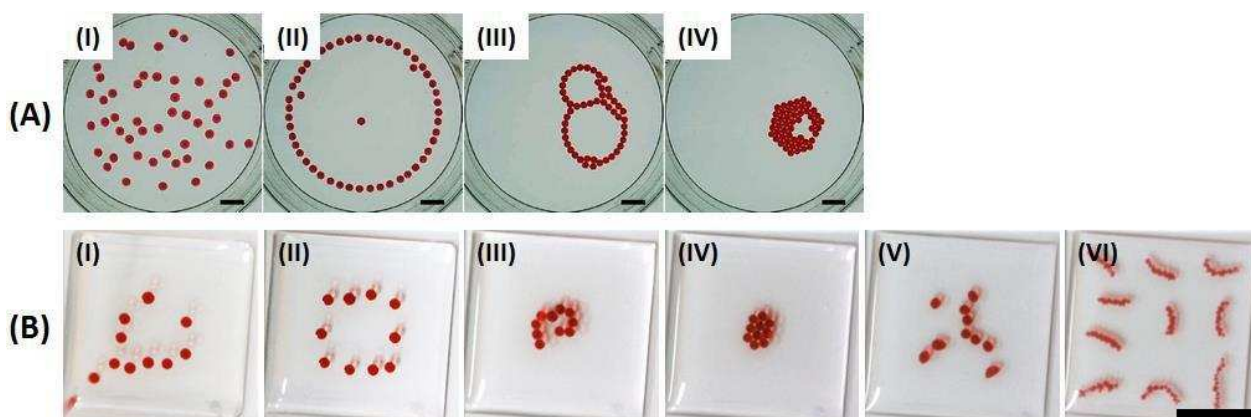


Figure. A comparison of behaviour of 50 ES droplets on a Petri dish (A) and 10 decanol droplets on a microscopic slide (B). (I) Initial phase. (II) A regularly ordered droplets. (III) The characteristic cluster oscillations. (IV) The static crystal-like cluster. (V) The cluster disintegration. (VI) Shape changes of decanol droplets. The scale bars correspond to 10 mm. See supplementary movie <https://youtu.be/dYftKfTmPJ0>.

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Magic colloidal clusters

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Small particle clusters exhibit discrete behaviour as a result of the interplay between bulk crystallization and effect of interface that separates them from their surroundings. An example is the extraordinary high occurrence of clusters of certain sizes in the mass spectrum of small noble gas and metal clusters [1]. These clusters are termed magic clusters for their superior thermodynamic stabilities.

Recently the study of particle clusters extends to the realm of colloids. The attractive force that holds together atoms is replaced by geometric confinement of weakly interacting colloids. Small numbers of colloids pack into clusters of various symmetries [2], whereas larger clusters favour icosahedral symmetry [3]. However, it is unclear whether the concept of magic cluster can be extended from the atomic scale to the scale of colloids.

We produce colloidal clusters of various sizes by confining colloids in emulsion droplets fabricated by microfluidics [4] and find a large library of magic colloidal clusters with defined surface features. With geometric modelling and electron tomography, we confirm the structure of magic colloidal clusters consist of closed shells of Mackay and anti-Mackay type. Simulation and free energy calculation show that these colloidal clusters are thermodynamically more stable than those of other sizes, in analogy to magic atomic clusters.

Our study of confined colloidal self-assembly provides insights into other natural self-organization process like virus capsid assembly and protein aggregates. Similar designing principle may govern structure formation across scales from nanoparticle, supramolecule to plasmonic nanocluster formation.

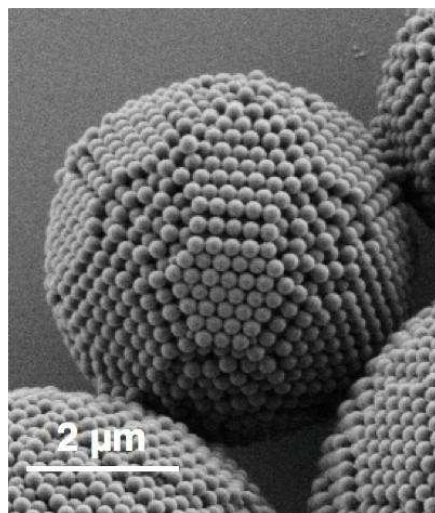


Figure 1. Exemplary magic colloidal cluster of 12 shells.

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Encoding Size and Shape of Electrostatically Self-Assembled Colloids

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Well-defined supramolecular particles can be formed through electrostatic self-assembly of macroions and multivalent organic or inorganic counterions in aqueous solution: assembly shapes range from spheres and cylinders over vesicles to networks [1-10]. Key to a targeted structure design is to fundamentally understand structure directing effects. In this contribution we reveal how the molecular building block structure directs the supramolecular nanoscale structure, in particular the colloid particle size and shape on a 10-100 nm level. Thermodynamics, interplay of interaction forces and dye-dye stack formation will be discussed in context with the resulting supramolecular nanostructures [2-6]. Self-assembled colloids are characterized by SANS, static and dynamic light scattering, AFM, ζ -potential measurements and spectroscopy. A general relationship of molecular structure, enthalpy/entropy balance and assembly size and shape will be presented.

In addition, we describe a light-triggered change of electrostatically self-assembled supramolecular nanostructures [7-10]. This new route for the conversion of light into mechanical energy is highly promising for applications in drug delivery, nanosensors and solar energy conversion.

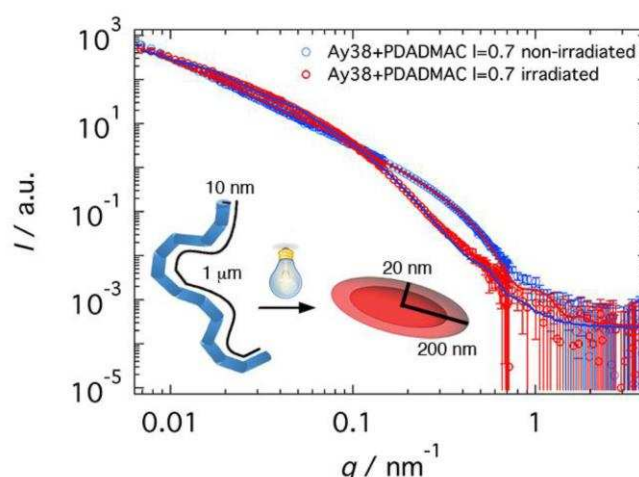


Figure 1. Light-switchable nanoparticle shape by electrostatic self-assembly: SANS for assemblies of a polyelectrolyte (PDADMAC= with a light-responsive dye “counterion” (Ay38) before and after irradiation ($l_c=0.7$). Well defined assemblies are formed in aqueous solution. Light induces a shape transition from flexible cylinders with 10 nm diameter and up to 1 μm length to more compact core-shell ellipsoids [10].

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Superparamagnetic colloidal crystals as candidates for neutron beam polarizers

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Spin-polarized neutron beams are required for many experiments in fundamental and condensed matter physics but current methods of polarization tend to be bulky and expensive, which limits the accessibility of polarized neutron beamlines. Polarizers based on magnetic gratings present a possible solution to this problem because they can likely be manufactured for a relatively low price and in business-card size, making it possible to quickly insert and remove such polarizers into the path of a neutron beam. By using a magnetic grating one can control the diffraction of neutrons by tuning the refractive-index modulation of the grating via an external magnetic field. If the magnetic part of the refractive index modulation exactly cancels the nuclear part for one of the neutron spin states, the grating will only diffract neutrons in the other spin state, thus producing polarized beams.

We have previously described holographic gratings functioning as neutron beam-splitters [1], as well as some preliminary results on using superparamagnetic nanoparticles to construct polarizing beam-splitters [2]. Our latest approach to fabricating magnetic gratings is based on using a colloidal crystal as a scaffold which is filled with superparamagnetic maghemite nanoparticles [3]. The crystals were produced via self-assembly from a suspension of maghemite nanoparticles and polystyrene beads. Different bead sizes and nanoparticle concentrations were tested to obtain a crystal of reasonable quality. Neutron diffraction experiments performed on the most promising sample show that the diffraction efficiency of such crystals can be controlled by an external magnetic field.

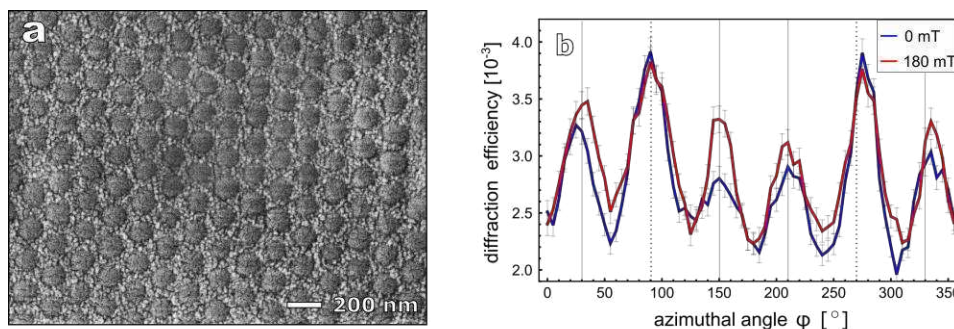


Figure 1. (a) SEM image of the surface of a colloidal crystal assembled from 202 nm (diameter) polystyrene spheres filled with superparamagnetic iron oxide particles. (b) Magnetic field induced change in diffraction efficiency of a magnetic colloidal crystal for different scattering directions.

Acknowledgements: The authors gratefully acknowledge the financial support from the bilateral project »BI-AT/18-19-009«, the ARRS grant no. P1-0192, and the hospitality of the Institut Laue Langevin. This work is partly based on experiments performed at the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland.

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Pathways for viscosity reduction in fatty-acid-containing micellar solutions

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In this work, we have studied the synergistic growth of giant wormlike micelles in three-component micellar solutions, which contain a zwitterionic surfactant (CAPB, cocamidopropyl betaine), an anionic surfactant (SLES, sodium lauryl ether sulfate) and a fatty acid. The solution rheology was characterized in terms of zero-shear viscosities and characteristic times for micellar breaking and reptation. For a given fatty acid concentration and fixed CAPB and SLES concentrations, the zero-shear viscosity η_0 exhibits a sharp and high peak, which in the case of octanoic acid (HC8) reaches 41 000 times the viscosity of water at low surfactant concentration (around 3.5 wt%). The peak height decreases as a function of the fatty acid chain-length until it completely disappears for hexadecanoic acid. Experiments with polarized-light microscopy and NMR showed that all examined solutions are isotropic (micellar), rather than birefringent (liquid-crystalline). The cryo-TEM imaging revealed complex phase behaviour: (i) growing rodlike micelles to the left of the peak; (ii) entangled wormlike micelles at the peak; and (iii) multi-connected structures for octanoic acid versus shape transition into dislike aggregates for dodecanoic acid after the peak; see Figure 1 and References [1,2]. The two scenarios in (iii) explain the viscosity reduction by making a direct relation between rheology and microstructure and thus they might be useful for the design of personal-care and household formulations.

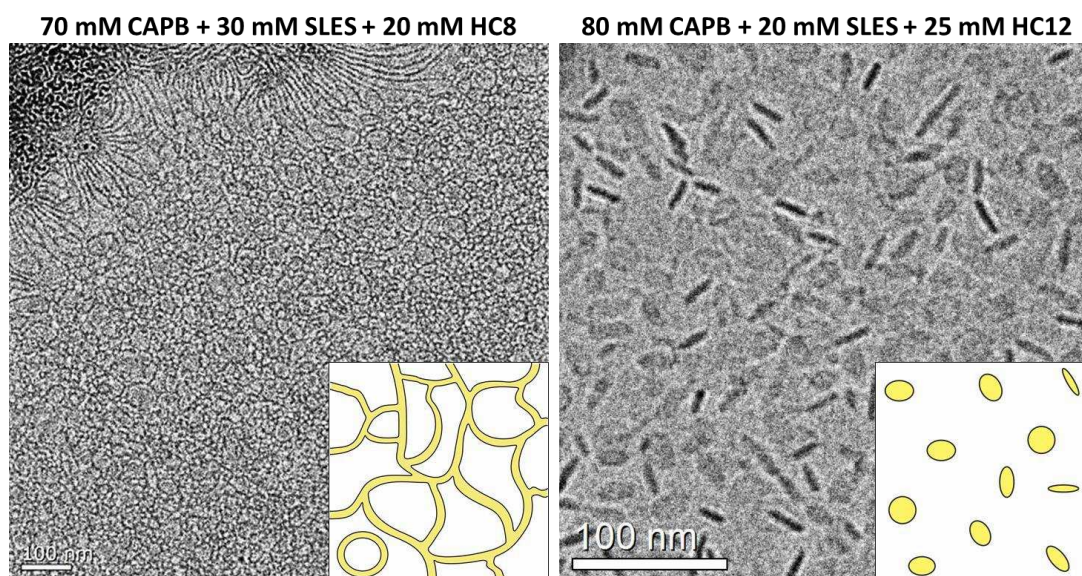


Figure 1. Micellar structures after the viscosity peak: with octanoic acid (left) and with lauric acid (right).

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Polyelectrolyte Microemulsion Complexes (PEMECs) with Structures Tunable by pH

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Oil-in-water (O/W) microemulsion droplets are thermodynamically stable liquid systems that allow to have a rather high content of hydrophobic material dispersed in aqueous solution, which otherwise could not be dissolved. Further, (O/W) microemulsion droplets have a well-defined spherical structure with low polydispersity, which renders them good model colloids. In that context, mixtures of charged microemulsion droplets and oppositely charged polyelectrolytes are very interesting systems, as the polyelectrolyte is able to bridge different droplets which allows further structural control on the microemulsion.

Accordingly, we studied the interactions of positively charged O/W microemulsion droplets with negatively charged polyelectrolytes. In our experiments, we varied size of the droplets and the type and Mw of the polyelectrolyte, as well as the mixing ratio (quantified by the charge ratio $z = [-]/([+]+[-])$). Based on a thorough determination of the phase behaviour and employing small-angle neutron scattering (SANS; see Fig. 1) it was possible to obtain a detailed characterization of the formed complexes in terms of size, shape and composition.

Additional tunability of the complexation arises from the pH-value since both the surfactant and the polyelectrolyte used are pH responsive. The surfactant (tetradecyldimethylamine oxide, TDMAO) is uncharged at neutral to basic conditions and becomes charged at low pH, while the polyelectrolyte (poly acrylic acid, PAA) is uncharged at low pH and becomes charged at higher pH values. This means we can tune the charge density in parallel on the droplet surface and on the polyelectrolyte chain, thereby systematically modifying the electrostatic interactions in the system. The electrostatic interactions in turn strongly influence the strength of binding and complexation and thereby the structures formed.

In our experiments we obtained a comprehensive picture of the formed complexes and how their detailed structure depends on their molecular composition, as well as the environment (pH). These aggregates serve as a model system for complexes with a high solubilisation capacity that could find potential applications in formulations which contain a large amount of hydrophobic agents.

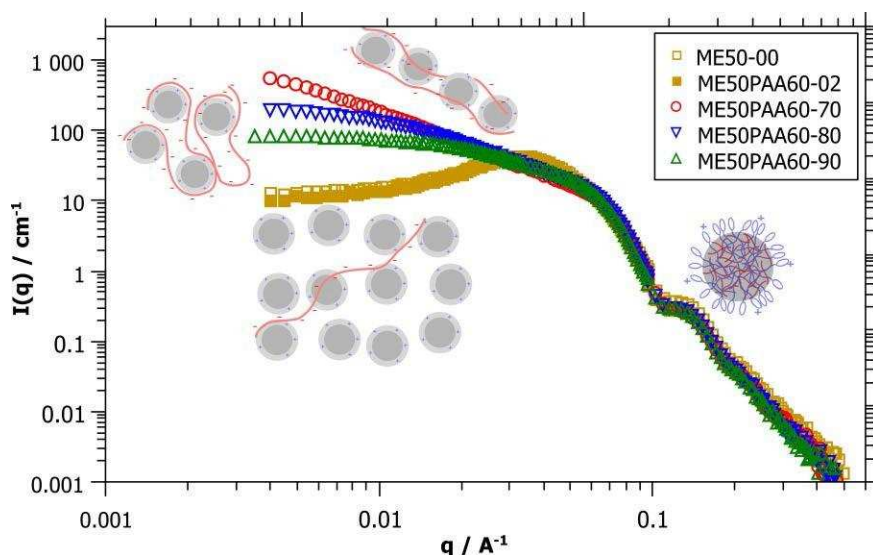


Figure 1. SANS curves $I(q)$ and corresponding structures of microemulsion – polyacrylate complexes for three different charge ratios $z = [-]/([+]+[-])$.

Assembly of Janus Fe_3O_4 -Au magnetic-plasmonic nanoparticles with sensing and molecular imaging capabilities

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Multicomponent nanoparticles have attracted strong interest in the last years due to the unique combination of properties present at the nanoscale that make them suitable for a high set of applications. Among them, Janus nanoparticles (with two chemically different surface regions) have emerged as exceptional candidates toward many technological and biomedical applications. Their strong interaction with interfaces has been used e.g. to create emulsified nanoreactors, filtering nanomembranes, or block-copolymers with optical and electronic properties. Other uses include: antireflecting surfaces, electronic displays, nanoswimmers, or as building blocks for more complex molecular colloids and supracrystals. They offer extraordinary potential in biomedicine, as they can mimic natural biomolecules, have directed interactions with cell membranes, or offer regions with high concentrations of bifunctional molecules, while keeping multiple functionalities.

Here, we report the synthesis of Janus nanoparticles composed of $\text{Au-Fe}_3\text{O}_4$ nanostar-nanosphere through two consecutive seed-mediated-growth steps [1, 2]. The nanoparticles showed superparamagnetic properties and a high plasmonic absorption at the near-IR. The extraordinary versatility of these nanoparticles has been tested in analytical sensing using Surface-enhanced Raman spectroscopy (SERS), and multimodal imaging. The resulting experiments showed the high Raman enhancement of these nanoparticles thanks to the Au nanostar part of the Janus nanoparticles that can be further amplified with the use of magnetic concentration, allowing nanomolar detection in very small sample volumes. Furthermore, with the use of combined gold and iron oxide in a Janus configuration we demonstrate how these magnetoplasmonic nanoparticles act as superior contrast agents in a high variety of imaging techniques, including cell imaging in dark and bright field, multiplexed SERS mapping and 3D tomography in magnetic resonance imaging (MRI) and computed tomography (CT) among others.

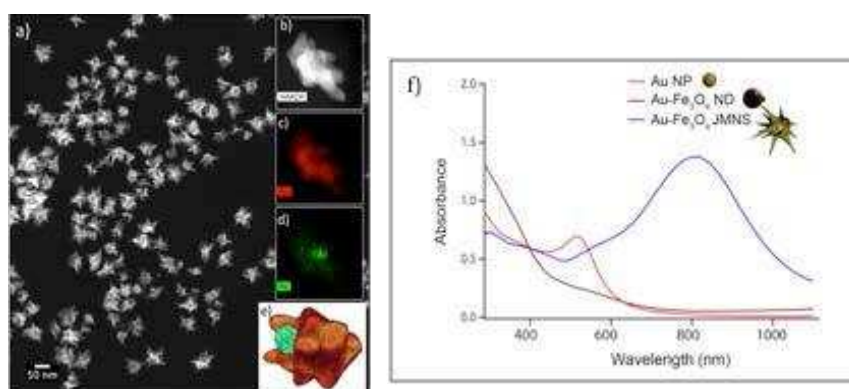


Figure 1. A-E) TEM image and electron microscopy tomography showing high uniformity and Janus type morphological configuration. F) UV-Vis spectra corresponding to the different synthesis steps. The final nanoparticles show a more intense absorption at the nearIR.

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Mesoscale solubility in liquid solutions and mixtures

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A vast majority of phenomena and processes in nature, industry, and research practice take place in the form of solutions and mixtures, not pure compounds. Understanding of solubility and solubilization/mixing mechanisms is therefore crucially important.

Here we report on a new paradigm in solution chemistry reflecting the fact that solubility is achieved not only by well known “like likes like” or “like dissolves like” based on molecular solvation but also on mesoscale solubilization of dislike compounds characterized in that the solubility (homogeneous distribution over the whole volume of the system) is achieved on a mesoscale level typically ranging from tens to hundreds of nanometers. As a result of mesoscale solubility, aqueous (and many nonaqueous) solutions and mixtures comprise of typically 10^{10} - 10^{12} nanoparticles/nanodroplets per milliliter which are formed by solutes not able to molecularly mix with solvent that mesoscopically segregate instead of being macroscopically phase separated. We show that mesoscale solubility is an everywhere present phenomenon usually met on a daily basis which was, however, bizarrely hidden and overlooked for a long time. The ever-presence of mesoscale solubilization, including binary mixtures of well miscible compounds, is coming from the fact that really pure chemical compounds are produced and used rather exceptionally. Even compounds considered commonly as pure, like for instance p.a. grade chemicals, are in fact multicomponent mixtures of the main compound plus several minority compounds with rather substantial concentrations 2-5 g/L (99.5% – 99.8% typical purity of the main compound). Dissolution of the main compound in a suitable solvent is then practically always accompanied by molecular solubilization and/or mesoscale solubilization of minority compounds based on their particular affinities to the solvent used.

From a practical point of view, the occurrence of mesoscale solubilization can be classified as unwanted and wanted solubilization, respectively. The former relates with the understanding of mechanisms of unwanted mesoscale solubilization (contamination) but also with very effective ways of decontamination based on contaminants elimination. Mesoscopically dissolved compounds can be much more effectively separated compared to molecularly dissolved compounds and also much more effectively detected (orders of magnitude better detectability). The latter represents intentional target oriented solubilization without surfactants or polymers as stabilizing agents (green detergentless or polymerless formulations). Mesoscale solubilization can be thus in many areas advantageous (not disadvantageous) compared to classical molecular solubilization. Best examples are nanomedicines, nanotherapy, and nanoimaging. It appears that hydrophobic compounds (potentially drugs or contrasting agents) can be mesoscopically dissolved in pure water without any need of carriers and with proper particulate size and stability.

We will present a very detailed characterization of mesoscale structures on the basis of light scattering techniques, ultramicroscopy, and semianalytical centrifugation. Our goal was also to map the occurrence of mesoscale solubility as a function of several parameters identified as the key ones. Further we will reveal its physical mechanism, discuss kinetics of the solubilization processes as well as the long-term stability of mesoscale structures.

Acknowledgements: This work was supported by the Scientific Grant Agency VEGA (grant no. 2/0177/17) and the Slovak Research and Development Agency (project NANOSEG No. 16-0550).

The Cyclobutane Scaffold in the Construction of Bolaamphiphiles: Effect of Diastereoisomerism and Regiochemistry on Their Surfactant Behavior and Aggregation

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New cationic bolaamphiphiles have been synthesized starting from meso-*cis* or chiral-*trans* 1,2-difunctionalized cyclobutane derivatives. They include *cis/trans* pairs of diastereoisomers, *cis*- and *trans*-**3** and *cis*- and *trans*-**4**, and *N*- or *C*-centered pairs of regioisomers, **3** and **4**, respectively (see figure 1). The goal of this work was to investigate the influence of the stereochemistry and the regiochemistry on their abilities as surfactants, molecular organization and self-assembly. Computational calculations were carried out to rationalize the experimental findings and a new methodology has been developed to calculate the structure of these bolaamphiphiles at the surface. Although the four surfactants adopt a wicket-like conformation, for *trans*-**3** the distance between polar heads is much larger than for the other three molecules, as suggested by calculations. This result and the fact that *trans*-**3** presents a larger area on the surface could explain that it is the less effective surfactant. The best one is *cis*-**3**. In the case of the two *C*-centered surfactants, stereochemistry has no influence on their effectiveness. Moreover, both *cis* diastereoisomers are more efficient than the *trans* ones. Therefore, relative *cis/trans* stereochemistry exerts a real influence on the properties of these surfactants in solution. Concerning aggregation, *N*-centered amphiphiles self-assemble forming vesicles while the *C*-centered amphiphiles form fibers as shown by cryoTEM (see figure 1). These results are in agreement with SAXS analysis suggesting that *cis*-**4** forms self-assembled cylinders while *trans*-**4** shows separated cylinders. Consequently, both stereochemistry and regiochemistry have an effect on the morphology of the aggregates. All these results must help in the rational design of new bolaamphiphiles with predictable properties and useful potential applications.

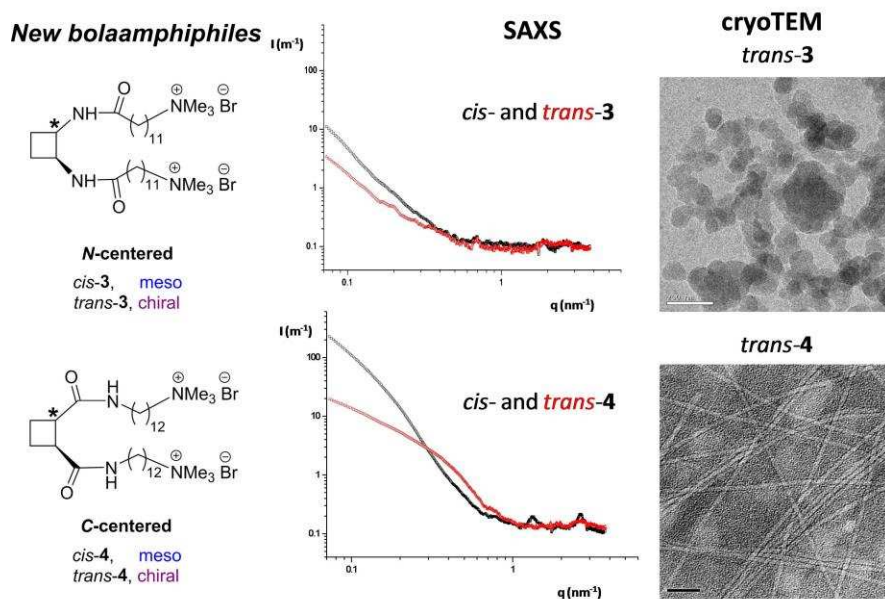


Figure 1 Bolaamphiphiles chemical structure and nanostructure selfassembly.

Morphogenesis of polycrystalline dendritic patterns from evaporation of a reactive nanofluid sessile drop

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From mesmerizing intricacy of an ammonite shell to chilled elegance of a snow flake, nature articulates language of shape and geometry fluently and delivers complex patterns and structures on all length scales with ease and panache *via* self-assembly. In nanoscience and nanotechnology, we aspire to study and harness such refined linguistic competence of geometry to create sophisticated hierarchical nanostructures with tailored geometry and enhanced functionalities. A widely studied system for spontaneous pattern formation is evaporative drying of a sessile drop containing non-volatile particles. The most familiar pattern is the “coffee ring”; mechanistically, this results from a competition between inter-particle forces and capillary and convective solvent flows. In previous studies, the dispersed non-volatile particles were *inert*; it remains little understood how *reactive* particles may alter evaporation induced patterns.

Here we show [1-3] that, upon fast evaporation of a mixed solvent sessile drop, dispersed ZnO nanoparticles transformed into ZnOH-derived surface-active clusters, accumulating at the drop surface and pinned periphery. As the drop thinned due to evaporation, Bénard-Marangoni instabilities were triggered and cluster flows caused concentration inhomogeneity in the surface cluster layer, manifesting in capillary ripples. Cluster coalescence radially along multiple Bénard-Marangoni flows resulted in cellular dendrites in the eventual polycrystalline surface pattern in the drop centre (**Fig.1d,e**), surrounded by a coffee ring also with micro-dendrites resulting from cluster coalescence at the receding peripheral contact line (**Fig.1b,c**). Our results reveal the mechanism for complex pattern formation upon evaporation of *reactive* nanofluid droplets.

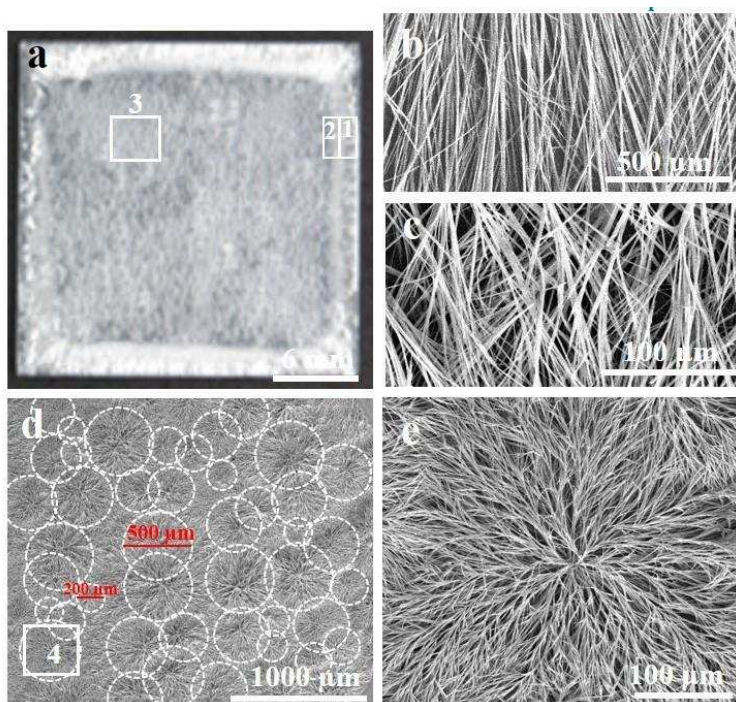


Figure 1. (a) Residual surface pattern from fast evaporation of a ZnO nanofluid droplet on a glass cover slip (24×24 mm); (b-d) SEM images of **regions 1-3** in figure (a) respectively; and (e) An enlarged view of an individual *Bénard-Marangoni cell* (**region 4** in (d)).

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Doxorubicin: a low molecular weight water gelator

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Aqueous solutions of the cancer antibiotic doxorubicin (DX) turn into gels upon the addition of a critical amount of salt (NaCl). The DX aggregation behaviour in these systems is markedly different from the self-association mechanism (dimerization) already described in the literature [1]. Instead of giving rise to dimers, when the gels are formed the DX molecules are arranged into long, highly chiral and flexible fibres made of hundreds of units. The joint use of spectroscopic, scattering, imaging and computational techniques allowed to shed light on the self-assembly process triggering the DX gelification. The supramolecular polymerization of DX leads to red shifted fluorescence spectra, very short fluorescence lifetimes and SAXS profiles compatible with long cylinders. It must be stressed that this feature is peculiar of DX, and is not shown by the closely related anthracycline molecules epirubicin and daunomycin (Figure 1) [2]. The involvement of specific chemical groups and the need of a specific stereochemistry of the monomers in the formation of a hydrogen-bond network stabilizing the supramolecular aggregates was supported by molecular dynamics calculations.

Variable temperature circular dichroism and fluorescence experiments allowed the thermodynamic details of the gelification process to be determined. The thermodynamics of supramolecular aggregation closely follows the predictions of the nucleation-elongation polymerization model that assumes that only at low enough temperature a small fraction of the drug molecules becomes active towards the polymerization. These active building blocks form upon aggregation of the pre-existing dimers (a process facilitated by the screening of the electrostatic repulsion). A salt-induced, T-dependent cooperative nucleation-elongation supramolecular polymerization of the doxorubicin molecules is therefore deduced (Figure 2).

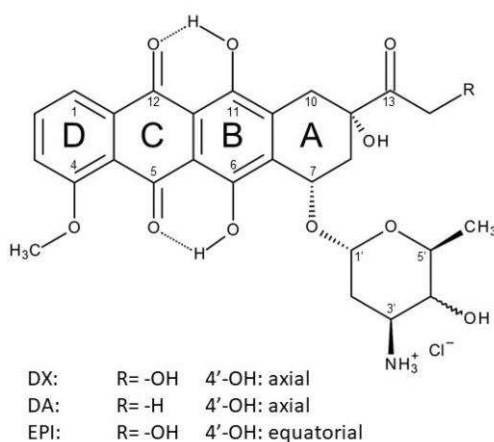


Figure 1. Doxorubicin (DX), daunomycin (DA) and epirubicin (EPI) chemical structures.

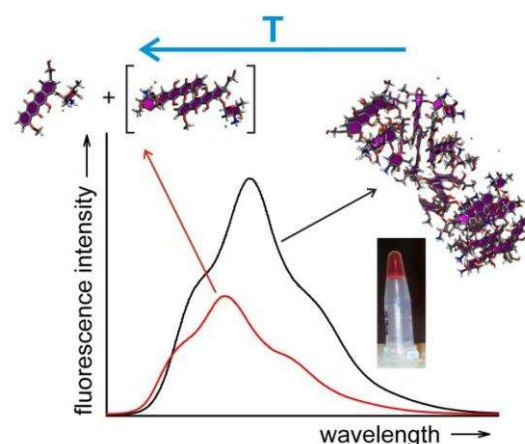


Figure 2. Sketch depicting the T-dependent DX gelification and the consequences on its fluorescence properties.

Acknowledgements: Financial support of CSGI and University "La Sapienza" is kindly acknowledged.

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A general comparison of kinetics with step-wise and fusion-fission aggregation in mono- and polydisperse micellar solutions

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The formation of stable aggregates of surfactant molecules in polar solvents at surfactant concentrations above the critical micelle concentration (CMC) is of great interest, both from fundamental and practical point of view [1]. Depending on the structure of the surfactant molecules and their concentration in the solution, one can observe the appearance of almost monodisperse spherical or polydisperse cylindrical micelles.

The most studied is the step-wise mechanism of micelle formation [2] when the change in the aggregation number occurs due to attachment/detachment of a surfactant monomer to/from an aggregate. This mechanism is described by the Becker-Döring kinetic equations, and its theory for spherical and cylindrical micelles was recently reviewed in [3]. With increasing the total surfactant concentration, fusions and fissions of aggregates influence on the micellar processes. Such processes, including capture and emissions of monomers, can be described by the generalized Smoluchowski equations [3-5]. Fusions and fissions of aggregates inevitably shorten the total time of relaxation to the final equilibrium and broaden the nonequilibrium distribution of micelles in aggregation numbers. In this communication, we present the results of the general kinetic study of micellar formation and relaxation with taking into account fusions and fissions of micelles by means of generalized Smoluchowski equations. A specific analysis of the dependence of the fusion coefficients for spherical and cylindrical aggregates on aggregation numbers is done. A direct comparison of the solutions of the generalized Smoluchowski equations under strong initial deviations from equilibrium with the corresponding solutions at the step-wise mechanism are given. This comparison is illustrated in the case on instant dilution of a micellar solution in Fig.1, where solid and dashed lines refer to the joint fusion-fission and the step-wise mechanisms and only the step-wise mechanism, respectively.

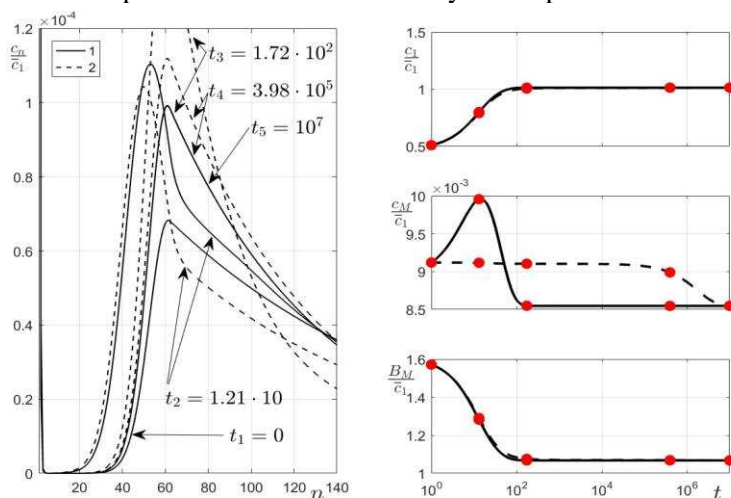


Figure1. Concentrations c_n of surfactant aggregates, monomer concentration c_1 , total micelle concentration c_M , total amount B_M of surfactant in micelles as a function of time at instant dilution of solution.

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On the self-assembly capacities of ionic liquid crystals

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Ionic liquid crystals have attracted, during recent years, a steadily increasing interest both in academic as well as in industrial research. This is – amongst others – due to the fact that their internal architecture can be tuned upon synthesis in order to optimize their material properties (such as mechanical, thermal, etc.). These particles are anisotropic in their shape and carry charges: thus they combine properties of charged particles and liquid crystals which are, for instance, reflected in their self-assembly capacities.

In an effort to understand the mechanisms that rule these self-organisation strategies a simple, yet faithful model for ionic liquid crystals has been put forward by Kondrat and co-workers [1] where these particles are shaped by impenetrable, ellipsoidal particles (characterized by their aspect ratio) plus a Gay-Berne type of interaction. In addition, these particles carry charges, located in equal distance from the particle center along the main axis of the ellipsoid of revolution. Varying the aspect ratio of the particle and the location of the charges, Bartsch and co-workers [2] could identify (using classical density functional theory and computer simulations) up rising new ordered self-assembly scenarios, among those a novel, wide smectic-A phase at low temperatures.

In our investigations we have systematically varied the parameters that characterize the interaction of these particles and identify the emerging ordered ground state configurations with the help of highly optimized minimization tools that are based on ideas of evolutionary algorithms.

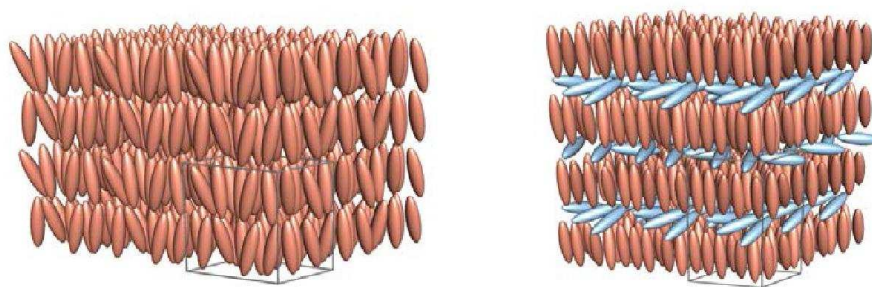


Figure 1. Snapshot of a smectic-A phase (left) and of the up rising novel, wide smectic-A phase (right) as obtained in local optimization runs.

Acknowledgements: B. Hartl acknowledges a DOC Fellowship of the Austrian Academy of Sciences.

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Microstructural characterization of dipolar building block assemblies

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Emerging materials technologies require advanced self-assembly strategies that can be amalgamated into an entirely solution-based low temperature processing. Deterministic assembly via a colloidal route is a core platform for exploiting the potential for variable property design/fabrication and deployment of mesoscale architectures with structural hierarchy, multi-functionality and programmed response to mechanical stress or external field, harnessing the physical properties originating from both the individual nanocrystals and collective interactions.

Colloidal shape engineering provides access to a class of entropically assembled morphologies encoded solely by the shape anisotropy inducing angularly specific interactions. The subsequent alignment of the complementary geometrical features is due to a directional entropic bond $\sim kT$ statistically emerging from the collective interactions [1]. In turn, employing competing or synergistic entropic/enthalpic anisotropies for purposeful valence engineering leads to a broader class of design strategies intended to target specific morphologies [2]. We present some instances of such design paradigm by exploiting the anisotropy of a basic dipole and that of a simplest space-tiling Platonic solid - cube, studied by numerical simulations in fair qualitative and quantitative agreement with experiments.

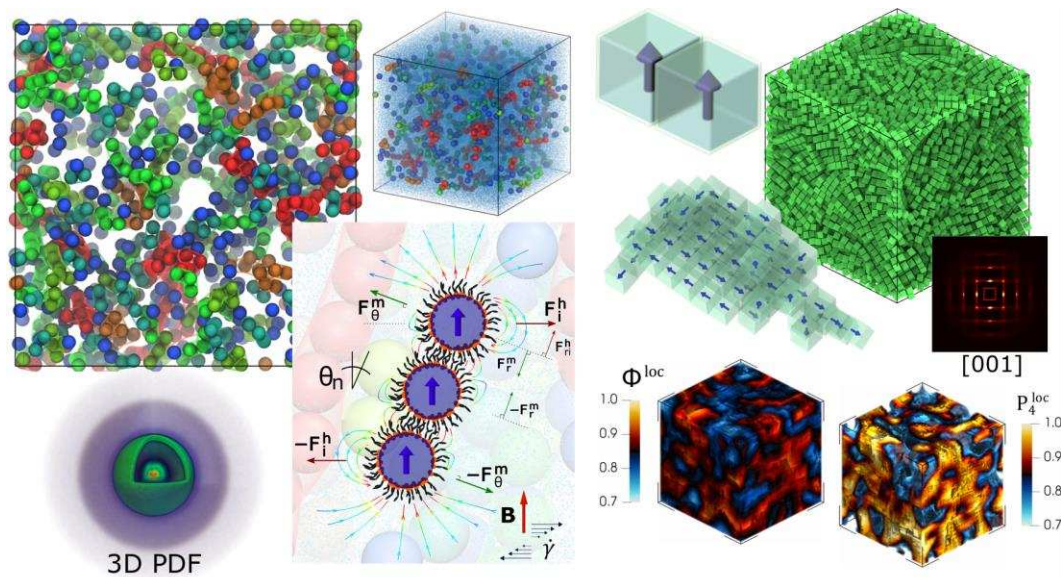


Figure 1. Self-assembly of dipolar spheres and cubes – systems with synergistic or competing anisotropies and their structural descriptors.

Acknowledgements: the support from the postdoctoral research program at the University of Latvia (project 1.1.1.2/VIAA/1/16/072) is gratefully acknowledged.

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Total description of COSAN aggregation: Calorimetry study and NMR probing

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COSAN (cobalt bisdicarbollide anion) belongs to anionic boron cluster compounds. Due to the chemical structure, COSAN clusters are only weakly hydrated [1] despite the fact COSAN alkaline salts are usually very water soluble. COSAN exhibit several features of classical amphiphiles even though it has no amphiphilic head-and-tail structure: solubility both in water and oil, surface activity, and micellization in water [2]. The driving force of the micellization is non-classical hydrophobic or superchaotropic effect [1,2].

Isothermal Titration Calorimetry (ITC) was used as an excellent tool for total description of COSAN salts micellization, the example of non-classical amphiphile aggregation. The parameters such as $\Delta_{\text{mic}}G$, $\Delta_{\text{mic}}H$, $\Delta_{\text{mic}}S$, aggregation number, degree of counterion binding, heat capacity change of micellization, and CMC were obtained from global fitting of enthalpogram temperature series [3] (Figure 1). The parameters were compared with results of scattering, spectroscopy and microscopy techniques showing that ITC is suitable alternative to other techniques. The ITC results clearly show that COSAN micellization is enthalpy driven with relatively minor entropy contribution; the aggregation number is very low as compared to classical amphiphiles; the degree of counterion condensation is almost zero for all studied salts; the heat capacity change of micellization is relatively small but still negative pointing to hydrophobic effect as the driving force.

To better understand the solution behaviour of COSAN, the mobility of counterions and the influence of co-solvent (acetonitrile) to COSAN micellization were studied by NMR spectroscopy.

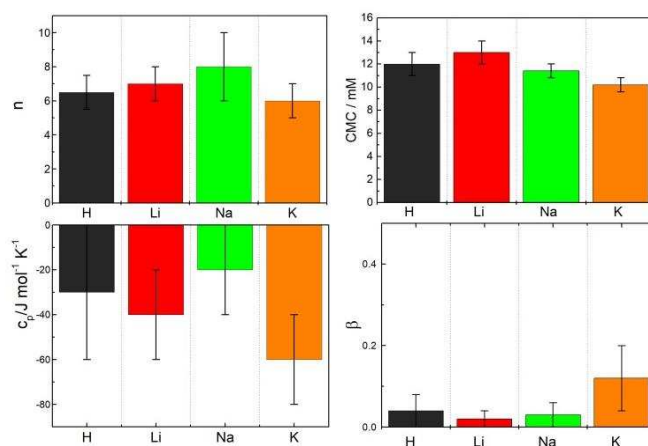


Figure 1. Parameters of fitting of ITC curves: aggregation number (n), degree of counterion condensation on micelles (β) and heat capacity change of micellization ($\Delta_{\text{M}}C_p^\theta$), and values of critical micelle concentration (CMC) at 298.15 K for various COSAN salts (marked by counterions).

Acknowledgements: The Czech Science Foundation grants 17-00289Y and 17-00648S, and GAUK grant 1588218 are gratefully acknowledged.

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Sphere-Tubule Superstructures through Supra -Molecular and -Colloidal Assembly Pathways

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While directed self-assembly of molecules on the supramolecular scale and aggregation of colloid-sized particles on the supracolloidal scale have commonly been investigated so far as two separate pathways toward the formation of respectively novel colloids and nanomaterials [1], the proposed study aims to combine supra -molecular and -colloidal aggregations as parts of a unique pathway, leading to a wide range of different supracolloidal frameworks. Hereby, supracolloidal aggregation as the outcome of controlled interactions between spherical fluorescent microgels and highly anisotropic supramolecular tubules was investigated using confocal laser scanning microscopy (CLSM). The interactions between the two species were modulated by changing parameters like particles charge, particle shape and electrolyte concentration. Under certain conditions positively or negatively charged microgels were found to specifically interact with catanionic surfactant tubules with tunable charge depending on the anionic/cationic derivative molar ratio [2]. The changes in the derivative molar ratio not only resulted to affect the charge of the tubular aggregates but also their structural design and size. Besides, we demonstrated that the microgels were able to interact with the extremities of the layers forming the tubules and hierarchically self-assemble into various superstructures varying from virus-like assemblies to microgels decorated tubules and finally to extended supracolloidal networks where the spherical particles act as colloidal responsive linkers, providing the basic framework of low density hybrid superstructures.

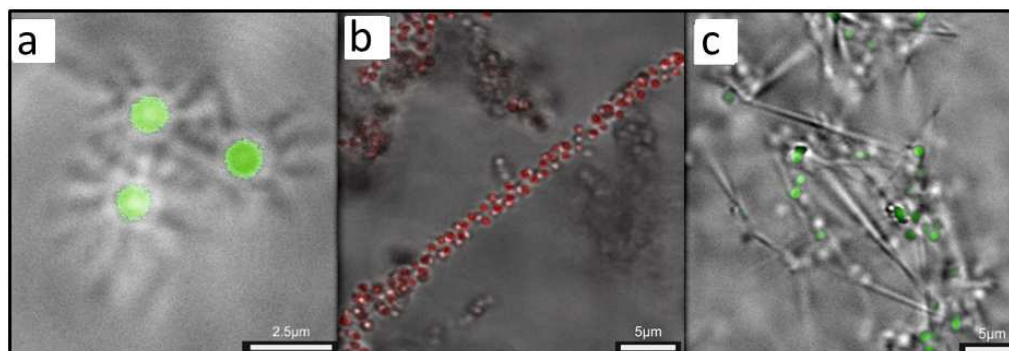


Figure 1. CSLM images of virus-like particles with a microgel core and a corona of tubules (a), microgel decorated tubules (b), clusters of tubules interconnected by microgels (c).

Acknowledgements: JJC acknowledges financial support from the Knut and Alice Wallenberg Foundation (project grant KAW 2014.0052). The authors acknowledge support from the European Soft Matter Infrastructure (ESMI) proposal E141000601.

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Self-assembly and transport of motile bacteria with light

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We use light-driven *Escherichia coli* bacteria for assembly using externally imposed light fields. With a spatial light modulator, light and dark areas are created. Inside the light areas, bacteria swim freely in all directions, however, swimming is halted abruptly upon reaching a dark area, where cells accumulate in time[1]. In this way, cells assemble into structures defined by the absence of light. Where static fields merely offer a switch between the motile and non-motile state, moving light fields also enable us to direct the motion, and transport bacteria toward specific target areas. We show examples of dynamic/moving light fields using this new class of "living active colloids" and discuss the mechanisms of directed motion.

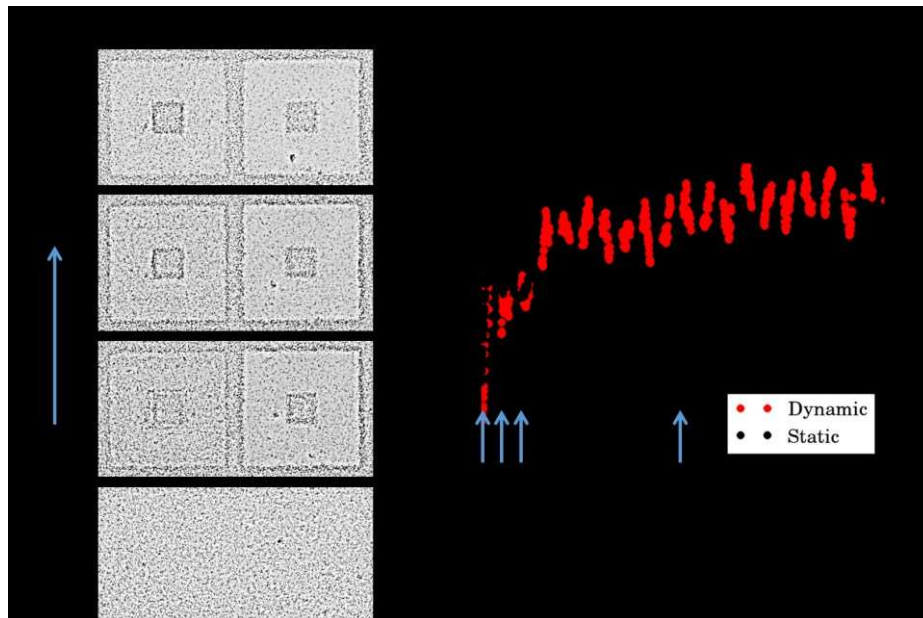


Figure 1. a) Phase contrast microscopy image snapshots of a static pattern and a dynamic pattern with the passage of time, b) Density in the centre of the patterns as a function of time.

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The molecular modelling and QSAR of Ebola VP35 inhibitors

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Ebola VP35 protein is a multifunctional protein, along with nucleoprotein and VP24; it is an essential part of the nucleocapsid which stores genetic material for viral reproduction. Another critical function of this protein is inhibition of interferon IFN- α/β production. Additionally, VP35 is also a cofactor of the viral RNA polymerase. This protein also inhibits the RNA-dependent protein kinase (PKR). All these properties are vital for the virus to live cycle and thus make it as an important therapeutic target.[1] The many high-resolution structures of the viral protein with bound ligands allow for performing additional research in the scope of the optimisation of the *In the Silico* activity of the ligands. The structure of VP35 consists of an N-terminal coiled-coil domain, required for its oligomerisation, and of a C-terminal domain, called the interferon inhibitory domain (IID), required for the interaction with the viral nucleoprotein (NP) and interferon inhibition. The high-resolution structure of the C-terminal domain has been recently solved. It is made up by two different subdomains an N-terminal α -helical subdomain and a C-terminal β -sheet subdomain. Recently, the high-resolution crystallographic structures of the VP35 with bound ligands were deposited into the PDB.[2] These complexes were then extensively studied by molecular dynamics and computational alanine scan to understand better the interaction between the protein and its inhibitors.[3]

In our work, we used the BioSolveit Seesar software to design an optimal ligand, which could successfully hinder the protein-protein interaction between VP35 and NP. From our experience, the Seesar [4] is very useful for *In Situ* modification of chemical structures, with the very detailed representation of atom based affinities. The proper use of Seesar may accelerate Drug Design projects. The collected data - inhibitors and its affinities have been used for QSAR modelling.

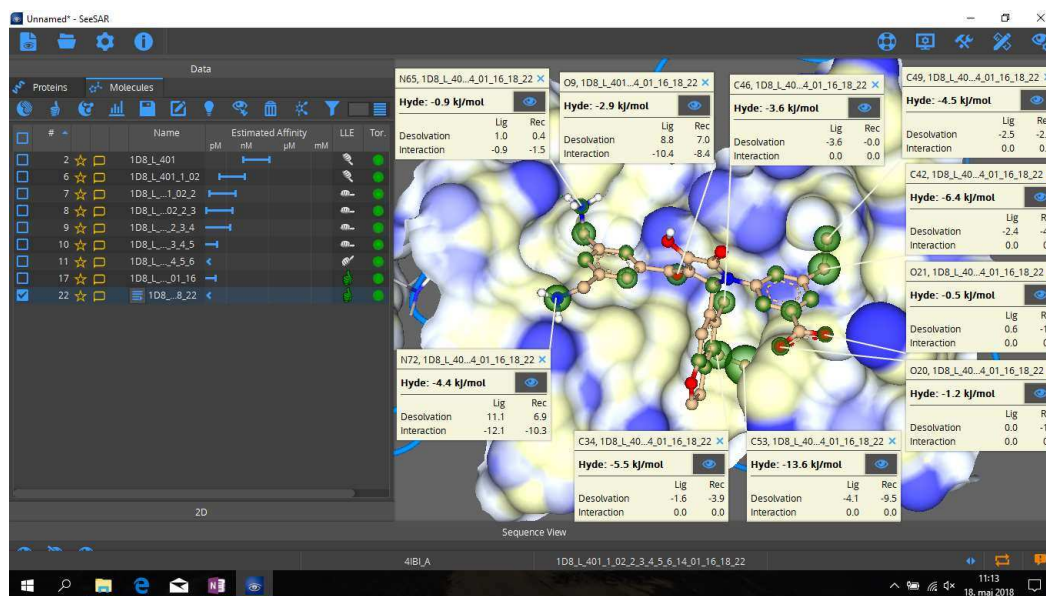


Figure 1. Improving the ligand preferences with Seesar.

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Viscosity B-coefficients of imidazolium based surface active ionic liquids in water

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Recently, a systematic study of aqueous diluted solutions of imidazolium based ionic liquids (ILs) $[C_n\text{mim}]\text{Cl}$ with different alkyl chain lengths ($n = 0, 1, 2, 4, 6, 8$) was carried out [1]. Based on the properties, derived from experimental density and viscosity data, structure making tendency of ionic liquids with longer alkyl side chain ($n = 4, 6, 8$) was confirmed. On the other hand, $[C_2\text{mim}]^+$ can be considered as border line ion, and cations with shortest side chain ($n = 0, 1$) express structure breaking tendency. According to experimental and computational study, based on MD simulations, hydrophobic hydration of the side chain on the imidazolium ring is most responsible for structure making/breaking properties of investigated imidazolium salts.

In this work, the study was extended to surface active (imidazolium based) ionic liquids (SAILs) $[C_{10}\text{mim}]\text{Cl}$ and $[C_{12}\text{mim}]\text{Cl}$. Despite the fact, that the investigated SAILs differ significantly in cmc [2], mobility and association tendency of $[C_{10}\text{mim}]^+$ and $[C_{12}\text{mim}]^+$ are very similar [3].

Measurements of density and viscosity were performed in the temperature range between 278.15 K and 313.15 K in steps of 5 K at concentration below cmc. From experimental values of densities, the volumetric properties of solute and solvent will be estimated as a function of concentration and temperature, whereas viscosities will serve for the B -viscosity coefficients determination. Obtained values will be related to changes in the structure of water affected by dissolved $[C_n\text{mim}]\text{Cl}$ depending on the temperature and the length of the cation alkyl chain. Computational analysis based on MD simulations (Figure 1) will give an additional insight into the interactions between constituting ions understanding better the interactions with water molecules.

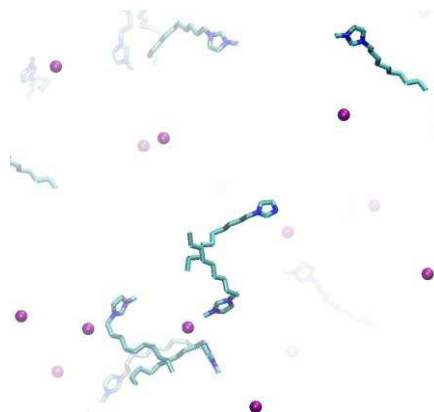


Figure 1. Visual representation of $[C_{10}\text{mim}]\text{Cl}$ aqueous solution at concentration below cmc

Acknowledgements: In case necessary, must be located at the end of the abstract, just before the references.

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Density and viscosity of aqueous solutions of functionalized quaternary octylammonium surfactants

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Surfactants are widely used compounds in industry and everyday life and especially quaternary ammonium salts such as alkyltrimethylammonium chlorides and bromides, have been widely studied [1-3]. But, no information can be found in the literature, how functionalization of a side alkyl chain on the quaternary nitrogen affects their surfactant properties, among which the value of critical micelle concentration, cmc, is regarded as one of the main characteristics at characterization of surfactants.

In this contribution five quaternary octylammonium surfactants will be investigated (Figure 1): a) N-octyl-N,N,N-trimethylammonium chloride – $C_8Me_3N^+Cl^-$, b) N-(2-hydroxyethyl)-N,N-dimethyl-N-octylammonium chloride – $(C_2OH)C_8Me_2N^+Cl^-$, c) N-(2-methoxyethyl)-N,N-dimethyl-N-octylammonium chloride – $(C_2OMe)C_8Me_2N^+Cl^-$, d) N-(2-(2-methoxyethoxy)ethyl)-N,N-dimethyl-N-octylammonium chloride – $(C_2OC_2OMe)C_8Me_2N^+Cl^-$ and e) N-(2-ethoxy-2-oxoethyl)-N,N-dimethyl-N-octylammonium chloride – $(C_2OOEt)C_8Me_2N^+Cl^-$.

Densities and viscosities of aqueous solution for all studied systems were measured before and after cmc in the temperature range from 5 °C to 55 °C (in steps of 10 °C). From the temperature and concentration dependence estimated properties the interaction in the systems will be discussed and compared with decyl analogues [4].

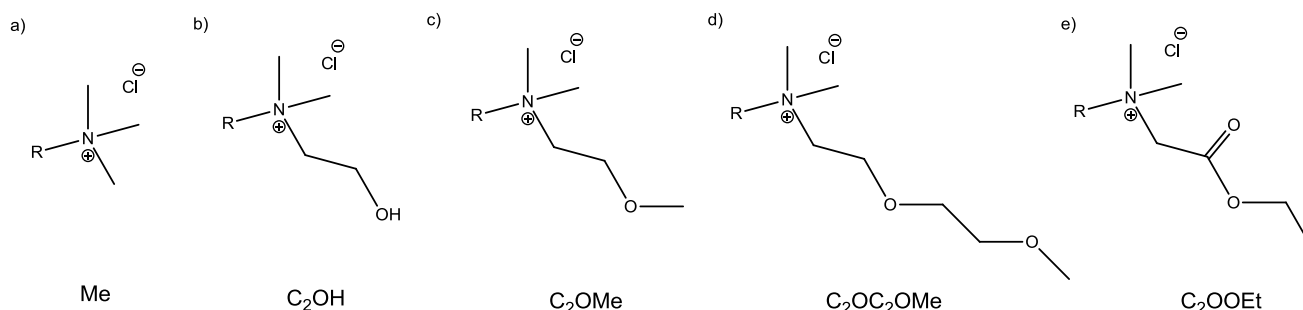


Figure 1. Studied quaternary octylammonium surfactants (R=octyl).

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Self-assembly of weakly acidic photoactive dyes in aqueous solution at varied pH and ionic strength

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The amphiphilic photoactive molecules self-assembled in aqueous medium have drawn significant attention in the past years due to their unique photophysical properties both in biological and functional materials sciences. Such compounds have been investigated in a variety of application fields such as solar cell production, development of pharmaceutical formulations and biomedical applications (e.g. photodynamic therapy) [1-3]. However, the formation of aggregates changes their figures of merit, and in the first place the photophysical properties by affecting their ability to absorb and emit electromagnetic radiation. Therefore, it is important to investigate the relationship between the aggregation state of the self-assemblies (size and type), and the electrostatic charge at their surface which depends on the pK of the compound, the bulk solution pH and ionic strength.

The poster presents an experimental methodology for the assessment of charge-structure relationship in the case of self-assembled weakly acidic or basic amphiphilic dyes. The studied molecules were synthesized by introduction *via* esterification of an aliphatic chain to some commercially available compounds that mimic the photoactive dyes: rhodamine B and Orange II. The size of the nanoparticles prepared by self-assembly of those molecules was measured by means of dynamic light scattering (DLS), as a function of pH, ionic strength and dye concentration. The critical micellization concentration (CMC) was measured in the pendant drop experiments for varied pH and ionic strength. The protonation speciation and surface charge was determined from the experimental proton binding isotherms measured in potentiometric and spectrophotometric titrations, also at varied ionic strengths. The interpretation of these measurements is proposed in terms of the established models for the self-assembly of ionic surfactants [4], whereby the obtained results should facilitate an evaluation of such dyes for the above mentioned applications.

Acknowledgements: This work was supported by the European Fund for Regional Development and the Ministry of Science, Education and Sports of the Republic of Croatia under the project Research Infrastructure for Campus-based Laboratories at the University of Rijeka (grant number RC.2.2.06-0001)

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Cationic cyclodextrin as counterion of anionic surfactants

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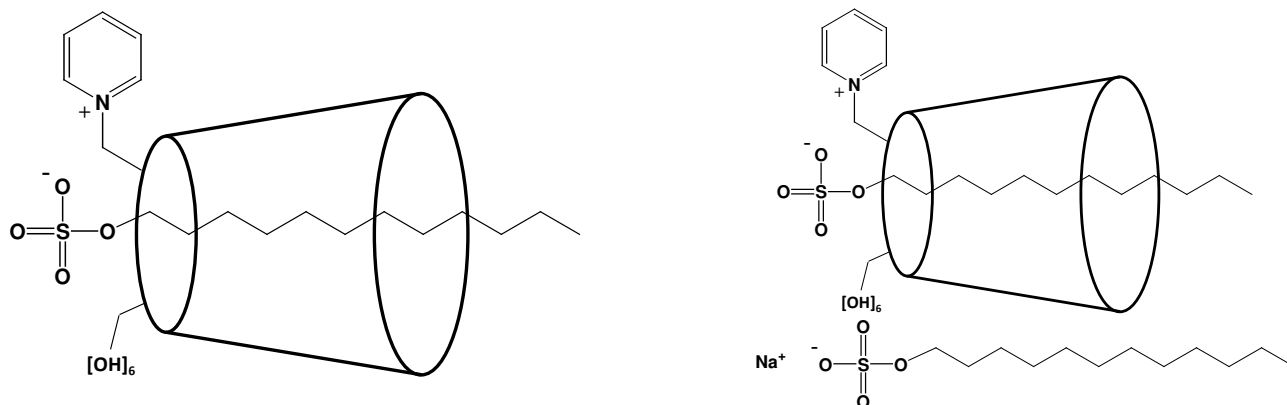
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Cationic derivatives of β -cyclodextrins are associated with dodecylsulfate such that a new anionic surfactants with bulky organic counterions are formed. In addition, β -cyclodextrins are able to bind the hydrophobic tail of the surfactant as an inclusion complex, which dramatically changes the surfactant properties in comparison to the classical sodium dodecylsulfate. Cationic β -cyclodextrins grafted with pyridinium groups are able to form inclusion complexes with organic molecules [1] such as surfactants owing to the hydrophobic character of their internal cavity. The cationic cyclodextrin acts both as a counterion to the anionic surfactant and a complexing agent to the hydrophobic chain of dodecylsulfate.

The surface-active properties of the mono-pyridinium β -cyclodextrin dodecylsulfate surfactant have been investigated together with the properties of the mixed system with sodium dodecylsulfate. Substitution of pyridinium β -cyclodextrin for sodium counterion increases the cmc with respect to sodium dodecylsulfate. Cmc measurements of the mixed systems show the non-ideal behavior of the association with sodium dodecylsulfate. Deviation from ideal behavior has been modeled with the regular solution theory, giving insight into the molecular origin of the non-ideal behavior of the mixed counterion system.



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Self-assembly of hollow colloidal silica cubes

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Among the multitude of recently synthesized non-spherical colloids, hollow silica cubes distinguish themselves by their charged surface and the strong influence of van der Waals forces on their behaviour. While their self-assembly has been observed in experiment, it has not yet been fully studied and characterized.

We take a three-pronged approach that combines analytical calculations, experimental results and computer simulations to elucidate how the self-assembly of the cubes is driven by the competition between electrostatic and van der Waals forces. This is centred around simulations that take the superball model of cubes developed in [1] for the study of hematite cubes [2] and expand it to consider the electrostatic aspects of the system.

First, we investigate the system through simulation and through analytical results based on the perfect superball equation. These simulations are then used to compute the interaction potential of the two cubes, which we examine at different orientations to understand the influence of their anisometry. We then move to small clusters of cubes and compare these to the experimental findings of the microstructures formed. Finally, we study the assembly of these cubes in bulk, under conditions comparable to those seen in experiment. Through the breadth of methods employed, we gain a multifaceted understanding of the behaviour observed in these systems and pave the way for future applications.

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Silica Coating of Tubular J-aggregates in Aqueous Solution

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Silica coatings can be a powerful tool for the study of colloidal systems. Thin shells of silica can enhance stability, permit solvent exchange, and provide a platform for functionalization. However, for some applications it is important that the addition of the silica shell does not disrupt the structure of the dispersed species being studied. Here we present attempts to perform silica coatings on a highly sensitive system that has well defined optical properties in its native state, as well as efforts to characterize the system. The colloid consists of very high aspect ratio double walled tubules composed of optically active amphiphilic molecules. The native arrangement of component molecules is indicated by narrowing and red-shifting of the molecular adsorption upon aggregation. Any disruption of this molecular arrangement results in changes in the absorbance and emission spectra. The shell formation is carried out in aqueous solution with the aid of organo-silane coupling agents. Initial characterization considers fluorescence of the coated tubules, as well as morphology as observed by direct microscopy.

Formation and Stability of Silica Nanoparticle Monolayers at Macroion (PAH)-modified Mica

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Even though silica nanoparticles and their monolayers find a broad field of applications, only a few studies providing a quantitative description of silica nanoparticle deposition at solid/liquid interfaces have been reported in the literature. Given the deficit of reliable experimental data, the goal of this work is to acquire thorough physicochemical characteristics of amorphous silica nanoparticle deposition.

In our studies, silica nanoparticle monolayers of controlled coverage were formed on macroion (PAH)-modified mica. The diameter of the particles determined by dynamic light scattering (DLS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) was equal to $dp \sim 28$ nm. The electrophoretic mobility and the zeta potential of particles were determined as a function of ionic strength and pH. Using the well-defined suspension, systematic studies on particle deposition kinetics were carried out. Particle deposition was carried out under diffusion controlled transport conditions. The coverage of the self-assembled particle monolayers was determined by AFM and SEM imaging. For long deposition times, the saturation coverage was attained, systematically increasing with ionic strength, up to 0.48 for $I = 0.15$ M NaCl. The deposition kinetic runs were adequately interpreted using the random sequential adsorption (RSA) model (see Fig.1). The same model was also used to determine the specific density of silica particles and confirmed their porous structure. Additionally, the particle desorption kinetics was studied using AFM and SEM methods. It was confirmed that silica nanoparticle desorption was practically negligible within the time period of 60 hours. Our experimental data proved, therefore, that it is feasible to produce uniform and stable silica particle monolayers of desired coverage in the self-assembly processes, controlled by the bulk suspension concentration and ionic strength. Such monolayers may find practical applications as substrates for selective protein and nanoparticle deposition

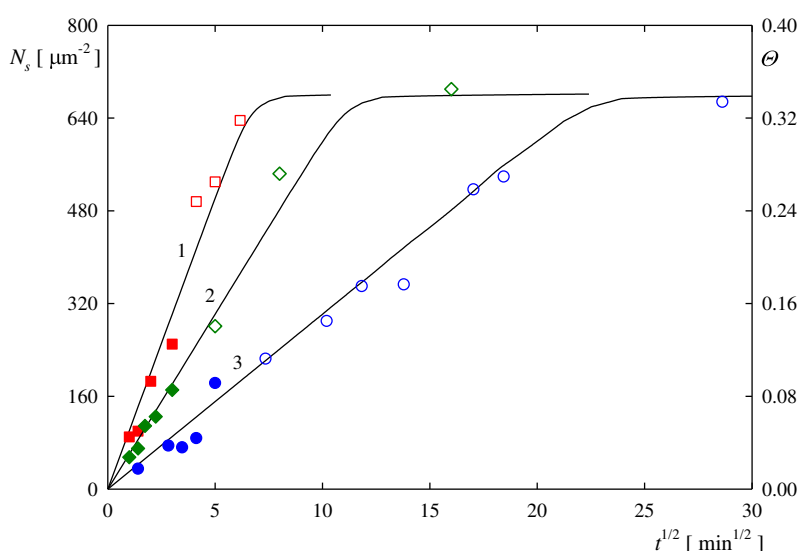


Figure 1. The kinetics of silica particle deposition on mica determined for various bulk suspension concentration. The points represent the results obtained for: (■, □) 50 mg L⁻¹; (◆, ◇) 30 mg L⁻¹; (●, ○) 15 mg L⁻¹, AFM (full points) and SEM (hollow points). Particle deposition conditions: $I = 10^{-2}$ M, pH = 5.8, $T = 298$ K. The solid lines show the theoretical results calculated from the RSA model.

Acknowledgements: This work was financially supported by the National Science Centre(NCN) Grant: SONATA UMO-2015/17/D/ST4/00569; The National Science Center Grant: UMO 2015/19/B/ST5/00847 and POIG 01.01.02-12-028/09-00.

Emission properties of fluorophores in plasmonic superlattices

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Dilute dispersions of gold and silver nanoparticles are known for their strong coloration due to absorption and scattering of visible wavelength light. This electromagnetic interaction can be attributed to the excitation of localized surface plasmon resonances (LSPRs). When placing a fluorophore in the vicinity of such plasmonic nanoparticles, a strong quench in emission can be observed because of energy-transfer between the emitter and the nanoparticle.[1] The energy transfer rate strongly depends on the distance between the two species and the near-field strength of the plasmonic particles.

In this contribution we present results from emission studies of fluorophores embedded into substrate-supported monolayers of plasmonic nanoparticles. We used steady-state emission measurements as well as lifetime analysis to identify energy-transfer and to quantify whether the fluorophore emission is quenched or enhanced by the plasmonic particles. Furthermore we provide insights into the role of periodicity in our monolayers that strongly alters the plasmonic response due to plasmonic/diffractive coupling.[2]

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Robust multilayer nanocoatings based on ionic silicones

A. Puciul-Malinowska, S. Zapotoczny

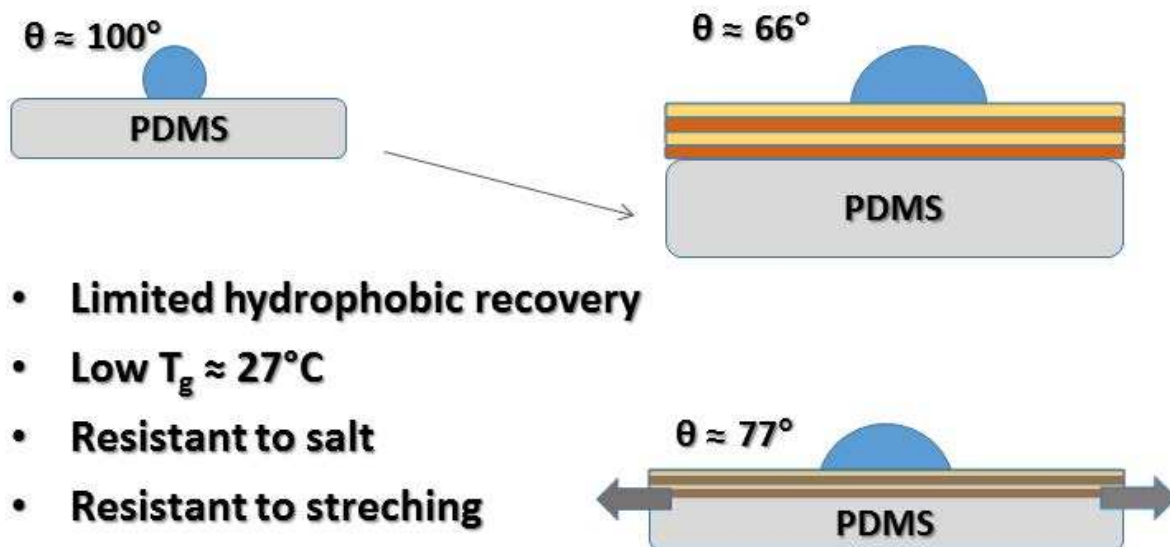
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Two oppositely charged water-soluble oligosiloxanes with the same main chain were synthesized and used for the formation of multilayer nanocoatings [1]. In spite of low molecular weight of the components, due to entropic reasons, linearly growing and robust multilayer films with hydrophilic surface were formed for the first time.

The multilayer films were found to be resistant to high temperature water treatment undergoing only reversible swelling and no surface recovery was observed after its prolonged exposure to air indicating permanent water wettability of this silicone-based coatings. High flexibility of the silicone chains resulted in low glass transition temperature (ca. 27°C) of both dry polyplexes and the films as determined using calorimetry and spectroscopic ellipsometry, respectively. Moreover, the thin coating was applied on plasma-treated poly(dimethylsiloxane) (PDMS) preventing the surface reconstruction in air and leading to long-lasting hydrophilization of the surface (water contact angles around 65°). Such water-borne systems may be used in common applications of silicones providing high flexibility and at the same time water wettability of the coatings.

Ionic silicones - nanocoating



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Stabilization of the gel phase of lipid bilayers by acetic acid and mononucleotides

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Lipids are major components of cell membranes. Being amphiphilic, they self assemble to form bilayers in polar solvents. Above the chain melting transition temperature (T_m), these bilayers are in the fluid state, whereas below T_m they are in the more ordered gel phase. It has been suggested that the non-enzymatic synthesis of RNA like polymers from mononucleotides in lipid environments has played an important role in the origin of life on earth [1]. With this motivation, we have studied the interaction of mononucleotides Uridine 5'-monophosphate (UMP) and Cytidine 5'-monophosphate (CMP) with DMPC (1, 2-Dimyristoyl-sn-glycero-3-phosphocholine) bilayers. We have used small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), Cryogenic scanning electron microscopy, Fluorescence microscopy and differential scanning calorimetry (DSC) techniques to study the influence of these molecules on the structure and phase behaviour of DMPC bilayers. We have also compared the effect of these mononucleotides on the bilayer with that of acetic acid, which is the simplest biologically relevant carboxylic acid [2,3]. Interestingly we find both acetic acid and mononucleotides have similar effect on the structural reorganization of bilayers. Though the solubilities of acetic acid and UMP are relatively high in water, these molecules showed preferential adsorption on the bilayer under excess water conditions. Adsorption of these charged molecules leads to an electrostatic repulsion between the bilayers, resulting in the formation of a swollen lamellar phase. From WAXS and DSC studies we find T_m of the lipid to increase in all the cases. The gel domains were also visualized by fluorescence microscopy using Rhodamine DHPE. We also find that for longer incubation time, the bilayers transform into the interdigitated gel phase. For different lipid to acetic acid/nucleotide molar ratios we have studied the phase behaviour of lipid bilayer as a function of temperature and incubation time.

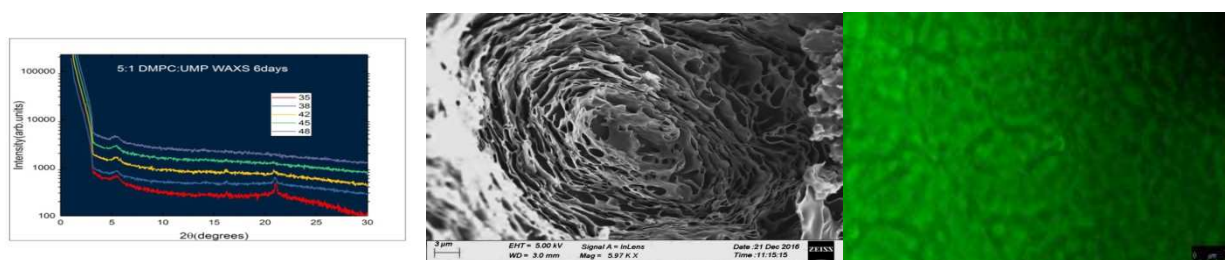


Figure 1. WAXS patterns obtained from DMPC bilayers containing UMP at molar ratio 5:1 (left). CryoSEM image of the swollen lamellar phase formed by DPPC in a 500mM acetic acid solution (center). Fluorescence microscopy image of DMPC multilayers containing UMP (molar ratio 4:1) at 31°C (right).

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Supramolecular assembly in *tert*-butyl alcohol/water mixtures

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In pure liquid alcohols two distinctly structured regions can be found [1-3]. Hydroxyl groups of the molecules form large branched networks, whereas alkyl tails of the molecules occupy the intermediate space. The introduction of a second component like water to such a system causes its restructuring leading to the supramolecular structure, which strongly depends on the system's composition. The structural characteristics of alcohol/water mixtures surely contribute to their anomalous properties (e.g. heat capacity, heat of vaporization, etc.) [4]. Among short-chain alcohols such anomalies are most pronounced in case of aqueous *tert*-butyl alcohol (TBA; 2-methylpropan-2-ol), presumably due to a rather bulky *tert*-butyl group. TBA mixes with water in all proportions. Its water mixtures are industrially important systems as they are extensively used as solvents. They find its use also in liquid chromatography as reaction media for various synthesis and even for protein aggregation – the structure of TBA/water system plays critical role in protein aggregation mechanisms [5]. In the present study, we were investigating the structure of TBA water systems by the experimental Small- and Wide-Angle X-Ray Scattering (SWAXS) technique combined with the Molecular Dynamics (MD) computer simulations. We directly compared the experimental scattering curves with the ones calculated from the simulation results according to the Complemented System Approach [6] and in this way validated the model used. As depicted in Fig. 1, we found very different structural situations in different composition regimes.

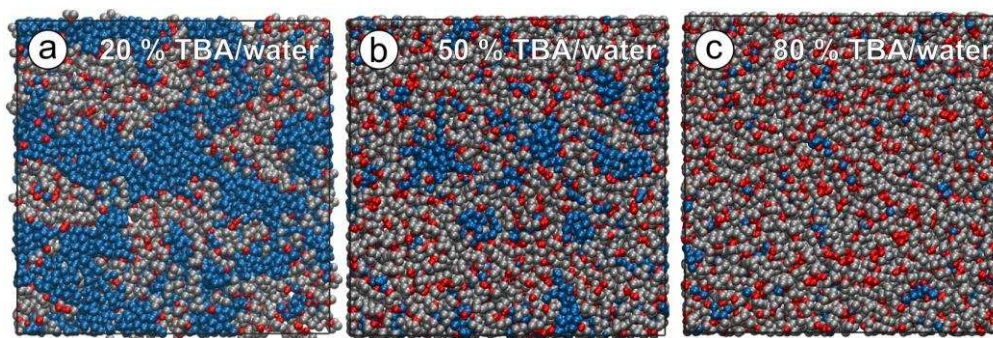


Figure 1. Thin slice ($z = 1$ nm) of the simulation box in case of a) 20, b) 50 and c) 80 % TBA/water mixtures. Blue colour denotes water molecules, red alcohol hydroxyl groups, and grey alkyl chains.

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Self-assembly of guanine-rich oligonucleotides into G-wires

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Guanine-rich DNA or oligonucleotides are able to self-assemble into complex four-stranded structures called G-quadruplexes. The basic assembly unit is a G-quartet: four guanines associated via Hoogsteen hydrogen bonding (Figure 1a). Subsequent π - π stacking of G-quartets produces the quadruplex core. When G-rich DNA or oligonucleotides self-assemble into long, continuous quadruplex superstructures they are termed G-wires. These nanowires have mechanical properties superior to dsDNA in regard to potential use in nanotechnology: they resist enzymatic degradation and are mechanically and thermally stable.

It is essential to build G-wires with an unperturbed quadruplex core in order to apply them in nanocircuitry. We recently showed that long G-wires can be constructed through cohesive self-assembly of GC- and CG-ends [1,2]. In this arrangement GC-overhangs are used to link two G-quadruplexes via (G:C:G:C) quartets based on Watson-Crick G:C base pairing (Figure 1b). A model sequence d(GCGGAGGCG) was deposited on mica substrate to test this principle. Atomic force microscopy (AFM) proved the formation of several hundred-nanometer long wires with an average height of 1.7 nm, a value that is typical for G-quadruplexes when studied by AFM.

In this study we extended our previous AFM work to establish prosperous candidates for the self-assembly of long, continuous G-wires [3]. We tested if magnesium ions have an effect on stimulating G-wire anchoring to the substrate. For comparison we also tested the effect of magnesium ions on G-wire growth inside solutions by dynamic light scattering. Our results showed that a number of G-rich oligonucleotides with GC-ends form G-wires. The wide distribution of G-wire heights, from 1.1 nm to 2.6 nm, indicated different self-assembly arrangements depending on the details of the molecular structure and substrate properties.

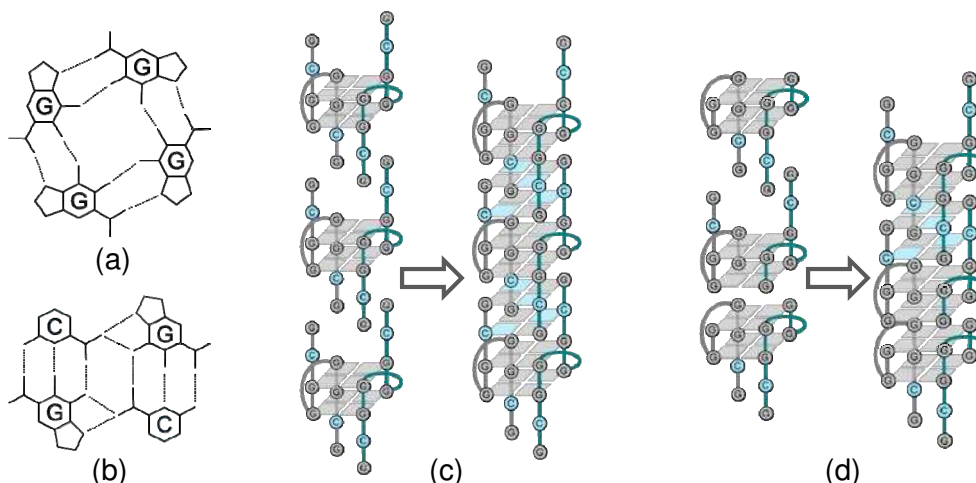


Figure 1. (a) Four guanines form a planar G-quartet. (b) A (G:C:G:C) quartet. (c) Self-assembly of G-wires with 5' and 3' GC-ends, and (d) without CG3' ends [2].

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Supramolecular assembly in terminal 1,*n*-diols

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Diols are industrially very important platform chemicals that contain two hydroxyl groups per molecule and can be successfully produced from renewable bioresources [1]. They are widely used in various functions and areas including solvents, fuels, polymer synthesis, cosmetics, and pharmaceuticals. Solvent properties of terminal 1,*n*-diols depend on their bifunctional nature and their relatively high viscosity that is likely connected to their molecular structure and supramolecular assembly in bulk. Investigating the structural properties of pure liquid systems, we hope to better understand the structure-function relationship that will govern the kinetics of the processes taking place in such solvents. With the present study of the series of terminal 1,*n*-diols from ethane-1,2-diol to pentane-1,5-diol at 25 °C (and higher temperatures) we expand our previous structural investigations of pure organic liquids [2-6]. Utilizing the experimental Small- and Wide-Angle X-Ray Scattering (SWAXS) technique and the Molecular Dynamics (MD) simulations we investigate how the elongation of the hydrocarbon part of the molecules effects the structuring in these systems. The simulations were performed utilizing the Transferable Potential for Phase Equilibria – United Atom (TraPPE-UA) force field model. The scattering of the modeled systems was calculated according to the Complemented System Approach [7], which offered a direct insight into the structuring of the systems and enabled the deduction on the origin of the scattering characteristics. Furthermore, the information on radial distribution functions, molecular end-to-end distance distributions, and size distributions of H-bonded hydroxyl aggregates was also obtained.

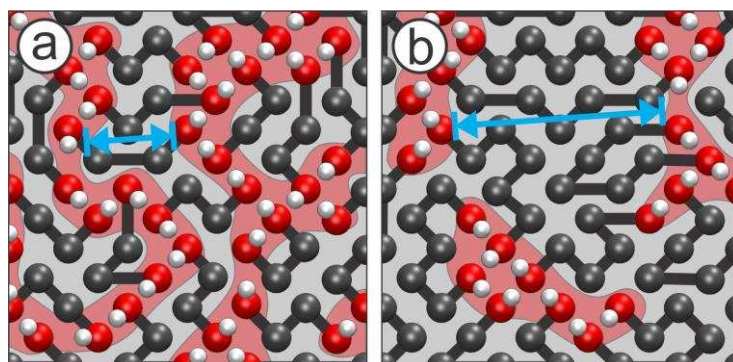


Figure 1. Scheme of the simulation box for (a) ethane-1,2-diol and (b) pentane-1,5-diol.

Acknowledgements: We acknowledge the financial support of the Slovenian Research Agency through the research core funding No. P1-0201 and the project No. N1-0042 (Structure and thermodynamics of hydrogen-bonded liquids: from pure water to alcohol-water mixtures).

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Self-Assembly of 3,4-ethylenedioxythiophene and the Surface Polymerization of the Adsorption Monolayer on an Au(111) Surface

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Electrochemical Scanning Tunneling Microscopy (EC-STM) and Cyclic Voltammetry (CV) are utilized to study the adsorption behavior of 3,4-ethylenedioxythiophene (EDOT) from phosphate buffer solution onto Au(111) surface, as well as the electro-polymerization of the EDOT monolayer into poly-ethylenedioxythiophene (PEDOT). The results show that EDOT molecules can spontaneously adsorption on an Au(111) surface at the open circuit potential (OCP, -0.15V vs Pt reference), forming a monolayer with various ordered adlattices, as confirmed by the observation of in-situ STM. The CV result shows that the EDOT adsorption is a surface oxidative reaction and is initiated at a potential of -0.25 V, and the corresponding desorption of the EDOT adlayer occurs at a more negative potential (-0.4V). If the adsorption process is initiated at a more negative potential and the electrode potential is increased gradually, the monolayer forms slowly and a highly order and uniform EDOT monolayer can be prepared as shown in Figure 1.

According to the CV study, a potential higher than 0.2 V should be applied to perform the polymerization of EDOT molecules. After preparing and observation of the EDOT adlayer, the polymerization of the EDOT adlayer is performed by applying a constant potential of 0.25V. However, the EDOT monomers in the solution will take part in the reaction on the electrode, leading to a disordered PEDOT layer with multilayered structure. Alternatively, if a cyclic potential between (-0.25 to 0.25 V) is applied, the polymerization will perform mainly on the adsorbed molecules and an ordered PEDOT monolayer can be obtained as demonstrated in Figure 2. An Electrochemical impedance spectroscopy (EIS) analysis indicates that the PEDOT film prepared by the dynamic potential treatment has a lower charge transfer resistance than that prepared using constant potential polymerization.

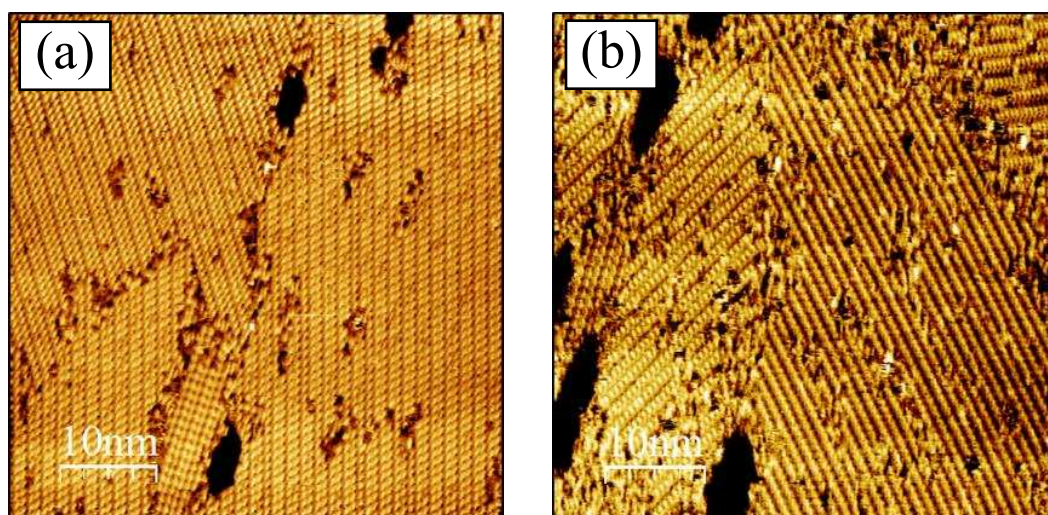


Figure 1. STM images of EDOT monolayer assembled by gradual increasing the adsorption potential (a), and PEDOT monolayer prepared by surface polymerization of the EDOT adlayer (b)

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Effect of temperature on self-assembly of poly(methacrylic acid) chains in the presence of multivalent counterions

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Natural and synthetic weak polyelectrolytes have an ability to self-organize into associates in solution. This process can be caused by changing different parameters such as polyion charge, temperature, solvent, adding other charged species into the solution or sometimes by acting with mechanical stress on it. The ability of self-assembly is widely studied because of numerous applications of the arising associates. They can be used in medical diagnostics as carriers for targeted drug delivery, in paints, coatings, composite materials, *etc* [1].

Suitable for studying the effect of polyion charge is poly(methacrylic acid) (PMA) as a synthetic polyelectrolyte, where charge can be easily varied by changing the degree of neutralization (α_N) of carboxyl groups. Recently it was shown that isotactic PMA (iPMA) forms nanoparticles in water at 25 °C at a so-called critical value of α_N ($\alpha_N \approx 0.2$) [2]. This α_N corresponds to the solubility limit of this homopolymer in water. It was discussed that iPMA chains first undergo a conformational change from coil to helix, which is followed by an intermolecular association [2-4]. Atactic form of PMA (aPMA) is soluble in water at any α_N . Our work aims at preparing stable associates by temperature-controlled self-assembly of aPMA and iPMA. The idea is based on recently published approach for inducing polymer self-assembly of poly(α -alkylcarboxylic acids) into stable polymeric nanoparticles without any assembly triggering additives, which involves heating of a homopolymer solution [1].

Possible self-assembly and structural characteristics of aPMA and iPMA chains was herein studied by UV-Vis, isothermal titration calorimetry (ITC), dynamic light scattering (SLS and DLS) and fluorimetric measurements in aqueous solutions of sodium (NaCl), magnesium (MgCl₂) and lanthanum chloride (LaCl₃) with ionic strength 0.01 mol L⁻¹ in the temperature range from 0 to 95 °C. Experiments were performed with samples of aPMA and iPMA, which differ in weight average (M_w) and number average molar mass (M_n), in polydispersity, tacticity, and α_N .

Nanoparticle formation was monitored by temperature-controlled UV-Vis experiments and further the associates were characterized by SLS and DLS. Using these two methods we determined the radius of gyration (R_g) and the hydrodynamic radius (R_h) of aPMA and iPMA associates. With ITC, the ionization enthalpies of both PMA isomers were obtained at different temperatures. With fluorimetric measurements we obtained information about the polarity of microenvironment in the formed aggregates of aPMA and iPMA.

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Electrochemical control of viscosity of aqueous solutions of gemini surfactant having ferrocenyl groups

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Ferrocene is hydrophobic in reduced form, whereas its oxidized state, ferrocenium ion, is hydrophilic. Thus, the hydrophilic-hydrophobic balance (HLB) of surfactants having ferrocenyl groups can be reversibly controlled by electrochemical redox reaction of ferrocenyl groups. The viscosity of aqueous solutions of threadlike micelles is higher than that of spherical micelles. It is expected that the control of the formation and disruption of threadlike micelles makes it possible to control the transportation of substance in flow systems. In this study, the electrochemical control of formation-disruption of threadlike micelles formed from a gemini surfactant having ferrocenyl groups has been investigated in terms of solution viscosity.

Gemini surfactant (**Fc11-4-11Fc**) (Figure 1) having ferrocenyl groups has been synthesized in our lab and 30 mM of **Fc11-4-11Fc** aqueous solutions containing 10 mM of LiBr were prepared. Oxidized solutions were prepared by oxidizing electrochemically the reduced solutions with an applied potential of +0.6 V. Re-reduced aqueous solutions were obtained by electrochemical reduction of oxidized solutions with an applied potential of -0.1 V.

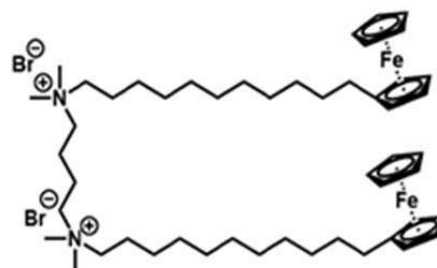


Figure 1. Chemical structure of **Fc11-4-11Fc**.

Reduced **Fc11-4-11Fc** solutions were highly viscoelastic fluids because of threadlike micelle formation (Figure 3a). The formation of threadlike micelles was confirmed by dynamic viscoelasticity measurements. As can be seen in Figure 2, the zero-shear viscosity (η_0) of the reduced solutions was almost 1000 Pa·s and decreased by oxidizing electrochemically for 24 hrs (Figure 3b). This will be due to the disruption of threadlike micelles. Further, the η_0 value of the oxidized solutions increased again by electrochemical reduction (Figures 2 and 3c). The formation-disruption of threadlike micelles by electrochemical redox reactions will result from the change in HLB of **Fc11-4-11Fc**.

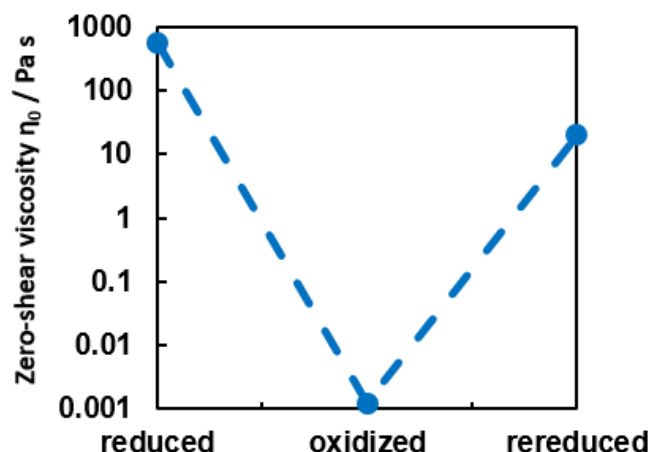


Figure 2. Change in the viscosity of aqueous solutions containing **Fc11-4-11Fc**.

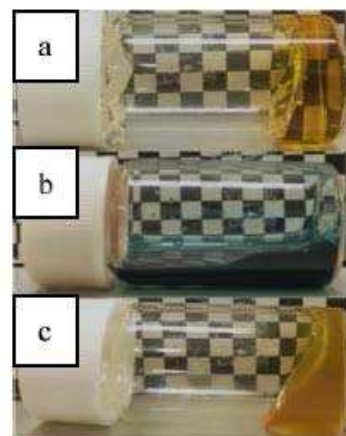


Figure 3. Physical appearance of aqueous solutions. a) reduced solution, b) oxidized solution, c) re-reduced solution

Wormlike micelles of alkyltrimethylammonium bromide-sodium salicylate in different aqueous binary systems

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Wormlike micelles (WLM) are formed by the self-assembly of surfactant molecules into long, cylindrical aggregates. A widely studied system is alkyltrimethylammonium bromide (C_n TAB), combined with sodium salicylate (NaSal). The quantity of NaSal in the WLM affects their relaxation mechanisms, thus affecting their zero-shear viscosity. Additionally, the relaxation mechanisms (reptation, and break and recombination) can be altered by adding polar additives, such as glycerol, to the solution[1,2]. The formation of the micelles is also affected by these additives, and this process can be observed through isothermal titration calorimetry, ITC. In this work, we studied the effects of several additives – glycerol, sucrose, dimethyl sulfoxide, 1,3-butanediol and urea – on the zero-shear viscosity and calorimetric profiles of the micelles[3].

Figure 1(a) shows the most relevant zero-shear viscosity profiles. 50% m/m of sucrose changed the profile very little, in comparison to 15% 1,3-butanediol, which greatly reduced the viscosity at the peaks. Additionally, 30% urea increased the viscosity at the 1:1 region and decreased in the other areas. This behaviour can be mostly explained by considering a few properties of these binary water/additive solutions, namely, refractive index n , dielectric constant ϵ , Gordon parameter G .

The best correlation between property and rheological behaviour is achieved by the Gordon parameter, Figure 1(b). For example, sucrose has little effect on G , on the viscosity and the calorimetric profile. 1,3-butanediol strongly decreases G , and it also has the strongest effect on the micelles. This property does not explain everything, however, as seen by urea. In this case, it is probably both the high dielectric constant of the medium and the strong interaction of urea with the surfactant cationic heads that results in the observed behaviour. The refractive index affects all systems by diminishing the attractive force between micelles through a decrease in the Hamaker constant, which depends on the difference of n between micelle and solvent. This accelerates the reptation mechanisms, diminishing the viscosity when the relaxation is reptation controlled, as was observed for glycerol. However, it is necessary to observe all parameters to fully comprehend these systems.

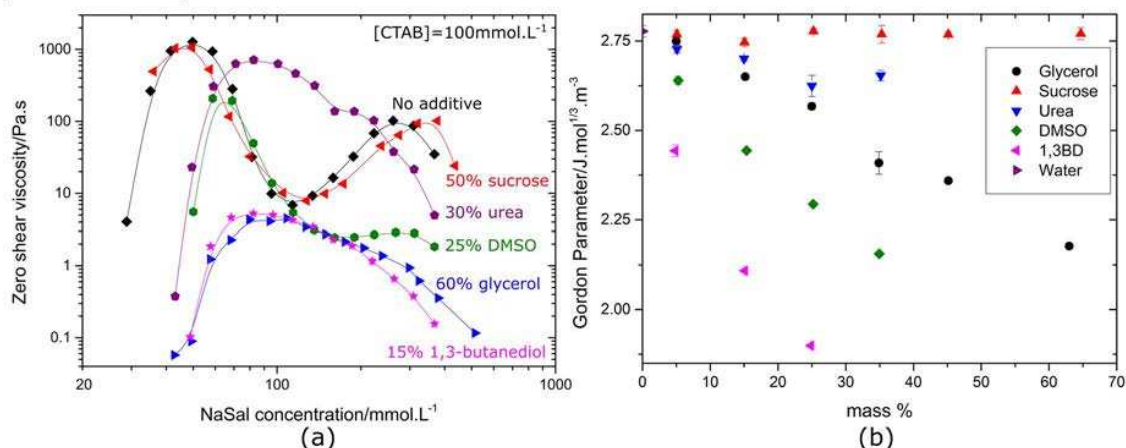


Figure 1. (a) Zero-shear viscosity of CTAB 100mmol.L⁻¹ at increasing NaSal concentrations in the presence of several additives (concentration in mass %). (b) Gordon parameter for the aqueous binary solvents.

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Self-assembled nanostructures in aqueous solutions of antennary peptides

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The antennary peptides are synthetic products, obtained as a result of preliminary molecular design. Their antennae of equal length built from several glycine residues are jointed by the C-end to an oligoamine branching core whilst the amine group at the N-terminus is exposed outside. The key outcome is that the peptides are capable to form well-organized supra-molecular assemblies (tectomers), bulk hydrophilic nanoplateforms and/or vesicles, in aqueous media, and ultra-smooth coatings on solid surfaces. The innate reason for the self-assembly is onset of highly cooperative arrangements of intra- and intermolecular hydrogen bonds (Polyglycine II motifs) [1].

Having in view potential practical applications of the antennary oligoglycines, we recently began systematic research on their behaviour in aqueous solutions. We demonstrated that properties of the self-assemblies can be finely tuned by variation in pH and/or by addition of charged entities (e.g. low or high molecular mass substances); the presence of soft or solid interfaces has significant effect and additionally modifies the resultant supra-molecular assemblies [2]. The study is focused on two types of peptides: (i) two-antennary with penta- or tetraglycine antennae linked to C_n-alkyl α,ω -diamine core (n=7,8,10); (ii) four-antennary with heptaglycine antennae linked to tetraaminomethylmethane core. A combined procedure is developed, including examination of properties of interfacial layers at solution/air and solution/solid boundaries, drainage and stability of foam and wetting films, to characterize the bulk and interfacial nanostructures and coatings. The applied experimental methodology includes several research techniques: microscopic thin liquid films, PAT, CA measurement, SEM, DLS.

The obtained results add new knowledge to structure-property relationships of the studied aqueous formulations giving valuable hints about the key factors related to possible applications in medicine, pharmaceutics, and environment protection.

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Mixtures of Amino Acid Based Surfactants

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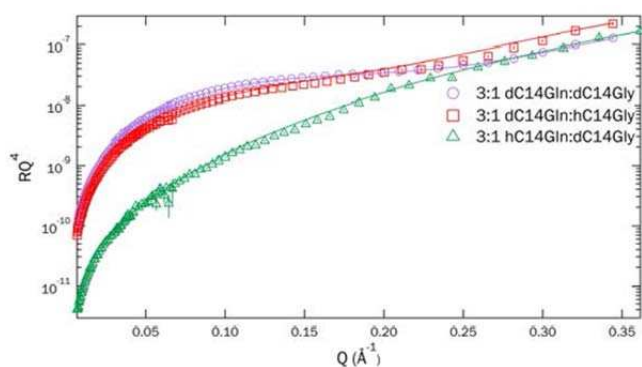
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The potential of amino acids as headgroups of surfactants has been recognised since the early 1900s. In more recent years they have been further investigated as greener alternatives to commercial surfactants [1,2]. In this work we have used renewably-sourced amino acids found in waste grain residue from the brewing industry; a mixture of glycine, glutamine and proline. These compounds have been used in combination with fatty acids including myristic acid to prepare surfactants. The physical properties of these amino acid surfactant mixtures have been investigated to determine the feasibility of amino acid surfactants synthesised directly from grain residue.

We have investigated the structural properties of myristic acid-based surfactants in detail, both in solution above the CMC using small angle neutron scattering, and at the air-water interface using neutron reflectivity. The surfactants were synthesised in both hydrogenated and deuterated forms using deuterated myristic acid, and where available, deuterated amino acids.

Neutron reflectivity allows determination of the relative absorption of the components of the mixtures by using selective deuteration of the different components, which allows the relative surface affinity of the two surfactants to be determined. Data shown in Figure 1 for myristoyl glutamine and myristoyl glycine indicates the higher surface affinity of myristoyl glutamine.

This talk will discuss and expand upon the data shown above, as well as discussing the effect of mixing these surfactants and others, on the structure at the air-water interface and the structure of micelles in solution.



Contrast	SLD (10^{-6} \AA^{-2})
dC14Gln:dC14Gly	7.10
dC14Gln:hC14Gly	5.88
hC14Gln:C14Gly	1.25

Figure 1. 3:1 Molar Ratio of Myristoyl Glutamine and Myristoyl Glycine fitted using Motofit software[3], relative Scattering Length Densities are Included in the adjacent Table

Acknowledgements: I would like to thank the ISIS neutron source ILL and Diamond for Beamtime, Dr Armando Maestro, Dr Maximillian Skoda, Dr Arwel Hughes and Dr Mario Campana for assistance with beamtime and fitting.

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Structure and cluster formation in size asymmetric soft electrolyte systems

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We examine the structure and thermodynamic properties of systems composed ions with rigid Gaussian charge distributions of differing widths that only interact electrostatically. These ultrasoft electrolytes [1,2] provide insight into the role of electrostatics in colloidal systems and have been observed to exhibit a liquid-vapor phase transition, as well as aggregation.

We perform molecular dynamics and Monte Carlo simulations over a broad range of ion densities and electrostatic coupling strengths for systems containing ions with different width charge distributions. Under certain conditions, these systems are observed to form large, finite sized clusters in an isotropic phase. The structure of these clusters, their charge and electrostatic potential distribution, and energetics of formation are analyzed in detail.

We compare and interpret the simulation results with a splitting field theory [3] framework that focuses on fluctuations in the electrostatic potential. Within this approach, the short wavelength and long wavelength fluctuations are treated within different approximation schemes. This theory can accurately describe the counterion mediated attractive interactions between like-charged plates [3,4] and the one-component plasma (OCP) [5] from the weak, intermediate, and strong coupling regimes. As the charge distribution of one of the ion species in the ultrasoft electrolyte broadens, the system more closely resembles the OCP, where the splitting theory is known to work well. We carefully examine the evolution of ultrasoft electrolyte as the width of one of the ions changes from being infinitely broad to smaller sizes. In particular, we present spatial correlations in the fluctuations of the electrostatic potential, decomposing them into short and long wavelength contributions. This information is used to extend the splitting theory to capture the region of cluster formation.

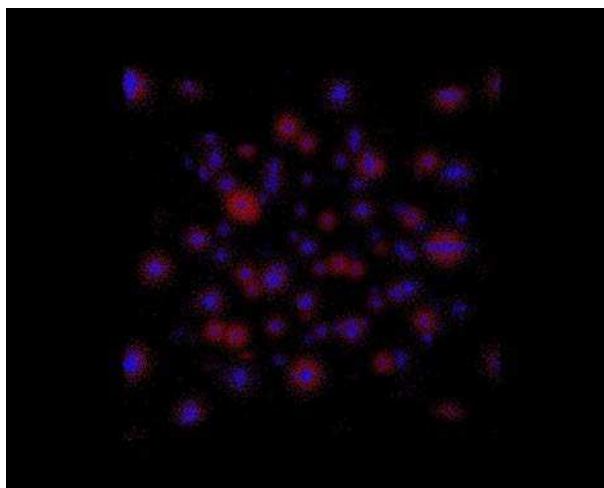


Figure 1. Cluster formation in a size asymmetric ultrasoft electrolyte: cations (red) and anions (blue).

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Investigating the self-assembly process of amphiphilic drugs using scattering techniques

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Amphiphilic drug systems widely used in antidepressant and cancer therapy are composed of hydrophilic and hydrophobic regions. This amphiphilic behaviour sets such systems the particular interest of drug industry. Amphiphilic molecules undergo molecular and supramolecular self-assembly processes resulting in hierarchical structures. Such hierarchical structures, like spherical or cylindrical micelles, vesicles, and lamellae, are organized on multiple length and time scales on the mesoscale. The mesoscale is the scale which connects the microscale (bottom) to the macroscale (top), in order to achieve the so-called bottom-top approach used for the description of self-assembled systems. The self-assembly process of amphiphilic drugs which occurs on the mesoscale is not yet well-studied and this is the particular interest of our study. In this study we aim to investigate the self-assembly process of amphiphilic drug micelles on the mesoscale using scattering techniques. Results from this study provide the knowledge to allow understanding of how the self-assembly process of amphiphilic drugs can be controlled and how the resulted hierarchical structures interact with other amphiphilic self-assembled and charged polymer networks. This could be useful for the industry, in order to create drugs with novel properties and to increase their compatibility with drug carriers.

Formation and stability of hematite/silver nanoparticle bilayers at mica: AFM and electrokinetic characteristics

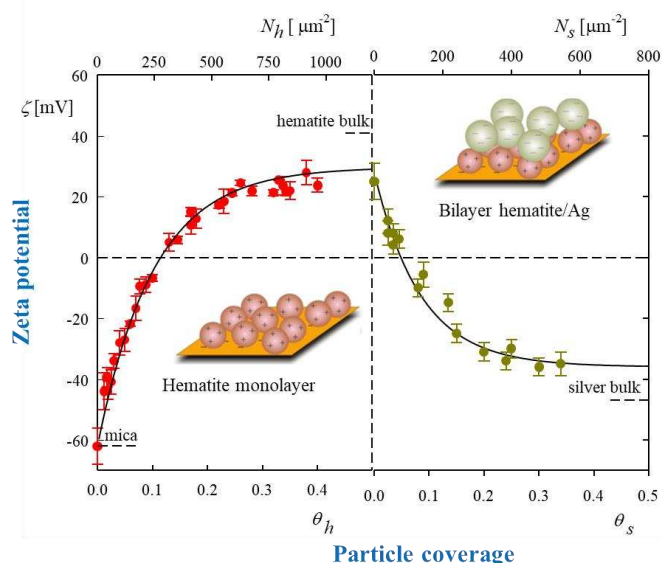
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Nanoparticles are recently the most prominent and promising components for technological applications. Self-assembly of nanoparticles has been identified as an important process in which nanometer-sized species are randomly organized into ordered structures. However in order to successfully exploit nanoparticle self-assembly and to ensure efficient and repeatable scale-up, a high level of consciousness and control is required.

Here we present quantitative studies on self-assembled bilayers of hematite/silver nanoparticles. The bilayers were thoroughly characterized using atomic force microscopy (AFM) and *in situ* streaming potential measurements. The coverage of the supporting layer, composed of positively-charged hematite nanoparticles ($d_H=26$ nm) was adjusted by changing the bulk concentration of hematite suspensions and the deposition time. Afterwards, negatively-charged silver nanoparticles ($d_S=28$ nm) were deposited under diffusion-controlled transport. The coverage of obtained hematite/silver bilayers was determined by a direct enumeration of deposited particles from AFM images and SEM micrographs. The kinetics of the hematite monolayer formation at the mica surface and the effect of the mica substrate and the coverage of a supporting hematite layer on the zeta potential and final coverage of obtained bilayers was determined. It was revealed that for the coverage exceeding 0.20, the zeta potential of bilayers was independent on the substrate and the supporting layer coverage. The kinetics of the bilayer formation was theoretically described in terms of the RSA model and 3D electrokinetic model. Additionally, using the streaming potential method, the quantitative studies on the stability of obtained bilayers were performed. It was shown that the electrostatic interactions are the dominant forces for the stability bilayers. Besides for significance in basic sciences, our studies allowed to develop a robust method of preparing nanoparticle bilayers of controlled properties. Such bilayers may find practical applications in catalysis or production of smart biointerfaces. In Fig. 1 the schematic view of $\alpha\text{-Fe}_2\text{O}_3@\text{Ag}$ nanoparticle bilayers is depicted.



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Transport properties of decanoates as a function of counterions and temperature: Experiment and theory

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Recently, an extensive thermodynamic study was carried out on the micellization processes of long-chain carboxylates in water [1]. It was found out that they can be successfully described by the two-step micellization model and that here the interactions with counterions are less expressed in comparison to those observed by other ionic surfactants.

In this contribution, the conductivities of sodium (NaC10), potassium (KC10) and cesium (Cs10) decanoate in aqueous solutions will be presented. The experiment was carried out from 5°C to 55°C in step of 10° C below and above their critical micellar concentrations (CMC) [2]. Experimental data were analyzed by a mean spherical approximation (MSA) transport theory which turned out as successful at the description of transport processes in relatively complex systems [3,4]. To reproduce experimental conductivity below CMC correctly, real association constants are introduced in the MSA-transport theory using activities calculated at the same level of approximation [4]. Above CMC the effective charge of the micelles and their degree of dissociation was deduced. From Figure 1 a) it is evident, that that premicellization association has to be taken into account and from Figure 1 b) that CMC is almost independent on counterions. Both findings are in agreement with the results from thermodynamic study [1].

In our presentation the applied experimental procedure and theory will be described and the counterion and temperature effects will be discussed.

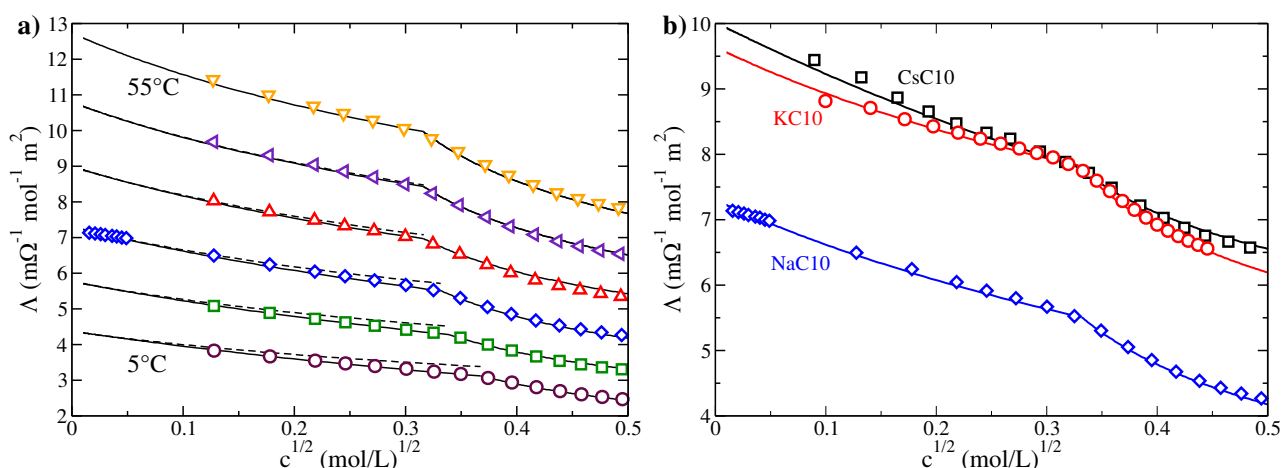


Figure 1. Molar conductivity of investigated micellar systems in water as a function of the square root of the total monomer concentration.

a) NaC10 from 5°C to 55°C by step of 10°C; **b)** NaC10, KC10 and CsC10 at 25°C; symbols: experimental values, lines: MSA-transport theory (solid line with association and dashed line without association).

Acknowledgements: PHC PROTEUS 2018 Code: 39668QL, BI-FR/18-19-PROTEUS-006.

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Self-assembly of low molecular weight organic compounds into stable nanohydrogel particles

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The growing interest in organic nanoparticles is linked mainly to their use in Nanomedicine as delivery vehicles for therapeutic or diagnostic applications.¹ Such nanoparticles include drug nanoparticles, liposomes, solid-lipid particles, polymeric hydrogels, protein-drug conjugates and dendrimers. However, the formation of gel nanoparticles from low molecular weight compounds remains practically unexplored. Following our extensive research on self-assembled fibrillar networks and macroscopic gel formation from low molecular weight molecules,² here we report on the use of low molecular weight (molecular) gelators for the preparation of nanosized gel particles.³

Several molecules capable of forming macroscopic hydrogels were used for the preparation of nanogel particles (Figure 1). The preparation of the particles was successful with different methodologies such as high dilution precipitation, ultrasound driven particle formation and microfluidics. Electron microscopy and DLS revealed rather uniform particle formation with diameters in the range of 50-200 nm depending on the compounds and methodology used. Interestingly, these particles are stable for several days in accordance with their zeta potential and present the capability of being loaded with fluorescent probes. In some cases, *in vitro* experiments reveal the successful transport into cells. Initial experiments of particle counting based on the combination of particle weight (SLS) and concentration of gelator (NMR) determinations indicate that nanogel particles are composed mainly by water.

Overall, molecular nanogels may represent an interesting new type of nanocarriers. The low molecular weight nature of the components imparts intrinsic stimuli responsiveness and presumably superior biocompatibility and biodegradation properties in comparison to polymeric systems.

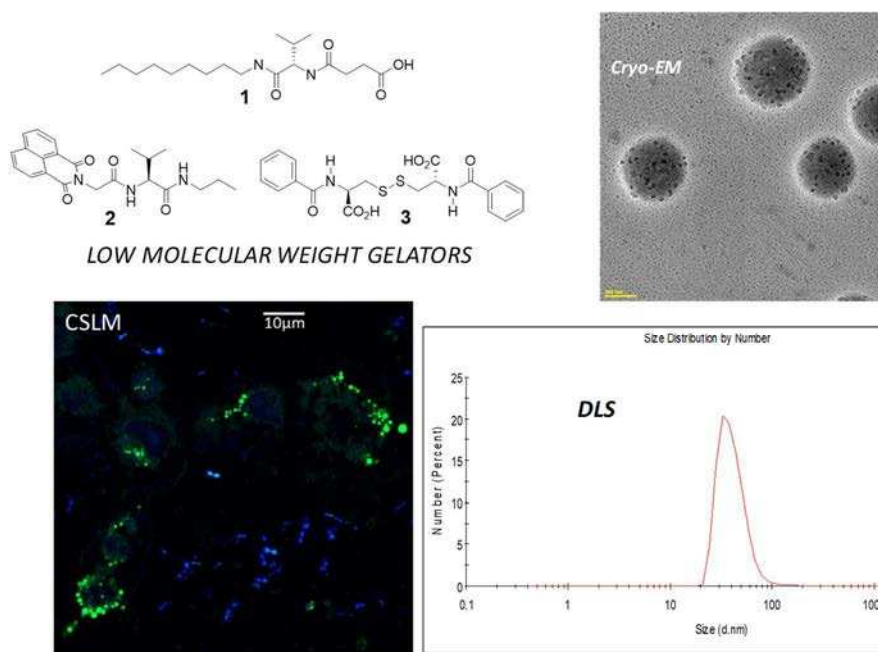


Figure 1. Structure of the compounds used to prepare nanoparticles. Selected Cryo-EM image and DLS size distribution. CLSM image of a cell culture in the presence of Rhodamine 123 loaded particles.

Acknowledgements: Ministerio de Economía y Competitividad of Spain (grant CTQ2015-71004-R) and Universitat Jaume I (grant P1.1B2015-76).

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New aspects of patterning via evaporation of colloidal drops

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Droplets are miniaturized reactors, hosting numerous physic-chemical processes within the span of a few millimetres or less. They are also devoid of the sophisticated infrastructures associated with microfluidic labs-on-chip. The ease of handling allows droplets to be used various configurations-levitated or sessile, vibrated or inclined, heated or cooled. Even the choice of solvent or the morphology of dispersed particles seem to produce effects unseen in the bulk form. Most of the configurations try to control the internal flow field in an evaporating droplet in a bid to hierarchically control the microstructure of the final residue. To this end we present some novel techniques. Droplets are free-standing liquid masses and can be stacked vertically. By controlling the delay between the deployment of two colloidal drops we can modulate the crack morphology of the final residue¹ (Fig 1a). Repeating this process with two different colloids, we investigated the aspects of in-situ mixing and subsequent transport of disparately sized colloids in evaporating droplets² (Fig 1b). In a separate line of work, we developed a cheap and indigenous method of printing wall-less containers for droplets³. When colloidal drops were deployed in such containers, they were morphed into myriad of exotic shapes. The internal flow field too displayed hybrid forms and the resulting residues show hierarchical features correlated to the design of the printed patterns (Fig 1c).

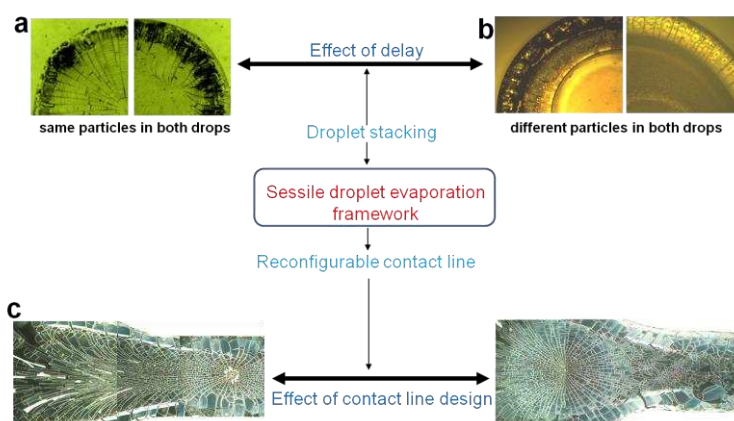


Figure 1. (a) how crack patterns were modified by delaying drop deployment for same type of particles (b) how deposit morphology was modified by using the droplet stacking method of (a) for two different particles (c) how deposits can be modified by deploying drops in different wall-less containers.

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Fatty acid self-assemblies in the presence of choline hydroxide: effect of the molar ratio

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In the current context of sustainable development, the use of agro-based molecules instead of petrochemical based product is one of the challenges of our century. Fatty acids are green molecules available in large amount in nature and present original interfacial properties [1]. Despite their attractive properties, the use of long fatty acid chains is restricted because of their low solubility in water. To improve their solubility, various strategies can be used such as mixtures with cationic surfactant to obtain catanionic systems or ion-pairing with organic counter-ions. In all cases, the main parameter is the molar ratio R between the fatty acid and the component used to its dispersion [1]. Contrary to fatty acid catanionic systems, few data are available in the literature about the effect of R in the case of organic counter-ion. Our aim was to investigate the impact of R on fatty acid assemblies in bulk for myristic acid and choline hydroxide as organic counter-ion. R was defined as the ratio between the molar number of choline and the molar number of myristic acid.

In a first step, we determined the phase diagram of the myristic acid/choline hydroxide system as a function of both temperature and R . We observed various phases (Figure 1). To determine the self-assembly structure in each phases, we performed SANS and TEM experiments. As a function of R and temperature, various fatty acid self-assemblies were obtained. At high R , only micelles were present for all the temperatures whereas at low R , lamellar phases, faceted or spherical vesicles were present [2]. Then, we determined the physical state of the fatty acid chain embedded in these self-assemblies by coupling NMR and DSC. We measured the chain melting transition from gel state to fluid state as a function of R . In a second step, we studied the ionization state of the fatty acid by coupling pH and infra-red spectroscopy analyses. At low R , fatty acid molecules were present under two forms: carboxylic and carboxylate. When the two forms coexist, hydrogen bonding formation can occur. By increasing R , the content of carboxylic form decreased until all fatty acids were under carboxylates. This change occurring at molecular scale is responsible for the structural self-assemblies transitions at the microscopic scale [3].

Our results show that by modifying the molar ratio between myristic acid and choline hydroxide, we can tune the ionization state of the fatty acid, the chain melting transition as well as the interactions at molecular state level leading to the formation of various self-assemblies in bulk [2-3].

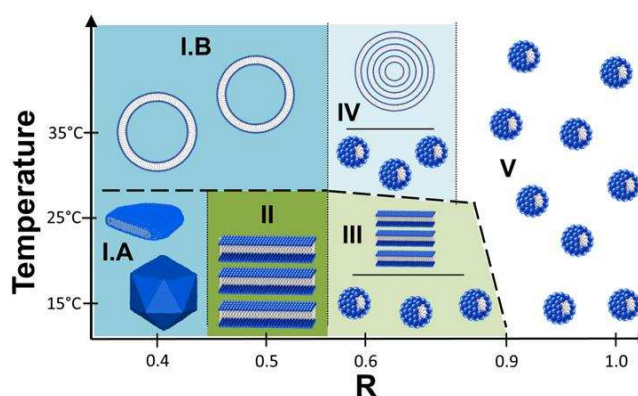


Figure 1: Illustration of the phase diagram of the myristic acid/choline hydroxide system as a function of both temperature and molar ratio (R).

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Investigation of quaternized chitosan - alkylethoxy carboxylate based complexes

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Polyelectrolyte - surfactant self-assembles (also PESCs) are interesting biomimic systems characterized by their highly complex, mesoscopically ordered structures which are sensitive to environmental stimuli, such as T and pH. One species of such a potentially functional material can be formed by the oppositely charged building blocks such as naturally derived chitosan plus the biofriendly surfactant alkylethoxy carboxylate which form complexes that were studied in our group by L. Chiappisi [1, 2]. The combined nm-structures from the surfactant molecules were controlled by the longer length scale polymer chains. This system has high potential for applications in biosensitive fields, e.g. cosmetic and pharmaceutical formulations or in detergency, especially as it shows marked pH-dependent behaviour.

Previous results showed that the local PESCs structure depends substantially on the surfactants packing parameter, such as the unilamellar vesicles formed by $C_{12}E_4COO$ are transformed to multilamellar vesicles (MLVs) by admixing the oppositely charged biomacromolecules. Recently, we embedded the chitosan with up to 100% possible substitution of the permanent charge by the methylation quaternization, which extends the systems working pH range (which for pure chitosan is restricted to values below pH 6) to the full range of acidic pH to neutral & basic. The ionically assembled structures for different types of surfactants and differently quaternized chitosan were investigated with different methods e.g. UV spectroscopy, static and dynamic light scattering, and small-angle neutron scattering (SANS). Different tunable assembly structures were revealed in the experiments. The interaction of the material with the biological environment was also evaluated with the antibiotic tests against different sorts of bacterium in our cooperating laboratory at the University of Maryland, US, thereby giving a rather complete picture of the applicability of this system.

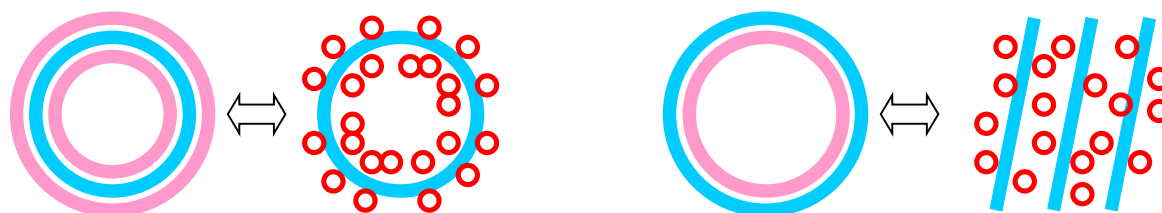


Figure 1. Suggested polyelectrolyte – alkyl ethylene oxide carboxylate complex structure in aqueous solution at different pH and concentration. Modified chitosan is showed in blue, surfactant vesicle bilayers are showed in pink, surfactant micelles is and showed in red. Left: at lower chitosan concentration; right: at higher chitosan concentration.

Acknowledgements: The authors are grateful to the TU Berlin for funding this research and Kao Chemicals for kindly providing the surfactant. B. D. also would like to thank the members of the Stranski-lab.

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Effect of particle size on pattern deposition

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Coffee ring formations in evaporating sessile droplets is a topic of active research. However, ring shaped residue is undesirable in many applications such as inkjet printing, photonic crystals, etc. Thus, there also have been many studies on suppressing the formation of coffee ring resulting in a uniform residue. Various methods used for coffee ring suppression are: (a) changing the particle shape from spheroidal to ellipsoidal [1], (b) adding surfactant to change the flow from capillary to Marangoni [2], (c) heating the droplet thereby transporting the particles from solution to air-water interface instead of edge [3], etc. In the present work, we report the effect of particle size on evaporation induced particle deposition (Fig. 1). We observe that as the particle size is increased from 50 nm to 860 nm, coffee ring effect is fully suppressed leaving behind a uniform precipitate. This is observed irrespective of the substrate roughness, internal flow field, initial droplet volume and initial particle concentration. We observe that higher attraction between larger particles results in early flocculation of particles thus suppressing the coffee ring formation. Hence, we present a methodology to alter the morphology of a dried pattern just by increasing the particle size. We also investigate the evaporation dynamics like temporal variations in contact radius.

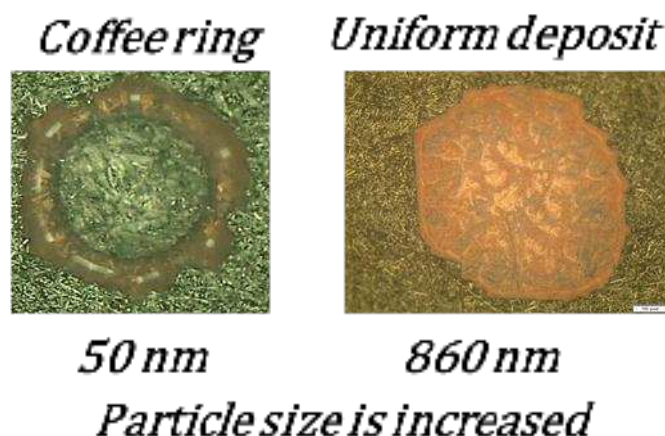


Figure 1. Effect of dispersed particles' size on the morphology of the final dried precipitate.

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Effects of vapor mediated interactions on the evaporation dynamics of confined sessile droplets

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An evaporating sessile droplet undergoes vapor mediated interactions with its surroundings. Vapor-mediated interactions induce alterations in the evaporation dynamics of a confined sessile droplet that depends on the form and extent of confinement droplet is subjected to. In the present work, a DI-water/nanoparticle laden sessile droplet is subjected to two different forms of confinement. In first, it is placed in a rectangular channel (Figure 1 (a)) and in second case it is surrounded by two neighbouring droplets placed in close proximity (Figure 1 (b)). In both cases, the extent of confinement is varied by manipulating the geometric parameters of the droplet system. A detailed study is conducted to ascertain the characteristic difference in the evaporation dynamics of an unconfined sessile droplet and a confined sessile droplet under the aforementioned confinement forms. It is observed that the close region between the droplet-air interface and the surrounding confinement entities incurs reduced mobility of diffusing vapor and hence its accumulation with relatively enhanced vapor concentration. Formation of region of vapor accumulation redistributes the evaporation flux around the confined sessile droplet, which results in alterations in the internal flow dynamics compared to its isolated/unconfined droplet counterpart. For nanoparticle laden droplets, the altered internal flow dynamics affects the nanoparticle transport and agglomeration kinetics, and hence affects the buckling dynamics as: shifting and increased number of buckling location(s), and complete suppression of buckling phenomenon for selective forms of confinement. In addition, the entrapment of diffusing vapor causes prolonged evaporation of confined sessile droplets resulting in increased lifetime compared to its isolated/unconfined droplet counterpart. The evaporation lifetime scaling is theoretically related to the form and extent of confinement (geometric parameters that define the droplet and its confinement entities). The semi-analytical formulation derived agrees well with the experimental data proving the unified theory of droplet lifetime scaling for different forms of confinement.

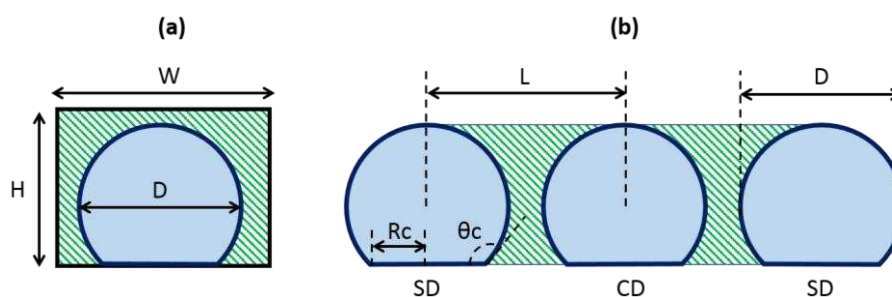


Figure 1. Two different forms of droplet confinement. (a) Sessile droplet is confined by a rectangular channel and, (b) CD (Center droplet) is confined by two closely placed SDs (Side droplets). Patterned green region depicts the region of vapor accumulation.

Insights into evaporation dynamics of an interacting three droplet system

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Studies on the evaporation dynamics of a single isolated sessile droplet resting on hydrophilic/hydrophobic substrates are abundant in literature. However, the most practical applications such as inkjet printing [1], DNA chip preparations [2] etc. utilize a framework comprising of an array of evaporating sessile droplets placed in close proximity of each other. The presence of neighbouring droplets in the close vicinity results in the vapor mediated interactions. In order to understand the evaporation dynamics of such droplet arrays, we have conducted a detailed study on the fundamental unit of such droplet arrays – an interacting three droplet system. In the present work, the characteristic evaporation dynamics of an interacting three droplet system (Figure 1) is distinguished from its isolated single droplet counterpart. The close proximity region between CD (center droplet) and SD (side droplet) is observed to have entrapped the vapor diffusing from the liquid-air interface. As a result there exists relative increase in vapor concentration (greater than the ambient vapor concentration). The redistribution of evaporation flux due to vapor entrapment causes alterations in the evaporation flow dynamics and contact line dynamics. In addition, a significant increase in evaporation lifetime of CD is observed compared to its isolated droplet counterpart. This scaling of evaporation lifetime is attributed to the formation of vapor confinement region which reduces the mobility of diffused vapor. A lumped model considering the two-step diffusion process is presented to semi-analytically predict the scaling of CD evaporation lifetime for a wide range of droplet spacing (L) values. The theoretical formulation shows excellent agreement with the experimental values. Further, the model is validated for an asymmetric placement of CD and a four droplet interacting system proving that the present case can be extended for a n -droplet array ($n \geq 3$).

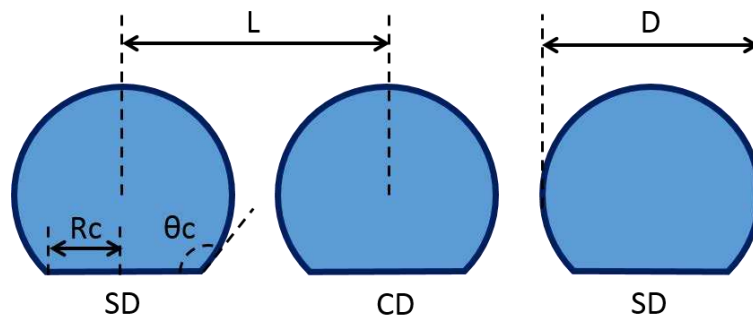


Figure 1. Schematic of an interacting three droplet system placed in close proximity. CD and SD denote the center and side droplets respectively. CD is equidistant (at a separation of L) from both SDs.

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Tailoring particle assemblies using substrate oscillated sessile drops

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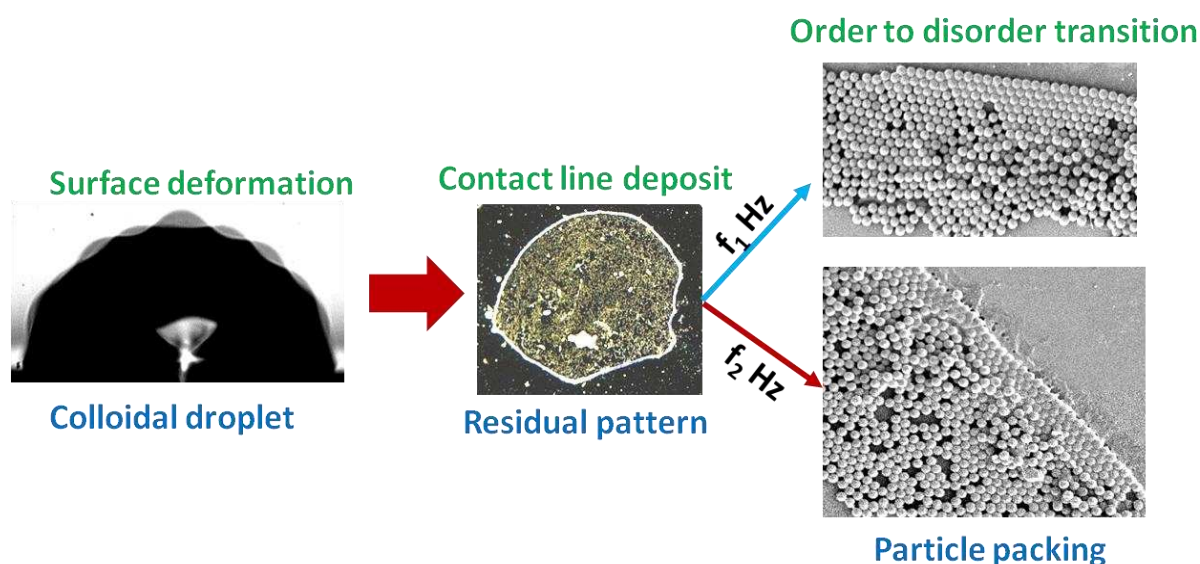
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The humble sessile droplet is imbued with an internal flow field which can assemble structures with distinct macroscopic (coffee-rings vs. uniform pattern) and microscopic (cracks, fingers, particle ordering) features¹. However, active research is needed to further understand and thereby control the exact trajectories of such flow driven assemblies. Oscillatory techniques seem promising. It is well known that a solid substrate with randomly scattered particles when vibrated at its resonance frequency displays Chladni figures. Oscillated droplets have known to display regions of particle accumulation based on ratio of attenuation of surface acoustic waves². Colloidal droplets on wettable substrates are sinusoidally oscillated in the low amplitude-high frequency regime. High-speed shadowgraph combined with a low speed fluorescence imaging provides crucial insight into the dynamics of droplet evaporation under forced oscillations. The resulting surface deformations lead to a decrease in the droplet lifetime (lifetime is inversely related to the frequency of oscillation). Additionally, the fluttering contact line leads to an increasing delay in deposition of the dispersed particles. Delayed deposition leads to an increase in the particle concentration which has a two-fold impact on the resulting precipitate. The lateral width of the final deposit is higher for higher frequency of oscillation. SEM of particles shows different regimes of order-disorder transition based on the frequency of oscillation⁴.



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Self-assembly of biopolymer nanocomplexes of almond gum and whey protein isolate

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Proteins and polysaccharides are natural polymers that are widely used as functional ingredients in food products. There is a particular interest in the use of polysaccharide–protein complexes in order to improve their functional properties. Almond gum (AG) is a novel biopolymer, which exudates from almond gum trees (*Amygdalus communis* L.). It has been attracting attention due to its potential capabilities to improve the stability, texture, and delivery as well as biodegradability, cost-effectiveness and water absorption capacity. Whey protein isolate (WPI) is a value-added ingredient with low thermal stability, which can be improved through electrostatic complexation with an anionic polysaccharide. In this study, soluble fraction of AG and WPI were used to produce soluble colloidal complex particles through electrostatic interaction. Moreover, for the purpose of disclosing the appropriate conditions for nanoparticle preparation, the formation of AG-WPI complexes was studied at different pH conditions. Visual appearance of the complexes of WPI:AG (3:2) at different pH conditions showed no sedimented particles, showing that soluble complexes were generated. Particle size using dynamic light scattering and electrophoretic mobility measurements presented that soluble complexes with a size range of 280 to 450nm and negative charges were formed.

This study has shown that soluble complexes of whey protein isolate and almond gum as a novel hydrocolloid can be successfully formed through electrostatic interaction. The formed nano-complexes can be potentially used as a replacement for synthetic surfactants and Pickering stabilization.



Figure 1. Visual appearance of nanocomplexes (almond gum-WPI = 3:2) at different pH conditions.

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Mixed micelles of cationic surfactants with hydroperoxides as a soft catalytic nanoreactor of free radical generation

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The catalytic action of cationic surfactants (S^+) on hydroperoxides resulted in the generation of radicals and the influence of various factors on this process (transition metal compounds, oxygen, and external magnetic field) are considered. In our previous studies it was established that hydroperoxides (ROOH), the primary amphiphilic products of oxidation of many organic substances, form with surfactants mixed micelles $\{mROOH \dots nS\}$, which has a strong influence on the ROOH decomposition, one of the key reactions in the oxidation process [1,2]. Other polar amphiphilic components such as metal compounds, inhibitors, etc. can concentrate in the interface and affect significantly the rate and mechanism of oxidation. The formation of mixed micelles was studied and confirmed by NMR, dynamic light scattering (DLS), and tensiometry for various surfactants (cationic, anionic, zwitterionic, nonionic) and hydroperoxides. However, the only cationic surfactants were found to catalyze the decomposition of ROOH into free radicals:



In micelles with cationic surfactants, the peroxide bond is located evidently in a strong electrical field of the electrical double layer with strength of $\sim 10^5\text{--}10^7 \text{ V}\cdot\text{m}^{-1}$, weakening this bond and stimulating the homolytic decomposition. The activation energy of the LOOH thermal decomposition is $90\text{--}120 \text{ kJ mol}^{-1}$, whereas in micelles with cationic surfactants the activation energy decreases to $40\text{--}60 \text{ kJ mol}^{-1}$. The cationic surfactants immobilized on a solid support retain the ability to catalyze the decomposition of hydroperoxides, producing radicals, and to initiate radical oxidation and polymerization.

Unpaired electrons of radicals formed are carriers of spin magnetism and can interact with magnetic fields. It is known that magnetic effects can appear only in multispin systems containing at least two spins, *i.e.*, radical pair (RP). Magnetic fields can induce spin triplet-singlet transitions in such pairs and change their spin state and reactivity [3]. The unexpected retardation effects of static magnetic field on the yield of radicals during tert-butyl hydroperoxide decomposition in the reverse mixed micelles with bromides of cetyltrimethyl ammonium (CTAB) and cetylpyridinium (CPB) have been discovered. In the case of $\{mROOH \dots nCTAB\}$, the field dependence of magnetic effect $ME_B = (W_{i0} - W_{iB})/W_{i0}$ was measured in the interval $0 - 150 \text{ mT}$, and high magnetic effect $ME = 60\%$ at 150 mT in the absence of O_2 has been determined. It is noteworthy that in the presence of paramagnetic particles such as oxygen and relatively stable radicals, the decrease of magnetic field effect is observed.

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Controlling the binding of hydrophobic drugs with supramolecular assemblies based on native cyclodextrins and CTAB

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The chemistry of quinoxalines has attracted considerable attention [1], because the quinoxaline moiety is present in a large variety of physiologically active compounds. Various quinoxalines exhibit biological activities including antiviral, in particular, against retroviruses such as HIV [2,3], antibacterial [4], antimicrobial [5], anti-inflammatory [6], antiprotozoal [7], anticancer [8], antituberculosis [9], antimalarial [10], antihelminthic [11], antidiabetic [12], and as kinase inhibitors [13]. Quinoxaline moieties are also present in the structure of various antibiotics such as echinomycin, levomycin, and actinoleutin, which are known to inhibit the growth of gram-positive bacteria and are active against various transplantable tumors [14].

Although the significance of this class of compounds is obvious, they have very low solubility in the aqueous medium. In the present work, the solubility of three 1H-quinoxalin-2-ones with unsubstituted and bromine- and fluorine-substituted oxindol-3-ylmethylidene moieties in aqueous solutions of natural α -, β - and γ -cyclodextrins (CDs) and cationic surfactant CTAB was studied for the first time. The structures of complexes and aggregates formed between macrocycles and unsubstituted 1H-quinoxalin-2-one, which have the greatest affinity for the internal cavity of CDs, were determined. A different solubilization capacity of this heterocycle in aqueous solutions of CDs, CTAB and their mixed solutions was detected. It can be concluded from the study of the spectral properties of heterocycle that its molecule is capable of being released from the hydrophobic nucleus of CTAB micelles with the participation of CD.

Acknowledgements: The financial support of the Russian Science Foundation (grant no. 14-23-00073) is gratefully acknowledged.

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Construction of nanocontainers through the self-assembly of supramolecular amphiphiles based on calix[4]arenes and surfactants

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Supramolecular assembly encompasses molecular self-assembled structures that are governed through non-covalent interactions such as hydrogen bonding, hydrophobic interactions, electrostatic interactions, π - π interactions, etc. [1]. Different calixarene and surfactant derivatives that are able to self-assemble in water and yield three-dimensional aggregates belonging to the class of vesicles or micelles have been reported in the literature during the last decade [2-4]. Calix[4]arenes have been shown to behave as versatile hosts for the complexation of molecular and ionic species with formation of supramolecular amphiphiles (superamphiphiles) [5,6].

Here we describe the complexation behaviour and self-assembly of anionic calix[4]resorcinols with cationic surfactants. The main point of interest of the present study is the possibility of the investigated calixarene-surfactant systems to exploit superamphiphilic nature for self-assembly into nanoscale 3D objects in water. We have shown that superamphiphilic calixarene-surfactant systems self-assemble in aqueous solution to generate micelle- or vesicle-like structures depending on the component ratio. Vesicular samples are uniformly built up via an electrostatic interaction between anionic groups of macrocycles and cationic headgroups of surfactants. When the all macrocycle ionic groups are electrostatically compensated by surfactants, the aggregates based on micelles take place, where molecules of calix[4]resorcinol are adhered on micelle surface playing the role of counterions [7]. The formulation of both micelles and vesicles is confirmed by a complex of physical-chemical methods, including DLS, TEM and solubilization of both hydrophilic and hydrophobic probes. This study is a first step forward towards the construction of self-assembled water-soluble nanocontainers that contain superamphiphilic units. Besides their importance for basic nanoscience, systems of this kind are of interest for biology (models for membrane channels) and medicine (drug delivery).

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Impact of Surfactants on the Dynamics of the Gelation Process of Low Molecular Weight Hydrogellants

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Low molecular weight gellants (LMWGs) with a molecular mass lower than 1000Da are capable of spontaneous thermo-reversible non-covalent self-assembling into a stable three-dimensional network of solid fibres that are able to immobilize the solvent in the meshes [1].

They have an increasing potential in industrial, pharmaceutical, cosmetic and food sections since they include properties and features like the high level of molecular organization which is the reason for the formation of a strong and stable gel network even by using a small amount of the gellant agent [2]. Furthermore, their properties can be tailor-made and they are biocompatible [3]. LMWGs often show an orthogonal self-assembled behavior in presence of surfactants which means that two self-assembled structures coexist within the same system without influencing one another [4].

In this study the kinetic behavior of a low molecular weight hydrogellant is investigated in pure water systems and in mixture with surfactants by rheology under defined shear conditions. The compactness of the gel network is determined by fitting the Dickinson model to experimental data which gives an indication for the gel structure [5]. In addition, the impact of nonionic and ionic surfactants on the gelation behavior of a low molecular weight hydrogellant is investigated for a deeper understanding of the interactions between gellant and surfactant during the aggregation of individual gellant molecules into a gel network. Finally, the sol-gel and gel-sol transition temperature are studied with different cooling and heating rates with surfactants below and above their critical micelle concentration (cmc).

It was found that the transition temperature is not influenced by surfactants which means that the low molecular weight hydrogellant orthogonal self-assembles in presence of surfactant. Moreover, the storage modulus G' at the quasi-equilibrium stage is independent on the presence of surfactants which also confirms the term “orthogonal self-assembly”. Nevertheless, the kinetic behavior of gelation is strongly influenced by surfactants. It could be highlighted that different behavior occurs by the addition of surfactants below and above their cmc. Below the cmc, surfactants promote the formation of a gel network which could possibly be understood as a consequence of the decrease of the interfacial tension and facilitation of the nucleation of individual gellant molecules. Above the cmc, the gel formation is delayed with increasing surfactant concentration which is presumably due to the hindered diffusion by surfactant aggregates. According to that behavior, an apparent decrease of the transition temperature in presence of surfactants is a result of a kinetic effect rather than an equilibrium thermodynamic tissue. It was shown that these findings hold for both, nonionic and ionic surfactants.

To gain insights into the morphology of the gel network in presence of surfactants, light microscopy, cryo-transmission electron microscopy and rheo-optical analysis have been employed as further methods.

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Self-assembly at interfaces: Probing molecular superstructures with computer simulations

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Surface-confined self-assembly of star-shaped functional molecules has been recently recognized as a promising method to fabricate extended superstructures with predefined morphology and physico-chemical functions. In this contribution, using theoretical modeling, we demonstrate how the architecture of 2D molecular assemblies formed at the liquid/solid interface and in ultra high vacuum conditions can be predicted and tuned based on individual properties of elementary building blocks at play. To that end model star-shaped tri- and tetra-topic molecules are used and their self-assembly on a (111) crystal surface is simulated using the lattice Monte Carlo method [1]. Several test cases are studied in which the probe molecules bear terminal arm centers providing interactions with differently encoded directionality. Moreover, the effect of molecular shape anisotropy is explored using building blocks equipped with arms having unequal lengths [2,3].

Our theoretical results show that manipulation of the interaction directions can be an effective way to direct the self-assembly towards extended periodic superstructures such as porous networks as well as to create assemblies characterized by a lower degree of order, including glassy overlayers, molecular ladders, cyclic aggregates and quasi one-dimensional molecular connections. The obtained structures are described and classified with respect to their main geometric parameters and further compared with the available experimental data. Special emphasis is put on new complex molecular patterns predicted with our theoretical approach. The obtained findings can be helpful in 2D crystal engineering and surface-confined polymerization techniques as they give hints on how to functionalize star-shaped organic building blocks which would be able to create superstructures with predefined spatial organization and range of order.

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Polyvinylpyrrolidone assisted self-assembly of cellulose nanocrystals resulted in nanorods with high aspect ratio

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Cellulose nanocrystals (CNC) refer to a type of rod-like cellulose nanomaterial with a typical length of 100-300 nm, a diameter of 10-20 nm, a moderate density, a high degree of crystallinity and a very high tensile strength and modulus [1]. The properties of CNC (anisotropic particle shape, high surface charge acquired upon sulfuric acid hydrolysis, high mechanical strength, the possibility of chemical modification of the surface hydroxyl groups and the formation of a chiral nematic liquid-crystalline phase in aqueous dispersions and films) attract considerable attention for the design of new functional materials [2].

Polyvinylpyrrolidone (PVP) is a water-soluble, non-toxic, non-ionic polymer with C=O, C–N and CH₂ functional groups that is widely used in nanoparticles synthesis [3]. The PVP molecule contains a strongly hydrophilic component (the pyrrolidone moiety) and a considerable hydrophobic alkyl group. PVP can serve as a surface stabilizer, growth modifier, nanoparticle dispersant, preventing the aggregation of nanoparticles via the repulsive forces that arise from its hydrophobic carbon chains that extend into solvents and interact with each other.

For the first time, in this work we have revealed PVP assisted CNC self-assembly which produces highly crystalline and reasonably uniform CNC nanorods with high aspect ratio (length/width). Morphological variations of pristine and PVP added CNC were evaluated by X-ray diffraction analysis and scanning electron microscopy, which revealed that the presence of PVP greatly increased the aspect ratio of the CNC nanorods. The aspect ratio of the CNC nanorods increased with increasing concentrations of PVP from 70 to 95 wt.% due to increasing the lengths up to fourfold while the widths remained constant.

A possible model of the PVP assisted CNC self-assembly is considered.

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Entanglements, Gliding Connections and End-Caps control Viscosity of Concentrated Giant Reverse Micelles

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Liquid-liquid extraction is the central technology in metal recycling. The extraction is always driven by oil-soluble surfactant molecules. TBP (Tributyl phosphate) is one of those widely used extracting surfactants, in short extractants. This molecule allows selective extraction of actinides in the framework of the nuclear fuel cycle as well as lanthanides for the life-cycle of electronic devices.

Emulsification and demulsification processes in extraction devices are only efficient when the difference in viscosity between organic and aqueous phase is small.

Even if the processes using TBP as selective extractant are known since world-war II, economic and technical reasons motivate the research for alternative extractants. One promising approach is the use of *N,N*-dialkylamides which also have good extraction properties and significant advantages over TBP [1]. The main disadvantage of *N,N*-dialkylamides is the viscosity of the organic phase which increases exponentially when processes are intensified by increasing heavy metal and extractant concentration.

By combining scattering and phase analysis, we show that the viscosity increase with heavy metal concentration can be rationalized by the formation of a three-dimensional living network. The mesoscopic structure consists of a one-dimensional ionic liquid of alternating metal-nitrate chains at a well-defined distance embodied in a “bottlebrush” microstructure. The main component of the network are w/o cylinders in equilibrium with endcaps and junction units.

We show a new minimal model at nanoscale that considers the chemical terms at molecular scale [2], the physical terms at meso-scale as well as the flow characteristics at macroscale to describe and explain the evolving structure. The number distribution of each microphase is given by the chemical potential associated with the defects as gliding junction points and end-caps. The resulting structure in two dimensions of the organic phase was obtained with a Monte-Carlo simulation based on the minimization of frustration energy.

The relative viscosity can be derived from works of Cates [3] and Khatory [4] introducing a characteristic effective length. The work finally allows to understand and explain the viscosity of some extracting water-poor microemulsions at elevated extractant and metal concentrations and proposes formulation principles for future extraction systems.

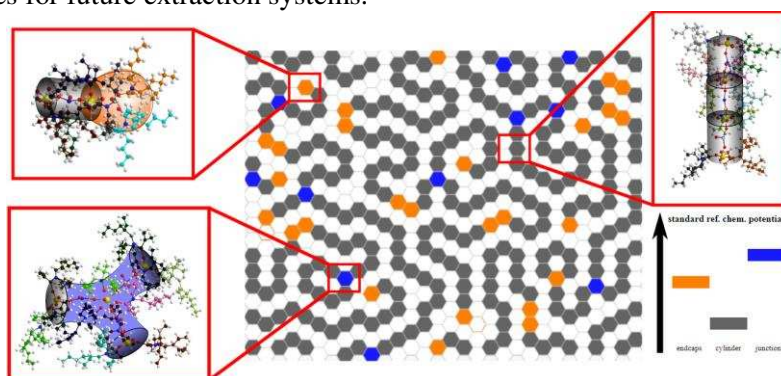


Figure 1. Schematic representation of the result of the mesoscopic model and Monte-Carlo-simulation. Endcaps are presented in orange, cylinders in grey and junction units in blue. The right representation shows a typical bottlebrush structure embodying a 1-dimensional ionic liquid.

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Aggregation Behaviour of New Thiazolium-Based Surface-Active Ionic Liquids and Salts – experimental and DFT study

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Two new thiazolium-based surface active agents – *N*-dodecyl-thiazolium bromide, [NddTz][Br] and *N*-dodecyl-4-methylthiazolium bromide, [4mNddTz][Br] were synthesized and their thermal stability determined by TG and DSC measurements. The self-assembly behaviour of newly synthesized surfactants in aqueous solutions was systematically studied experimentally and applying molecular dynamics. Obtained results of surface tension and electrical conductivity showed that both salts possess a superior surface activity in aqueous solutions compared to imidazolium-based surface active ionic liquid (SAIL) *N*-dodecyl-3-methylimidazolium bromide, [3mNddIm][Br]. Also, thermodynamic parameters of micellization were calculated and compared with results obtained by volumetric measurements. Applying molecular dynamics (MD) simulations it was shown that additional methyl group on the thiazolium ring has an important role in the formation of micelles. Antimicrobial activity of these salts was tested by microdilution method on Gram-positive and Gram-negative bacteria and yeasts. *In vitro* toxicity study has been performed using human fetal lung fibroblasts (MRC-5) and colon adenocarcinoma (HT-29) cell line.

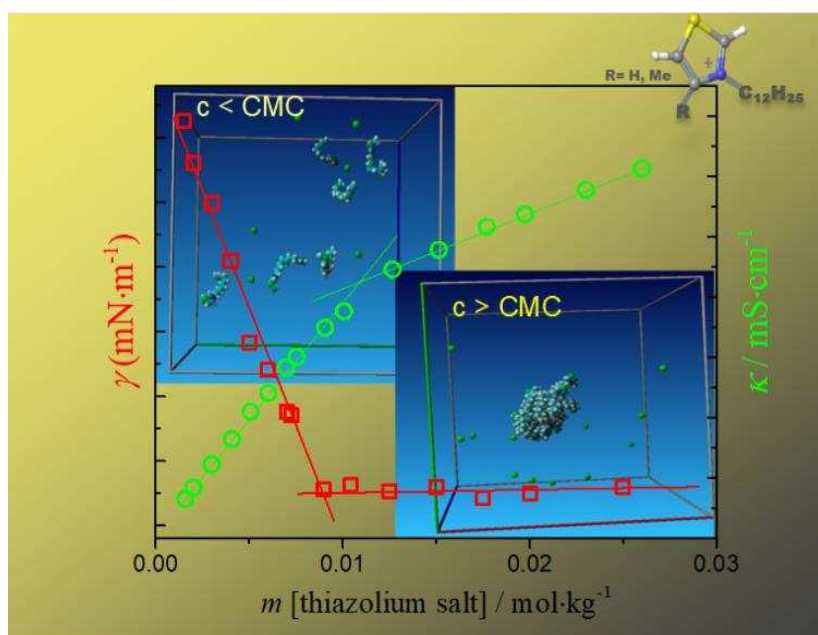


Figure 1. Comparison between surface tension and electrical conductivity measurement.

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Sweet and sour responsive gel nanoparticles

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Synthesis of linear polymers and nanoparticles based on N-vinylcaprolactam are discussed, together with properties of aqueous solutions and dispersions. Poly(N-vinylcaprolactam), PVCL, is a biocompatible thermoresponsive polymer showing LCST behaviour in water [1,2]. Examples of controlled radical polymerisation of the monomer through RAFT/MADIX technique will be discussed [3,4], this including an example of polymerization induced self-assembly, PISA, where nanoparticles build up spontaneously during the polymerisation process.

Sterically stabilised PVCL nanoparticles show ultimate colloidal stability even at elevated temperatures [5]. Recently, however, our focus has been on nanoparticles stabilised with carboxylic acids (the *sour* particles). Because the particles are further functionalised with click reactions we avoid the use of stabilising chains which create a steric barrier for surface chemistry. Gel particles functionalised with gold nanoparticles are of special interest because the thermal collapse of the gel may be induced by light or RF field.

To widen the possibilities of utilising the responsive nanogels we study the colloidal stabilities of their derivatives coated with monomeric or dimeric sugars (the *sweet* particles). The hypothesis is the sugars strengthen the biocompatible character of the particles.

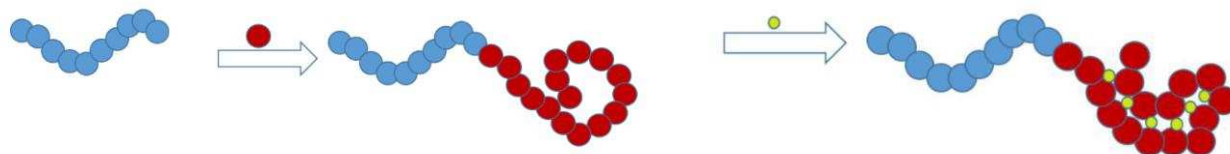


Figure 1. PISA: vinylcaprolactam is polymerised in water using a PEO-CTA, $T > \text{LCST}$. The particles are locked with salicylic acid.

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Exploring the pH sensitivity of poly(allylamine) phosphate supramolecular nanocarriers for intracellular siRNA delivery

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Silencing RNA (siRNA) technologies emerge as a promising therapeutic tool for the treatment of multiple diseases. An ideal nanocarrier (NC) for siRNAs should be stable at physiological pH and release siRNAs in acidic endosomal pH, fulfilling siRNA delivery only inside cells [1]. Here, we show a novel application of polyamine phosphate NCs (PANs) based on their capacity to load negatively charged nucleic acids and their pH stability. PANs are fabricated by complexation of phosphate anions from phosphate buffer solution (PB) with the amine groups of poly(allylamine) hydrochloride, Figure 1A, as carriers for siRNAs [2, 3]. PANs are stable in a narrow pH interval from 7 to 9, and that they disassembly at pHs higher than 9 and lower than 6. This dependence with pH can be used to load PANs by adding water soluble drugs at high or low pH where the polyamines remain as free molecules in solution and then decrease or raise the pH to neutral values to induce NC formation. PANs will trap molecules present in the solution. Alternatively, if the molecule of interest is negatively charged it can form a complex with the polyamines and then by addition of phosphate salts NCs will be formed. We show that the formation of complexes is particularly suitable for encapsulating and delivering siRNAs. NCs with encapsulated siRNAs are stable in cell media without disassembling. Once internalized in cells, following endocytic pathways, the NCs will not be any longer stable and disassembly at the low endosomal pH releasing the siRNA into the cytosol. The efficacy of this approach is shown for the silencing of the Green Fluorescence Protein (GFP) protein in the GFP-A549 cell line. Confocal Laser Scanning Microscopy (CLSM) experiments using Green rhodamine labelled PANs (GR-PANs) and Cy3-labelled siRNA show from co-localization experiments that siRNAs are released from the PANs, Figure 1B. Co-localization experiments with labelled endosomes and either labelled PANs or siRNAs prove the translocation of PANs and siRNAs into the cytosol, Figure 1. As a proof of concept, it is shown that PANs with encapsulated green fluorescence protein (GFP) siRNAs are able to silence GFP in A549 cells expressing this protein, Figure 1C. Silencing efficacy was evaluated by flow cytometry, CLSM and western blot assay. These results open the way for the use of poly(allylamine) phosphate nanocarriers for the intracellular delivery of genetic materials.

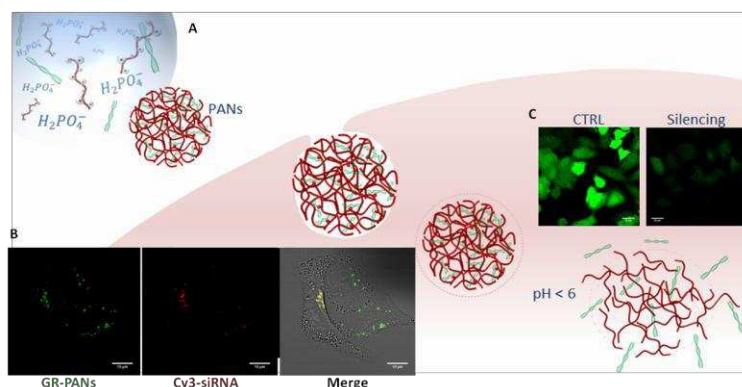


Figure 1. Schematic representation of the co-localization and silencing efficacy of PANs loaded with siRNA.

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Reinforced polymer micro(nano)capsules templated on solid and liquid cores as promising microreactors and drug carriers

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Polymeric microcapsules fabricated by layer-by-layer (LbL) electrostatic self-assembly technique are very attractive material as carriers of different sensitive substances and active agents (e.g. drugs, dyes, enzymes, proteins). As microreactors they are valuable especially for catalytic, enzymatic and photochemical reactions, protecting reagents from environmental influences.

The crucial features of the polyelectrolyte microcapsules, which directly affect delivery of the encapsulated substances, are their mechanical robustness and long-term stability. Strong pressure exerted on the capsules walls during removal of the solid cores or cellular uptake often results in deformation and rupturing of the capsules. Therefore, there is a need to develop robust capsules with sufficiently long shelf-life as well as facile loading/unloading procedure.

We have recently demonstrated a facile route to incorporate Multiwalled Carbon Nanotubes (MWCNTs) in polyelectrolyte microcapsules walls by precipitation method [1]. MWCNTs wrapped with polyanions were co-precipitated with porous CaCO₃ microparticles, which were then used as templates for deposition of polyelectrolyte multilayers. After removal of the cores hollow capsules with MWCNTs crossing and stabilizing the walls were obtained. Very significant improvement of mechanical properties and reduction of overall permeability of the obtained capsules was observed with respect to the unmodified capsules. Importantly, the permeability of the capsules could be increased by irradiation with nearIR light absorbed by MWCNTs enabling facile loading/unloading of the cargo molecules.

Novel micro(nano)capsules with oil liquid cores stabilized with amphiphilic graft copolymers have been also developed [2,3]. The formed capsules were shown to serve as high capacity and long-term stability reservoirs of lipophilic molecules. They were not sensitive to dilution and variation of pH in relatively broad ranges. Such capsules may be further modified by applying LbL coatings for tailoring the release rate of the cargo molecules. Hydrophobically modified natural polyelectrolytes (e.g. hyaluronic acid) were also applied as shells of such capsules implying their biocompatibility and ensuring long term stability (> 15 months) of the aqueous suspension at room temperature [4]. The obtained nanocapsules may find applications not only serve as stable carriers in controlled delivery of drugs, but also as. e.g. (photo)nanoreactors for realization of efficient reaction in confined environments or at the interfaces.

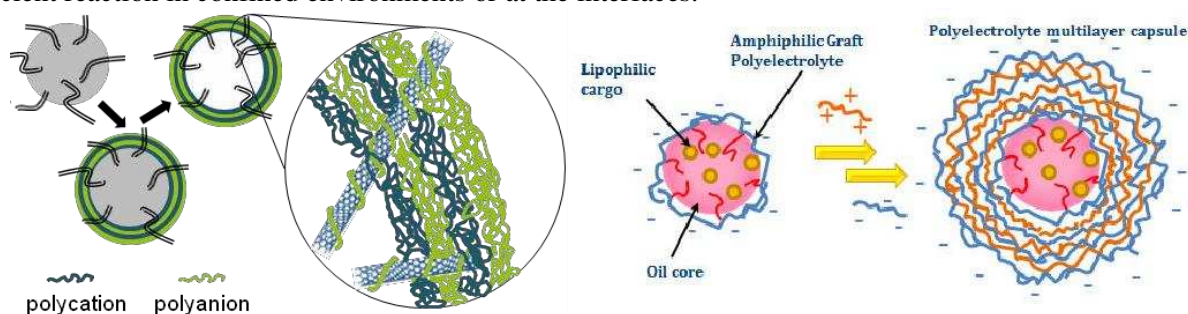


Figure 1. Fabrication of solid core-based microcapsules reinforced with carbon nanotubes (left) and liquid core-based capsules stabilized with amphiphilic polyelectrolyte (right).

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Unexpected rheological behavior of concentrated poly(methacrylic acid) aqueous solutions

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Poly(methacrylic acid) (PMAA) is an interesting polyelectrolyte, the conformation of which may be tuned by pH and/or ionic strength but also by temperature. Concentrated aqueous solutions of poly(methacrylic acid) (PMAA) display a sharp increase of their viscosity over time under shear. This phenomenon known as antithixotropy has been studied as a function of both polymer concentration and ionization degree. Both shear and oscillatory shear experiments are used to characterize the rheological behavior of PMAA solutions, with a peculiar attention to the semi-dilute regime. In the linear regime, non-ionized PMAA solutions tend to behave like associative polymers with a highest exponent for the power law describing the concentration dependence of the viscosity. The rheological behavior of such solutions may be controlled by the balance between intra and intermolecular interactions involving both hydrophobic and hydrogen bonding interactions. Under shear, PMAA solutions display a classical Newtonian behavior in the low shear rate region followed by a sharp increase in the viscosity for higher shear rates when the PMAA concentration is high enough.

This shear induced gel formation is characterized by a critical shear rate that sharply decreases as the PMAA concentration increases. However, the critical shear stress associated to the gel formation is independent of the concentration (figure 1) and only related to the ionization degree. In this presentation, we will present this unusual shear-thickening behavior of a polyelectrolyte and try to understand structures formed during this shear thickening.

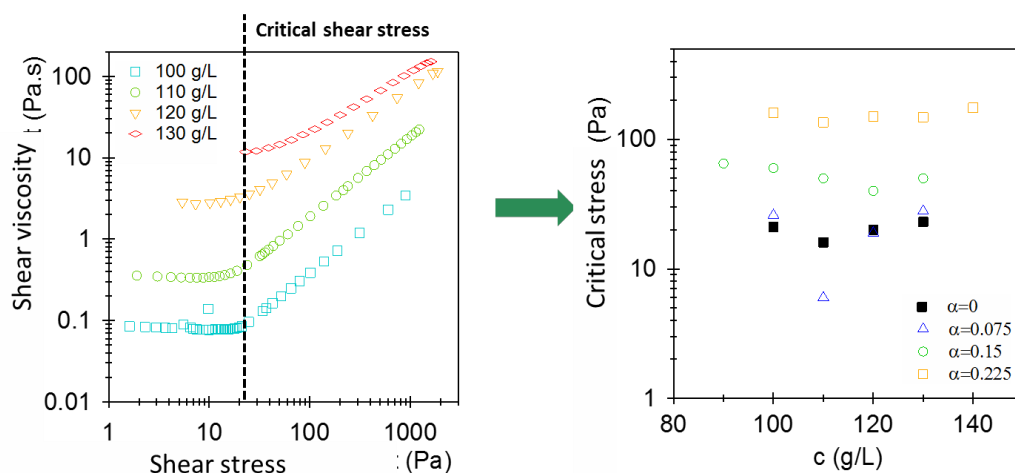


Figure 1. Shear viscosity as a function of PMAA solutions concentration at ionization rate $\alpha=0$. We can note the presence of a critical shear stress beyond which shear viscosity increases sharply (on the left). This critical shear stress depend on ionization rate (on the right).

Smart microgel based surfaces and free standing membranes

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Stimuli-responsive surfaces are in the focus of interest for a multitude of applications such as sensors [1], anti-fouling coatings [2], drug delivery [3] and cell culture substrates [4]. For the latter, coatings made of thermoresponsive Poly-(*N*-isopropylacrylamide) pNIPAm microgels have been found to allow reversible switching of cell adhesion upon heating and cooling [3-5]. In these works the microgel layer had to be prepared on the substrate intended for use. Hence, the dimensions and material properties of the substrate can strongly influence the adsorption of the microgel particles.

The aim of the present contribution is the presentation of the recent results related to the use of microgels as surface coatings and the extension of these works towards preparation of free standing membranes from cross-linkable microgels. The approach is based on the deposition of microgels, containing aromatic moieties, by spin-coating the particles on a sacrificial-polyelectrolyte layer.

During this work a new monomer, *N*-Benzhydrylacrylamide, for copolymerization with NIPAm has been synthesized. In a precipitation reaction copolymer particles from NIPAm and the aromatic comonomer were obtained, with different comonomer concentration ranging from 1 to 30 mo-%. To confirm the incorporation of the aromatic component into the microgel structure the purified particles were analyzed with IR-spectroscopy. The microgels itself were characterized using Photon correlation spectroscopy (PCS) and UV/Vis-turbidity measurements.

Monolayers of the copolymer microgels were spin-coated onto a silicon-wafer covered with a polyelectrolyte. Atomic force microscopy (AFM) was used to study the surface coverage, topography and the thickness of the coatings. The layers are subsequently cross-linked by e-beam irradiation. They are transferred to Si-Nitride chips for the use in electrochemical cells. We are able to show that such membranes exhibit thermoresponsive ion flux.



Figure 1: Left: AFM image of an electron beam cross-linked microgel based membrane. Right: Macroscopic membrane transferred to a silicon nitride chip with funnel hole for conductivity measurements

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Transport and solvation of penetrant molecules in thermoresponsive hydrogels

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The catalysis by metal nanoparticles is one of the fastest growing fields in nanoscience. However, the optimal control of catalytic activity and selectivity in nanoparticle catalysis remains a grand scientific challenge. Here, we present our ongoing endeavors how to theoretically derive design rules for the optimization of nanoparticle catalysis (in the fluid phase) by means of stimuli-responsive carrier systems [1–3]. In the latter, nanoparticles are stabilized in solution by an encapsulating thermosensitive hydrogel shell. The physicochemical properties, in particular the permeability, of this polymeric 'nanogate' react to stimuli in the environment and thus permit the reactant transport and with that the catalytic reaction to be switched and tuned [3].

In order to gain insights into the permeability at the nanoscale, we employ molecular dynamics simulations of a Poly(N-isopropylacrylamide) (PNIPAM) hydrogel with explicit water [4–5]. We focus on the transport and thermodynamic properties of various sub-nanometer-sized molecules ('penetrants'), ranging from non-polar to polar molecules and ions, in the PNIPAM matrix in its swollen as well as in the collapsed state. We find that the water distributes in fractal-like cluster structures embedded in the nanometer-sized voids of the matrix. The nano-clustered water acts as an important player in the diffusion and the solubility of the penetrants. The latter two properties are the key determinant for a total selectivity and permeability of a thermosensitive hydrogel shell.

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Colloidal charge effects on defect-gel stability in lyotropic nematic phases.

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When colloids are dispersed in a liquid crystal (LC), they induce defect lines or disclinations due to competition between the anchoring of molecules at the colloid surface and elastic distortion in the bulk [1]. We present the first experimental study reporting on the viscoelasticity of a colloid in lyotropic nematic media for a wide range of volume fractions, $0.1 < \phi < 50\%$. Furthermore, we explore the effect that colloid charge has on the elastic character of the composite.

The lyotropic nematic calamatic (NC1) phase was made from ternary system of 24.8% sodium dodecyl sulfate surfactant, 4.8% decanol and 70.4% water. The colloidal particles used to probe the LCs were; sterically stabilized polymethylmethacrylate (PMMA) particles, anionic polystyrene-block-poly (N-vinyl-2-pyrrolidone) PS-b-PVP particles and cationic polystyrene (PS) particles. Oscillatory measurements were performed on a strain-controlled ARES rheometer from TA instruments using 40mm cross hatched parallel plate geometry at a gap of 1000 μm .

We show that the viscoelasticity of colloids in lyotropic nematics is analogous to that of colloids in thermotropic nematics, as shown in Figure 1. The storage modulus (G') increases steeply at high volume fractions, $\phi\% \geq 10\%$, reaching values of $G' > 10^3$ Pa because particle networks induce the formation of, and support, disclinations that span the substrates [2]. A defect-stabilized gel can only be created in a lyotropic calamatic nematic if the nematogens, in this case the uniaxial micelles, anchor with normal orientation to the colloid surface, as observed for sterically stabilized particles. Anionic particles present a storage modulus two orders of magnitude lower and we attribute this to charge repulsion between the anionic surfactant and the colloid. Preliminary measurements indicate that the storage modulus recovers for cationic PS since the nematogens anchor to colloid surface leading to gel formation. Postulated director configurations of both positively and negatively charged PS particles are illustrated in Fig 1, b - c.

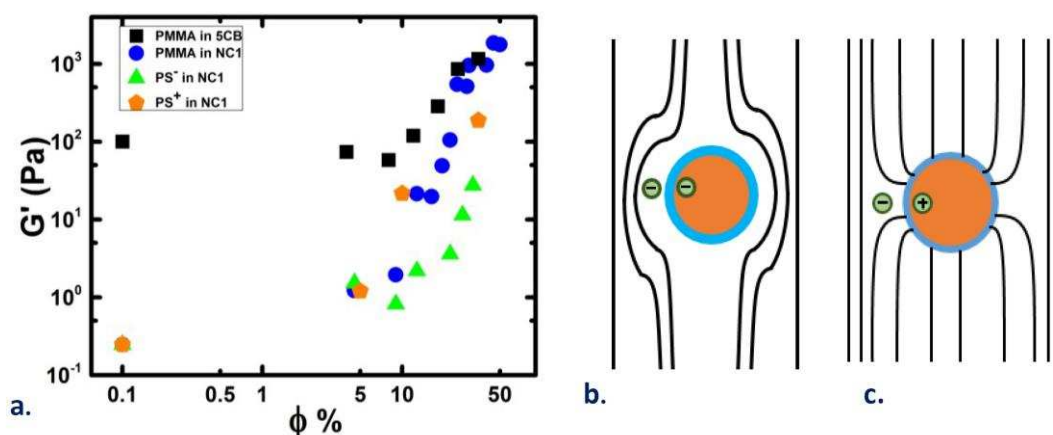


Figure 1. a. Plot of storage modulus (G') as a function of $\phi\%$ of charged and uncharged colloids in lyotropic nematic liquid crystals; black square = PMMA in 5CB, blue circle = PMMA in NC1, green triangle = anionic polystyrene in NC1 and orange pentagon = cationic polystyrene in NC1 LCs, b. Schematic of director configuration of anionic PS in NC1 LCs, c. Director configuration of cationic PS in NC1 LCs.

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Hierarchical Structure of Multicomponent Polysaccharide-Peptide Hydrogels

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Over the past two decades, the potential of polysaccharide hydrogels as a three-dimensional cell microenvironment has been widely explored. To better emulate the functionality of the natural extra cellular matrix (ECM), current efforts in the engineering of synthetic extracellular matrixes has focused on installing molecular features (proteins and bio-interactive polymers) within insoluble scaffolds, either by self-assembly or through covalent modifications of polymer or biopolymer networks.

Combining polysaccharides and peptides for creating hydrogels as a cell microenvironment for tissue engineering is of particular interest, due to the complementary properties of both molecules: Bio-functionality of the peptides on one hand, and similarity to the natural ECM of the polysaccharides on the other.

However, apart from their direct role in cell interaction, peptide sequences may also affect the hierarchical structural organization and mechanical properties of the resulting hydrogel, thus indirectly affecting the cellular response.

Our overall aim is to develop a fundamental understanding of the structure-mechanical properties relations of multicomponent polysaccharide hydrogels used in tissue engineering applications, by conducting systematically exploring the effect of arginine-glycine-aspartic acid (RGD)-containing peptides on the hierarchical structure of polysaccharide-peptide hybrids (solutions and gels). Polysaccharide type, ligand incorporation method (covalently attached or self-assembled) as well as peptide nanostructure and amount are some of the factors we have tested using advanced tools including small angle X-ray scattering, electron microscopy and rheology.

Here, we present a systematic investigation of the effect of three RGD-containing peptides, G₆KRGDY, A₆KRGDY and V₆KRGDY, on the physical properties of alginate-peptide hydrogels. These peptides differ in their self-assembled structure in water: A₆KRGDY forms spherical micelles; V₆KRGDY forms cylindrical micelles while G₆KRGDY did not form specific aggregates.

Rheology measurements showed that the storage modulus of Alginate-A₆KRGDY and Alginate-V₆KRGDY gels is an order of magnitude higher than that of Alginate-G₆KRGDY gels. Small angle X-ray Scattering (SAXS) measurements suggest that the difference in the mechanical properties of the gels is due to the formation of larger peptide junction zones additional to the ones formed by the calcium ions.

These findings show that the peptide's sequence plays a significant role in determining the spatial organization of the polysaccharide and the mechanical properties of the alginate /peptide hybrid hydrogels. Indicating the importance of possible intermolecular interactions between the peptide and the polymer in determining the hydrogel's properties.

Microgel Interaction with Amphiphilic and Peptide Drugs

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Polyelectrolyte microgels have the capacity to store large amounts of amphiphilic drugs, peptides and other types of biotherapeutics in a protective environment. This makes them particularly interesting as delivery systems for drugs that need to be protected against degradation and as components of slow-release and depot drug formulations. Drugs of opposite charge to the network can be loaded into the microgels at low ionic strength and released at high ionic strength. This principle has been used almost paradigmatically to develop drug release systems. However, surprisingly little attention has been paid to the importance of the self-assembling properties of drugs and the interplay between electrostatic and hydrophobic interactions in this respect. Recently, we pointed out [1] that the release of amphiphilic drugs to solutions of physiological salt concentration are not fully captured by a simple ion exchange process, as has been proposed in the literature.

In the first part of the paper we investigate the binding and release of several cationic amphiphilic drugs to microgels (DC bead[®], diameter $\sim 200\ \mu\text{m}$), used clinically in the treatment of liver cancer, by means of micropipette-assisted microscopy of single microgels (Fig. 1) and μDiss apparatus release studies. The data are interpreted by means of a theoretical transport model based on the Nernst-Planck equation, taking into account local equilibrium between aggregated and free drug molecules. The results highlight the importance both of the electric coupling of diffusive fluxes and the amphiphilic self-assembly.

In the second part we investigate the distribution of cationic peptide chains in a suspension of colloidal poly(acrylamide-*co*-methacrylate) microgels (diameter $\sim 0.2\ \mu\text{m}$) by means of Nano Particle Analysis (Nanosight). For intermediate peptide loadings, the systems display multi modal microgel size distributions, believed to reflect a non-uniform distribution of the peptide among the microgels and aggregation of microgels. The result is interpreted by means of statistical thermodynamic model calculations (Fig. 1) using a recently developed model [2-5] suggesting that the non-uniform distribution is driven by electrostatic free energy.

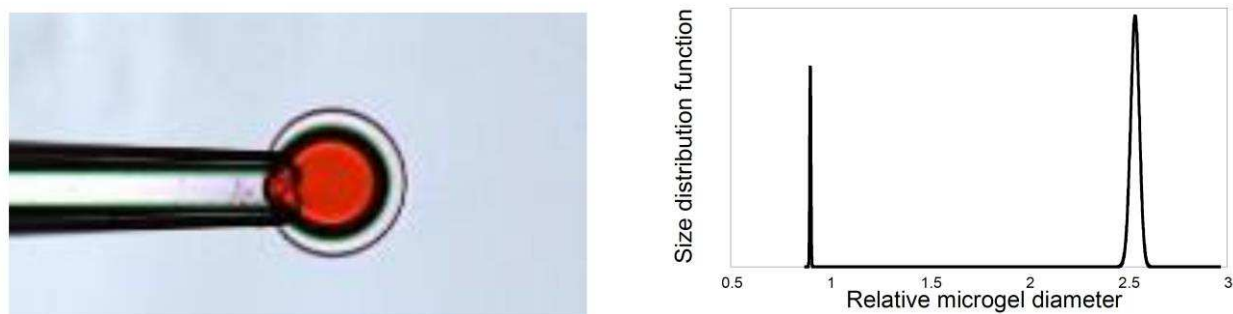


Figure 1. Microscopy image of doxorubicin-loaded microgel during release (left), and theoretically calculated bimodal distribution of peptide in a suspension of colloidal microgels (right).

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Chiral fluctuations & the origin of chirality in cholesteric phases of DNA origamis

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Lyotropic cholesteric phases are commonly observed in many bio-colloidal and polymer solutions, characterised by a complex interplay between thermal fluctuations, entropic and molecular forces. The difficulty of achieving accurate microscopic descriptions of these many competing factors has led to the introduction of strongly coarse-grained theoretical models, whose microscopic underpinnings are highly non-trivial. Furthermore, the wide lengthscale discrepancy between typical particle sizes and experimental pitches has largely thwarted direct numerical investigations of cholesteric self-assembly for all but the simplest model systems [1,2].

We here present an extensive numerical framework based on density functional theory [1] to investigate the cholesteric behaviour of arbitrary particles in the weak chirality limit. This approach, built upon the use of highly-efficient Monte-Carlo methods for the computation of virial-type integrals, enables us to tackle a vast range of complex mesogen models and interaction potentials [2]. We illustrate its application to experimentally-relevant systems of DNA origamis [3] as described by a well-documented molecular model coarse-grained at the nucleotide level [4] (Fig. 1), and investigate the respective influence of excluded volume, electrostatics and particle flexibility on phase behaviour and cholesteric pitch. It is shown that intra-molecular mechanics play a crucial role in the supra-molecular organisation of such systems, and need to be accurately taken into account in theoretical investigations of the cholesteric assembly of semi-flexible polymers.

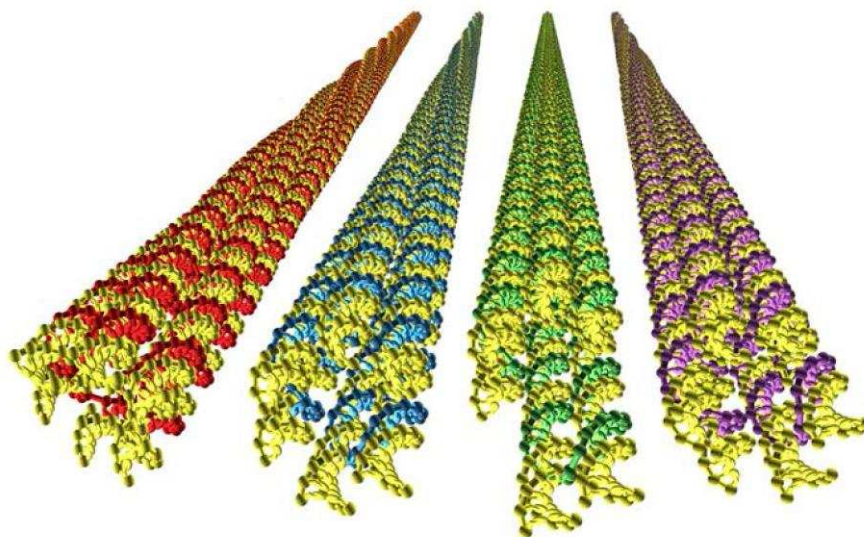


Figure 1. Fully-extended conformations of 15k base-pair DNA origamis [3] as represented by the oxDNA model [4].

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An aqueous copper(II) luminescent sensor based on Tb(III)-containing coordinated gel composites

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Cu(II) plays a key role in a variety of chemical, biochemical and environmental processes. Copper is an essential trace metal in human nutrition; however, as it general happens, an excess of copper in human diet can be dangerous to health [1, 2]. Thus, methods for the quantitative detection and quantification of Cu^{2+} ions, in aqueous solutions, have gained considerable attention in recent years. In particular, fluorescent sensors have been developed because of their simplicity (e.g., samples do not require pre-treatments) [3, 4].

This communications reports the synthesis of a new coordinated gel composite composed by terbium(III) chloride and poly(sodium acrylate) (PSA). The Tb(III)/PSA gel composite shows excellent luminescent emission and visible luminescent colors; consequently, it arises as a good candidate for acting as a luminescent sensing material. To investigate the ability of these gels to detect different cations, a series of mono-, di- and trivalent cations have been tested (Figure 1). It can be seen that the emission intensity of luminescence (at 545 nm) of the gel composite changes by changing the metal ion. In general, in the presence of different metals, the color of the fluorescent gel composite changes from green to light green. However, in the presence of Cu(II) a significant luminescence quenching is observed: this observation suggests that the Tb/PSA gel composite can be developed for detection of Cu^{2+} ions. The selectivity of Tb(III)/PSA gels towards different anions was also checked; from all anions studied, nitrite ions have shown the strongest luminescence quenching. Additionally, it can be concluded that results with different cations are not affected by nitrite as counter ion. The interference of other competing metal ions toward Cu(II), in aqueous solution, was further ascertained by using solutions containing more than one metal ion. The interaction between Cu(II) and the gels does not seem to be affected by any competing mechanism. Indeed, we have good evidences that Tb(III)/PSA gel can be used to detect, in a selective and precise way, the presence of copper ions, even in the presence of the other metal ions and therefore, is a promising material to act as Cu(II) sensor. The possible mechanism of luminescence quenching is discussed and further complemented with the analysis of SEM, UV-Vis and EDX mapping data.

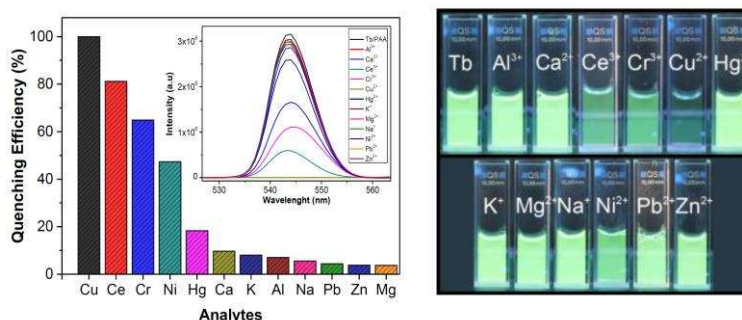


Figure 1. (a) Comparison of the quenching efficiency (545 nm) with different metal ions in aqueous solution (inset: emission spectra of Tb(III)/PSA) and (b) fluorescence photographs changes of Tb/PAA (green) in the presence of 3.33 mM of metal ions under UV light (365 nm) in aqueous solution.

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Polyelectrolyte-surfactant complexes and their use in drug delivery: Study of cetylpyridinium-alginate complex nanoparticles

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Complex polyelectrolyte nanoparticles have attracted a lot of attention recently in pharmaceutical research due to the simplicity of formation and formulation, good biocompatibility and relatively high drug encapsulation yield [1]. Interactions between polyelectrolytes and oppositely charged surfactants have also been frequently investigated [2]. However, their use in drug delivery with implications in development of innovative carriers for different types of drugs is rarely studied. Here we have investigated the mechanism and thermodynamics of polyelectrolyte complexation with surfactants, the possibility of nanoparticle (NP) formation and the use of these NPs as drug delivery platform for poorly soluble drugs.

Alginate, a bioadhesive and biodegradable polyelectrolyte was used as the model polyanion, and cetylpyridinium chloride (CPC) as the crosslinking agent for NP formation. CPC is a cationic quaternary ammonium compound and is also an effective antibacterial agent that is already used in oral rinses [3]. Due to its amphiphilic structure, CPC molecules are associated into micelle-like aggregates, which are threaded on an alginate polymer chain like pearls on a string, which we proved by potentiometric measurements using a cetylpyridinium cation (CP⁺) selective membrane electrode. The cooperative nature of the interaction between CP⁺ and alginate and the formation of the polymer-surfactant complex was confirmed by the sigmoidal shape of the binding isotherms. In the CP⁺/alginate molar ratio range from 0.2 to 0.8 in the dilute regime the size of these polymer-surfactant complexes was in the nanoscale range. In this way we were able to obtain polymeric NPs, as shown by both the dynamic light scattering and atomic force microscopy. CPC, as a drug, was in this way ionically entrapped in the alginate chains and its release sustained over 7 days [4].

Furthermore, the underlying thermodynamics and molecular interactions in the polyelectrolyte complexation process were investigated and compared for different types of crosslinkers. With the use of isothermal titration calorimetry and infrared spectroscopy we were able to show that the main forces involved in complexation process are the ionic interactions accompanied by hydrogen bonding and the hydrophobic effect. However, the complexation itself is not an enthalpy driven process. There is a significant entropic contribution due to counterion release and desolvation. Altogether, polyelectrolyte complexation is a mild procedure which can be further utilized for drug incorporation [5].

In addition to CPC inherent antimicrobial and crosslinking properties, we wanted to exploit its solubilisation capacity to increase the solubility of poorly soluble lipophilic model drugs (i.e. duloxetine and ibuprofen). These drugs were chosen due to their similar inherent lipophilic properties but different basic (duloxetine) or acidic (ibuprofen) properties that can affect their solubilisation. Firstly, the solubility of both drugs and the solubilisation capacity of CPC were determined. Then the optimal ratio between the drug, CPC and alginate was determined in order to form ternary complexes preferably with a size in the nanometer range. The main goal of these CPC-alginate complexes with incorporated poorly soluble drugs would be to increase the drugs solubility as well as to modify their release and protect them from the harmful gastrointestinal environment. In this way the unexploited potential of the polyelectrolyte-surfactant complexes in drug delivery could be used.

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Novel approach to study the intracellular fate of siRNA/polyamine complexes by Fluorescence Cross Correlation Spectroscopy (FCCS)

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Silencing RNA (siRNA) therapies are a promising technology for the treatment of a large number of diseases [1]. The concept behind this technology is the inhibition of the expression of target genes. One of the principal obstacles for the success of siRNA therapies is that the siRNAs must be protected from the degradation in bloodstream and the release of the siRNAs must take place in cytosol. Excellent agents for siRNA delivery are cationic lipids and polycations, i.e. polyelectrolytes bearing multiple positive charges [2]. In both cases the negatively charged siRNAs associate with the positive charges of the lipids or polycations, forming complexes through electrostatic interactions.

This study addresses the stability issues and intracellular translocation of polyamine/siRNA complexes based on poly(allyl amine hydrochloride) (PAH) intracellularly applying Fluorescence Cross Correlation Spectroscopy (FCCS)[3], a variation of the Fluorescence Correlation Technique (FCS) and Confocal Scanning Laser Microscopy (CSLM).

Complexes based on green rhodamine labelled PAH (GR-PAH) and cy5/7-siRNA (R-siRNA) were formed in solution and studied in different media. Then, experiments were performed inside the cells following cellular uptake of the complexes.

From our experiments it is possible to describe the fate of the siRNA complexes intracellularly and to determine the timeframe for the dissociation of the complexes inside the cells.

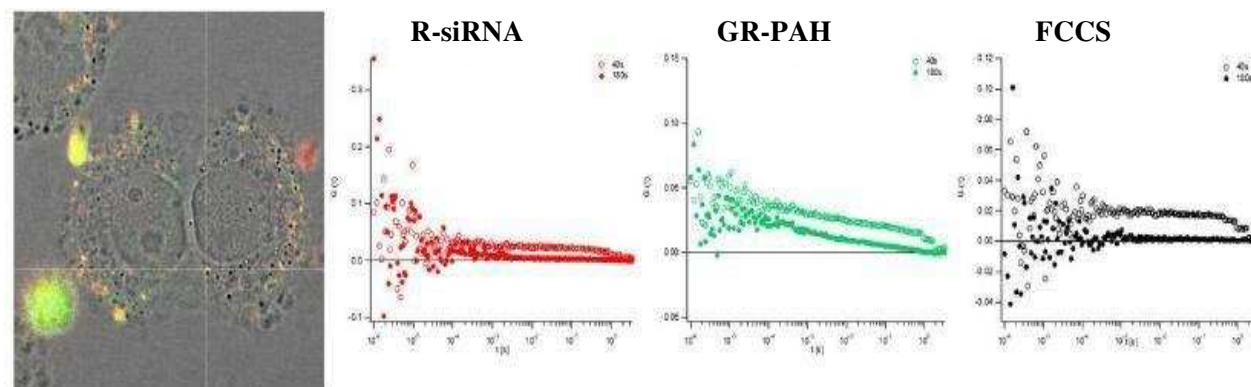


Figure 1. Confocal micrograph and FCCS curves collected after 30 min incubation.

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In-situ measurements of light-induced phase transitions of AuNP- microgel hybrids by an extended DLS setup

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The stimulus sensitivity of poly(N-isopropylacrylamide) (PNIPAM) microgels is well known and studied. PNIPAM microgels respond to stimuli like temperature, solvent, pH, light or magnetic fields depending on the incorporated comonomers or nanoparticles [1-3]. To trigger size changes of the microgel particles by light, gold nanoparticles (AuNPs) are embedded into the microgel network. The irradiation of the AuNPs leads to a conversion of the light energy to heat emission into the PNIPAM network and causes a size reduction in the thermoresponsive PNIPAM microgel particles.

The photothermal effect was studied using an extended dynamic light scattering (DLS) setup [4], where the size determination of the hybrid particles and the irradiation of the AuNPs happened simultaneously. The AuNPs in the microgel network were irradiated at the surface plasmon resonance (SPR) wavelength range by the added Sapphire laser (532 nm). The size of the microgel particles was determined by HeNe laser irradiation (633 nm). In the two-laser setup the AuNP- microgel hybrid particles were investigated at various temperatures, scattering angles, and excitation laser intensities.

Not only the amount of incorporated AuNP influences the response to light trigger but also the distribution of AuNP within the network. The distribution is affected by the architecture of the microgel network. Due to the batch synthesis and the higher conversion rate of the cross-linker molecules compared to NIPAM, the PNIPAM microgel particles exhibit a radial variation in mesh size with a highly cross-linked core and a fuzzy shell. The AuNP are incorporated only in regions where the mesh size is large enough for the AuNP to permeate through the network which is the fuzzy shell. This is indicated by results from DLS measurements and from TEM images [4].

The feeding of monomer and cross-linker into the reaction mixture during the synthesis leads to microgel particles with a homogeneous cross-link density distribution [5]. Incorporating AuNP in those microgel particles results in hybrid particles which exhibit a volume phase transition not only induced by temperature but also by light. In these hybrid particles the degree of deswelling upon irradiation is more pronounced compared to the hybrid particles prepared from heterogeneously cross-linked microgels. Additionally, less incorporated AuNP are necessary to observe a full volume phase transition upon irradiation.

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Segmental dynamics of planar polymer brushes

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The physical properties of stimuli-responsive polymer brushes still receive vast interest in basic research. Polymer brushes undergoing a temperature induced phase transition are of major interest for technical applications such as (bio-)functional coatings. Polymer brushes are polymers end-tethered to a solid surface. A variation of the chemical composition, brush height or grafting density allows for a wide range of different polymer coatings with distinct properties.

Among them, thermoresponsive polymer brushes based on PNIPAM serve as a prominent model system, while P(MEO₂MA-*co*-OEGMA) copolymer brushes are, due to their biocompatibility, promising candidates for smart biocoatings. In particular, P(MEO₂MA-*co*-OEGMA) copolymer brushes have a tunable phase transition temperature in the physiological range. Moreover, their biocompatibility makes these brushes well-suited candidates for bio-functional coatings. Due to the novelty of these macromolecules a limited number of studies on their physical properties exists [1,2].

Beside knowledge of the structural properties also the investigation of the brush dynamics is important for understanding the fundamental properties of polymer brushes. Here, we focus on recent grazing incidence neutron spin echo spectroscopy (GINSE) experiments probing the dynamics inside polymer brush layers. GINSE is a newly developed method to gain insight into the brush dynamics in proximity to planar surfaces on the nanometer length and nanosecond time scale [3,4].

At different penetration depths of the evanescent neutrons into the brush we explored the segmental dynamics well below the LCST. Exploration at different neutron penetration depths enables a better understanding of the segmental dynamics along the vertical brush profile. For the investigated p(MEO₂MA-*co*-OEGMA) and PNIPAM brushes we found that with increasing distance from the surface the available space for the individual chains increases. This agrees with theoretical considerations regarding the non-uniform blob size model. Within the framework of the Zimm model for polymer dynamics, this leads to an increase of the effective solvent viscosity at increasing distance from the surface.

The results proof the suitability of GINSE experiments for the investigation of the dynamics in thin polymer coatings which broadens the general understanding of polymer-substrate-interactions. This will be vital for the development of new bio-materials and the understanding of the physicochemical properties of polymer brushes.

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Preparation of doubly crosslinked microgel photonic crystals from novel core/shell microgel particles

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The preparation of novel hierarchically structured „smart” gels is a challenging area of modern material science. Contrary to the traditional approach, when macrogels are prepared by the copolymerization of monomers, in the recent years a new approach has been established to prepare covalently crosslinked gels by the crosslinking of microgel particles (doubly crosslinked microgels) either by the free-radical crosslinking of glycidyl methacrylate (GMA) functionalized microgels [1-2] or by coupling poly(*N*-isopropylacrylamide-*co*-acrylic acid) copolymer microgels with epichlorohydrin [3].

Here we report a novel approach for the preparation doubly crosslinked microgels using unique core/shell microgel beads with poly(*N*-isopropylacrylamide) (pNIPAm) core and poly(vinyl alcohol) (PVA) shell as the building blocks. These unique core/shell microgels represent a new family of sterically stabilized gel beads, which have a hydrophilic shell that allow their simple functionalization under mild conditions. To prepare the core/shell microgels we used a single-pot polymerization method developed recently in our laboratory. This method allows the formation of polymer shells with unrestricted composition on a pNIPAm-based core. As a first step we prepared core/shell microgels with a pNIPAm core and a poly(vinyl acetate) shell. We got the final pVA shell by the hydrolysis of the pVAc. Dynamic light scattering measurements proved the formation the core-shell structure and the expected steric stabilization provided by the pVA shell.

We used the prepared core/shell microgel particles as building-blocks to produce 3D gel structures by crosslinking the pVA shells of the microgel particles with glutaraldehyde. When the microgel beads were allowed to form a colloid crystal before the crosslinking reaction the crosslinking resulted in the formation permanent colloid crystals that showed intense iridescent colors. The crosslinked gels preserved their temperature responsiveness and the macroscopic samples (d~cm) produced a volume phase transition on a few a minutes time-scale.

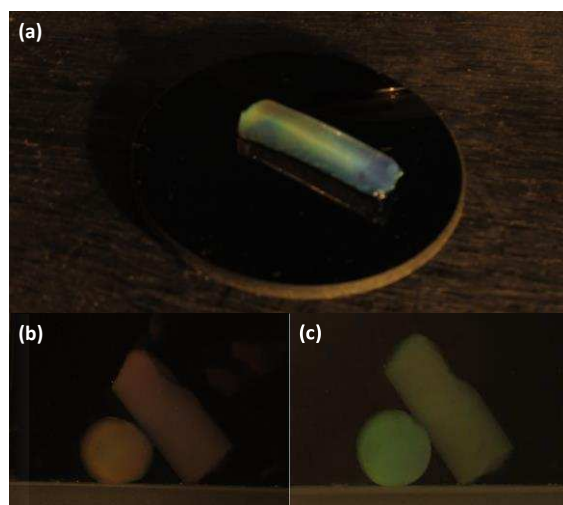


Figure 1. Doubly crosslinked pNIPAm-shell-PVA microgel photonic crystals.

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Computational Investigation of Microgels: Effect of the Microstructure on the Deswelling Behaviour

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Microgels are unique soft-matter systems due to their tunability in terms of architecture, softness, permeability and deformability. Their conformational changes in solution can be achieved by changing, e.g., temperature and pH. The importance of these molecules relies on their huge amount of potential applications such as drug delivery, photonic crystals or purification technologies, just to name a few.

Unlike the case of regular network frameworks, usually assumed in simulation studies of microgels, we modeled and simulated a realistic and efficient synthesis route, mimicking cross-linking of functionalized chains inside a cavity. This model is inspired, e.g., by experimental microfluidic fabrication of microgels from macromolecular precursors [1], and is different from polymerization routes [2]. The assembly of the chains is mediated by a low fraction of interchain crosslinks.

In order to deeply understand the microgel structure and eventually improve the synthesis protocol we characterize in detail the equilibrium structure and deswelling kinetics, and compare results with those found for microgels obtained via underlying regular structures. The specific microstructure of the microgel has no significant effect on the locus of the deswelling transition, but strongly affects its kinetics. The coarsening process during the deswelling and collapse of the microgel is apparently given by two universal time scaling laws: stretched exponential for the regular networks and power-law for the disordered ones.

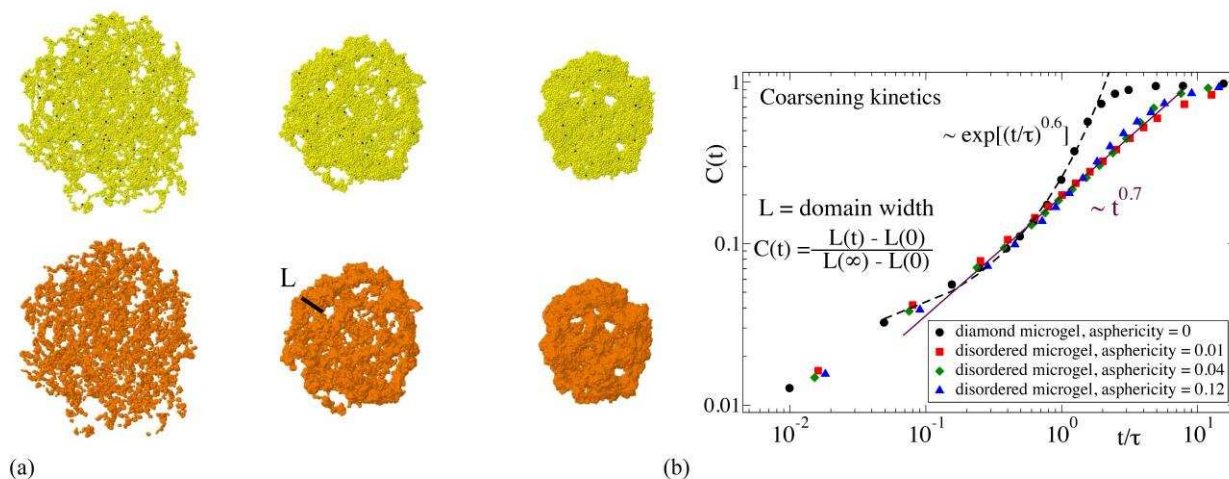


Figure 1. (a) Collapse and coarsening of the microgel in real coordinates (top) and density field representation (bottom). (b): Scaling behaviour of the domain growth during the collapse, for a diamond-like microgel and for disordered microgels of different microstructures.

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The unstable flow of concentrated solutions of very high MW polymers at low Reynolds number - and some important consequences.

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This talk focuses on unstable flow in confined environments exhibited by solutions of very high MW viscoelastic polymers: predicting the onset of the flow instability; demonstrating an unexpected dependence of the onset on polymer concentration; and showing that the behaviour is of potentially enormous industrial consequence.

Polymer solutions are often used to enhance crude oil recovery to increase viscosity thereby preventing viscous fingering. “Flooding” an oil reservoir with a polymer solution exhibiting elastic properties has been reported to result in a sustained doubling of the recovery enhancement compared to that with conventional viscous polymer flooding [1]. Flooding with viscoelastic polymer solutions is claimed also to increase recovery more than expected on the basis of conventional understanding of based on capillary number alone [2]. However, within the oil industry there are doubts that a genuine effect is observed, or that potential improvements could be realized in real-world conditions [3].

In this talk, I will demonstrate that flooding with viscoelastic polymer solutions can indeed increase recovery more than expected from changes in capillary number. That the improvement in recovery arises from fluctuations in flow at low Reynolds Number. This fluctuating flow, known as elastic turbulence [4], is an effect previously unrecognised in oil recovery. I will demonstrate that the effect may be obtained at field-relevant flow rates and provides an underlying mechanism explaining both the extra recovery enhancement and the observation of apparent flow thickening for these viscoelastic solutions in porous media [5].

Flow in micromodels, rheometers, and even inside rock cores will be described with both viscous and viscoelastic polymer solutions. The circumstances under which viscoelasticity is beneficial will be demonstrated. The findings are applicable to the design of formulations for enhanced oil recovery by polymer flooding. The data lead to a mechanism that may be used to explain the observations of improved displacement efficiency and why the improvement is not seen for all viscoelastic polymer floods.

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Effects of different starches and hydrocolloids on model dough properties and quality of gluten-free bread

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Native starches do not generally have ideal properties for the preparation of food products. That is why blending of starch with hydrocolloid is crucial in modifying rheological and thermal properties of the system. Hydrocolloids interact with starch and modify viscosity, texture and sensory properties. Many studies have been done with a goal of understanding how and why the addition of hydrocolloid influences the properties of starch-based product [1-4].

To better understand the physicochemical changes imparted by hydrocolloids on gluten-free dough we prepared 15 model dough samples with different starch/hydrocolloids ratios. Corn and potato starch were mixed together in water with hydroxypropyl methylcellulose (HPMC) and xanthan. Properties of prepared starch/hydrocolloids systems were determined by differential scanning calorimetry (DSC) and rheometry. Samples with different corn/potato starch ratio exhibit different thermal but almost identical rheological properties. On the other hand, xanthan and HPMC have strong influence on rheological properties of the mixtures since they increase thickness and viscosity.

The formulations investigated by thermal and rheological methods were used to prepare doughs and bake loaves of bread. Hyperspectral imaging and sensory evaluation were used to analyze baked loaves. Hyperspectral imaging allowed us to obtain spectrum for each pixel in the images of bread slices and perform PCA analysis of spectral data. Our goal was to determine whether a correlation exists between data obtained from thermal and rheological analysis of model dough samples, data obtained from spectral analysis of baked loaves and sensory analysis data. Understanding such correlations could allow us to develop better-textured and more appetizing bread without unnecessary ingredients.

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The Critical Fluctuation of Poly(*N*-isopropylacrylamide): Hydration Behaviour and Additional Microscopic Order Parameter

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It has been generally accepted that a coil-to-globule transition of a thermo-responsive polymer in aqueous media is driven by enhanced hydrophobic interaction between its hydrophobic side chains at an elevated temperature. Poly(*N*-isopropylacrylamide) (pNIPAm) has been extensively studied as an ideal model for water-soluble thermo-responsive polymers undergoing a coil-to-globule transition at about 32–34 °C [1, 2]. A couple of more detailed mechanisms of the phase transition of the thermo-responsive polymers have been suggested so far, such as solvent fluctuation-induced dewetting [3], cooperative-hydration [4], and energetic state of aqueous medium [5]. Despite these prevailing ideas, there is still much unsettled dispute over the counter-intuitive phase behavior of aqueous pNIPAm. A recent Raman-MCR study revealed that significant changes in the OH-band frequency range occur only above the cloud-point temperature, where the pNIPAm chains collapse [6]. In appearance, this unexpected observation is not fully consistent with the solvent-fluctuation induced transition mechanism.

Our small- and wide-angle X-ray scattering (SWAXS) and dielectric relaxation spectroscopy (DRS) study on aqueous semi-dilute pNIPAm, covering a wider range of the length and time scales (0.07–28 nm⁻¹ and 0.2–89 GHz) has solved several unsettled issues. The results have elucidated (1) close-coupling of critical fluctuations and dehydration of the polymer chains, (2) deuterium isotope effects on the critical fluctuations, (3) microscopic agglomeration formation even in the one-phase (random-coil) region, and (4) a high-density state of the micro-globules above the spinodal temperature T_s . The real-space analysis of the scattering intensities using a Fourier inversion technique (**Figure 1**) leads to successful identification of the local number density of these micro-globules to be an additional microscopic order parameter monitoring the coil-to-globule transition of pNIPAm.

We will also talk about subsequent investigation into the critical fluctuations of pNIPAm in water/methanol mixed solvent at methanol molar fractions $X_m = 0.05, 0.10, 0.15, 0.20, 0.45, 0.80$, and 1, focusing on the so-called cononsolvency. We have found that the singular concentration for mixing schemes in methanol/water mixtures as revealed by previous DRS study seems to be strongly linked with the phase boundary of pNIPAm in methanol/water mixtures. We observe critical fluctuations depending on T as well as X_m , the correlation length exhibiting diverging behaviour when either a spinodal temperature or a critical composition is approached. Addition of methanol to water reduces hydrophobic hydration and enhances hydrophobic interaction between the sidechain groups of pNIPAm.

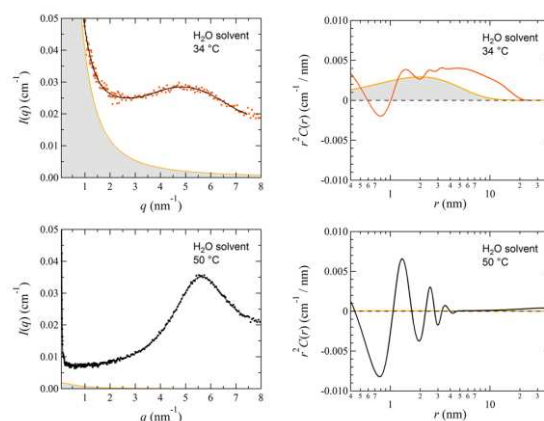


Figure 1. SAXS intensities (left) and the resulting density autocorrelation functions (ACFs), $r^2C(r)$ (right) of aqueous pNIPAm below and above T_s . The Ornstein-Zernike contribution is indicated by the shaded areas.

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Polyelectrolyte Surfactant Complexes (PESCs) of Hyaluronan and Cationic Surfactant – Structural Progression and Rheological Behaviour

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Hyaluronan (HA) is a very important biopolymer that is essential in giving elastic and viscous properties to biological tissue and also relevant in tumor progression. It is a glycosaminoglycan that under neutral conditions is a polyanion and its Mw can range from a few thousand to several million g/mol. In our experiments we investigated mixtures of hyaluronan with cationic surfactant such as simple tetradecyltrimethylammonium bromide (TTAB) but also other cationic surfactants. In our studies we determined first the phase behaviour with a focus on physiological conditions but also compared to the behaviour at other ionic strength and pH, where it can be noticed that for lower ionic strengths the tendency for precipitation is largely enhanced.

In a larger range of the composition space single phases are observed where PESCs are formed, which were characterized in detail by means of static and dynamic light scattering (SLS, DLS), and for further structural details by means of small-angle neutron scattering (SANS). These experiments show a marked aggregation behaviour already for the addition of as little as 0.5 mM TTAB and the formation of relatively large aggregates of ~ 80-120 nm size. However, further TTAB addition does not lead to more of these aggregates or their growth but instead one observes the formation of small, elongated complexes. SANS combined with cryo-TEM (Figs. 1 and 2) give a consistent picture of these large aggregates which are very open and consist to 98-99% of water, as well as of the cylindrical aggregates. Interestingly the surfactant addition has almost no effect on the rheological properties and one has even no significant effect for a large surfactant excess [1].

Our investigation was extended then to HA in the Mw range of 150-2200 kDa, and we observed complex structures that are strongly correlated with the Mw of the HA, forming only rather small elongated structures for short HA and very extended structures for long HA. In contrast the rheological behaviour is largely dominated by the HA itself and the phase behaviour is rather similar for all Mw's. Interesting is the marked salt dependence of the phase behaviour of these systems, which was then further characterized by comprehensive ITC and scattering experiments that show how the HA surfactant interactions change in a systematic fashion here.

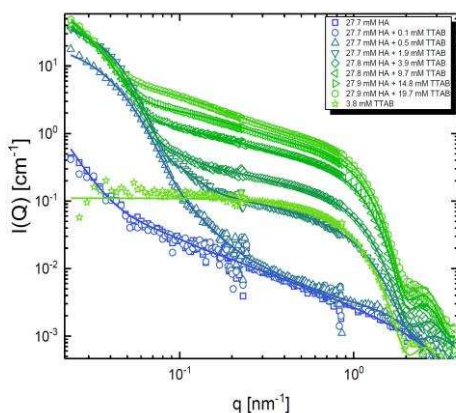


Figure 1. SANS curves of HA/TTAB complexes.

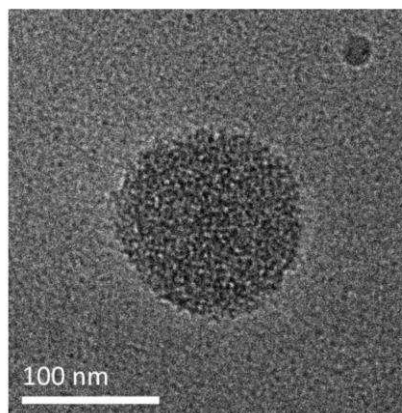


Figure 2. Cryo-TEM image of 28 mM HA/6 mM TTAB

Acknowledgements: Financial support by the ILL through a PhD scholarship for P.B. is thanked for.

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Coarse-grained Monte Carlo simulations of complexation between weak polyelectrolytes and oppositely charged nanoparticles

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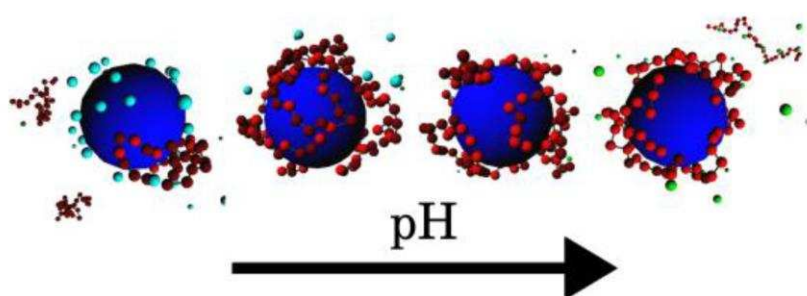
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Systems comprising of nanoparticles and oppositely charged polyelectrolytes have a great technological interest, being major components in formulations used in pharmaceutical, food, cosmetics, detergents, and paint industries. The stability of colloidal suspensions and the interaction of its constituents are important issues in formulations, and a large effort has been made to understand how the properties of each individual component affect the overall characteristics of the formulations.

Of special interest are weak, or annealed, polyelectrolytes. Contrary to strong (quenched) polyelectrolytes, the ionization of annealed polyelectrolytes is pH dependent. This allows for fine-tuning of the properties of the polyelectrolyte and the resulting complexes they form with other macroions. In addition, annealed polyelectrolytes exhibit charge mobility, where protons are mobile along the chain, giving rise to non-uniform charge profiles [1, 2].

Using Monte Carlo simulations, we have studied the complexation between charged nanoparticles and oppositely charged, annealed, polyelectrolytes. In particular, systems consisting of a single nanoparticle with multiple polyelectrolyte chains, and systems of two nanoparticles and a polyelectrolyte chain were considered. We have found that the titration behavior is dependent on the mixing ratio between nanoparticles and polyelectrolytes, and varies mildly with its chain length. Furthermore, the mobility of charges in the polyelectrolyte allows for a maximization of the electrostatic interactions between nanoparticle and polyelectrolytes by concentrating the charge in the adsorbed chains, which coexist with nearly neutral and non-adsorbed chains [3]. The influence of chain ionization on bridging between nanoparticles has also been looked into.



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Structure, persistence and hydrodynamics of high generation denpols

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Dendronized polymer (denpol) are a subclass of hyperbranched polymers. They consist of dendrimer side chain, covalently linked to a linear polymer main chain. Their unique structure is expected to lead to “sausage”-like persistent nano-object. When dispersed in good solvents, the swelling of the dendrimer side chains is expected to lead to increase rigidity of the backbone, in a similar fashion than in bottle brush polymer. The dendrimer side chain is expected to lead to a dense cross section.

We investigate the conformation of well-defined dendronized polymers (denpols) based on poly(norborene) (PNB) and poly(*endo*-tricycle[4.2.2.0]deca-3,9-diene) (PTD) backbones and ester dendrons. Their synthesis by ring-opening metathesis polymerization (ROMP) of macromonomers led to fully grafted and large degree of polymerization denpols with narrow polydispersity. The structure and conformation of denpols with a 4th, 5th and 6th generation side dendron were investigated in dilute solutions, by a combination of scattering techniques.

Careful analysis of GPC couple with Multiple Angle Laser Light Scattering (MALLS) allowed measure of the evolution of the gyration radius R_g with the molecular weight or the degree of polymerization. The evolution were analyzed with the Benoit Doty expression for the R_g of semiflexible chains, and persistence length were measured for every denpol fraction. The form factors were measured by Small Angle Neutron Scattering, and analyzed by fitting with the Kholodenko semiflexible cylinder model form factor. Good fit were obtained and values for the cross section radius, the contour length and the persistence length could be reliably measured. Good agreement between the persistence length measured by SANS and GPC-MALLS were obtained with values ranging from 5 nm (G4) up to almost 20 nm (G6), much larger than the main chain or the lower generation denpol [1]. The cross section radius were measured between 1.8 nm and 2.8 nm. The evolution of the measured dimensions (cross section radius, persistence length) are compared to models and also to the case of bottle brush. The rather high values of the aspect ratio L_p/R_{cs} attained in the high generation denpol could possibly lead to formation of liquid crystalline phase at larger concentration.

The diffusion coefficient were measured by Dynamic Light Scattering and were found to compare well to semi-flexible cylinders using Winkler models.

The increase of the cross section density with increasing generation number is expected to lead to excluded volume effect, towards soft colloidal properties. Different macromolecules do not overlap but rather form territories. Results of DLS and SANS in semi-dilute regime confirmed that tendency.

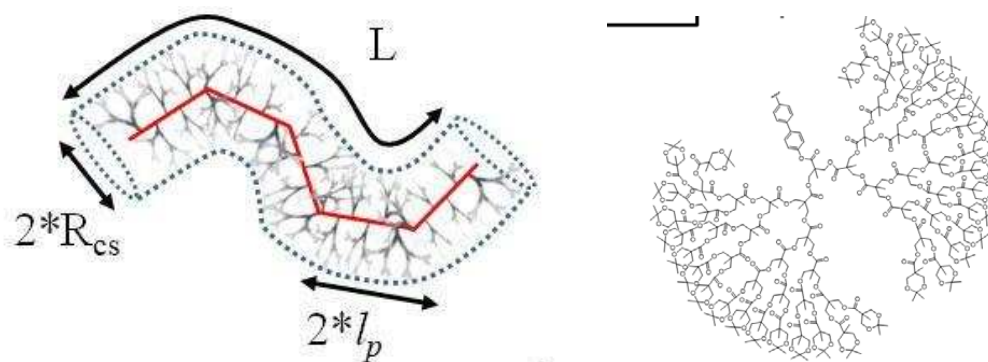


Figure 1 : Denpol as semi-flexible cylinder and 6th generation ester dendron (G6)

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Electrostatic Formation of Polymer Particle Stabilised Liquid Marbles and Metastable Droplets – Effect of Latex Shell Conductivity

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Small liquid droplets encapsulated and stabilised by hydrophobic powders which exhibit low friction on surfaces, known as liquid marbles, have increased in research interest in the last 15 years. Traditionally, liquid marbles have been produced by rolling the liquid droplet on top of a bed of particles, resulting in the particles attaching at the gas-liquid interface and stabilising it via Cassie-Baxter wetting [1-3]. More recently, we have shown that the production of liquid marbles is achievable using an alternative, non-contact electrostatic method to transfer the particles to the air-water interface [4]. This method has allowed the study of the electrostatic transfer of a range of particles, including polymer latexes which can exhibit lower contact angles than required for the direct contact rolling method. It is hoped that this method will open up new possibilities for contactless particle handling.

A 5 μL earthed water droplet was suspended above a bed of 85 μm diameter polystyrene particles, and a potential applied between 0.5 and 3.0 kV. Certain potentials allow for the electrostatic transfer of the particles to the droplet interface, which was monitored as a function of bed-droplet separation distances. As a result of the low water contact angle of these particles, they were partially wetted and the end result was a metastable particle-stabilised droplet rather than a liquid marble. Adding a shell of conductive polypyrrole (Figure 1) to each polystyrene core particle alters the particles' charging and transport behaviour, resulting in differing bed- droplet separation transfer distances for a given applied potential. Further modification of the polypyrrole shell thickness and dopant properties allows for the particle cohesion, hydrophobicity and conductivity to be tuned, thus changing conditions where liquid marbles can be produced using this novel electrostatic method.

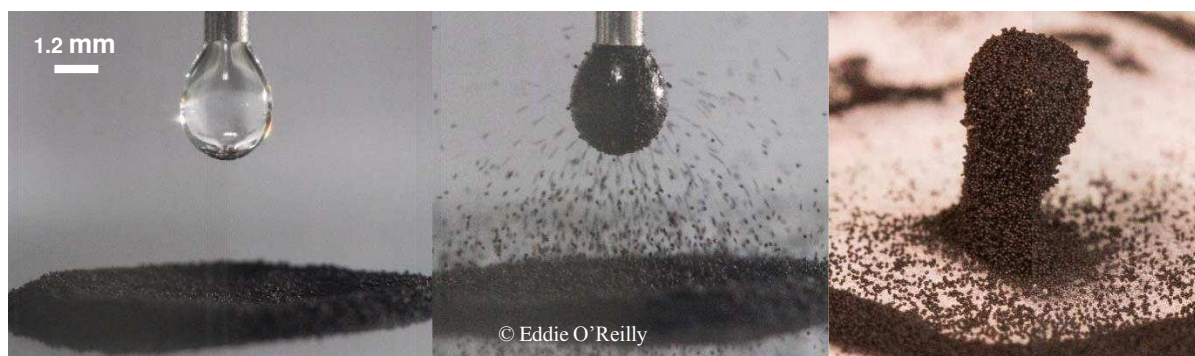


Figure 1. Electrostatic coating of an earthed water droplet (left) by polypyrrole shell-polystyrene core particles (middle) to form a liquid marble (right).

Acknowledgements: This research was supported by the Australian Research Council (DP170100578) and the Japan Society for the Promotion of Science (16039901-000541). C.A.T. thanks the Australian Government for a Research Training Program (RTP) Scholarship.

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Development of a novel drug delivery system comprising biopharmaceuticals for dermal and nail delivery

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Predominantly, the majority of fungal infections (dermal and nail) are caused by dermatophytes, such as *Trichophyton rubrum* known as one of the most prominent. Among fungal infections, nail infections or onychomycosis exhibit the most difficulties and limitations in their treatment. Onychomycosis affects around 5-10% of the population in the world.

Onychomycosis is a common infection of the nail caused by dermatophyte affecting mostly toenails in adults being associated with limited treatment options [1]. In this study novel dosage forms were prepared and evaluated for their suitability in treatment of onychomycosis. Films were prepared comprising polymeric excipients such as chitosan, (hydroxypropyl)methyl cellulose, hydroxyethyl-cellulose, carboxymethylcellulose according to solvent evaporation method. Developed formulations as shown in Table 1 were evaluated in terms of physical appearance, stability and adhesiveness.

Furthermore skin and nail irritation studies were conducted. Five potential formulations (F1-F5) were designed while F1 and F4 exhibited the most promising results in terms of stability with 26 min and 40.67 min, respectively, and suitability in nail application. F1 as the most favorable dosage form revealed with 2.9438 kg/m/s in terms of adhesive force the most adhesive properties in contrast to the other preparations. All formulations were found to be non-skin irritating and safe to use. Taken together, these findings suggest novel designed films containing polymeric excipients as a fruitful platform for the treatment in onychomycosis.

Table 1: Composition of formulations containing polymers.

Ingredients	Chitosan [g]	Ethanol [mL]	HCl [mL]	HEC [g]	HPMC [g]	NaCMC [g]	PPG [g]	PVP [g]	TEC [mL]	Water [mL]
F1	-	20	-	1.0	0.2	0.4	0.23	-	-	-
F2	-	20	-	-	-	0.4	0.23	1.0	-	-
F3	0.5	20	10	-	-	-	0.23	0.4	-	-
F4	-	20	-	1.0	0.2	-	-	-	0.5	-
F5	-	20	-	1.0	-	0.4	0.23	-	-	10

HCl: Hydrogen chloride; HEC: Hydroxyethyl cellulose; HPMC: Hydroxypropyl methylcellulose; NaCMC: Carboxymethyl cellulose sodium salt; PPG: Polypropylene glycol; PVP: Polyvinylpyrrolidone; TEC: Triethyl citrate

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Acquisition of bioflocculant from *Rhodococcus opacus* FCL1069 strain

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Flocculation is known as a dynamic and an exceptionally efficient process which removes suspended solids, colloids or cell debris of organisms from water solutions. The substances that carry out the flocculation process are called flocculants and, due to their source, they can be divided into three groups: inorganic flocculants (e.g. aluminium sulphate, iron chloride), synthetic organic flocculants (polyacrylamide derivatives) and natural flocculants (bioflocculants) [1]. Especially promising are natural substances obtained from bacteria, fungi and algae, which are able to replace toxic products, without significant changes in their efficiency and exploitation costs. Microorganisms isolated from soil and wastewater are the most efficient producers of bioflocculants [2]. However, there are studies of bioflocculant-producing bacteria isolated from deserts, glaciers of Antarctica and caves.

Bioflocculants mainly consist of polysaccharides and proteins, however the composition and properties depend on type of microorganisms which produce these substances [3]. Despite many different properties of natural flocculants such as biodegradability, a high efficiency, a non-toxicity and a lack of secondary pollution, only few have been commercially applied. Therefore, it is important to adjust the bioflocculant receiving procedures to industrial standards. Studies indicate a significant effect of extraction methods on the properties of natural flocculants.

In the present work, *Rhodococcus opacus* FC1069 was analysed due to synthesis of bioflocculant. Bacterial strain was cultivated in Erlenmeyer flasks containing 1 L of liquid medium for 11 days on a rotary shaker (150 rpm, 28 °C). Supernatant obtained from culture broth was examined for flocculating activity using mixture of kaolin and calcium chloride. Additionally, bioflocculant was extracted from culture broth using cold ethanol as a precipitant and lyophilized to obtain partially purified product. The incubation time of *Rhodococcus opacus* culture broth was established based on flocculating activity and mass of vacuum-dried bioflocculant obtained on the subsequent days of cultivation. The chemical components of the studied bioflocculant were estimated by series of spectrophotometric analysis. Additionally, the basic extraction parameters were tested to obtain the bioflocculant. Several variables were used, including the type and the volume of the precipitating factor, the mixing time after addition of precipitating factor and the total precipitation time of the bioflocculant.

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Polyester fabrics modified with zwitterionic polymer brushes to reduce biofilm formation

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Biofouling is a problem affecting the efficacy of a broad range of systems and applications. These include implants, biosensors or textiles used in the medical sector, where the contamination by bacteria and microorganisms is a major cause of infections [1]. In recent years, lubricant-infused surfaces have been found to reduce lateral adhesion of all types of liquids and to induce bacteria and microorganisms to slide off [2]. A major drawback concerning these surfaces is that liquid lubricants are easily removed by shear stress or evaporation. Several strategies have been adopted to limit the depletion of the lubricant, yet further efforts are needed to improve the performances of slippery surfaces. A long term stability might be achieved using highly hydrated polymer brushes to replace the lubricating layer. PEG or zwitterionic polymers proved to be highly effective for this purpose, since several coatings that prevent the attachment of proteins and bacteria have already been synthesized [3,4]. In this work, we aim at functionalise a polyester fabric with zwitterionic brushes. The high motility of the polymer chains and the strong hydration effect associated with the charges make these materials promising candidates for the fabrication of lubricant-infused surfaces.

Acknowledgments: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722497

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Diffusion of sodium hyaluronate in aqueous solutions: the influence of the electrolyte presence in the medium

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This work focuses on the investigation of the influence of the following ions: Na^+ , Mg^{2+} , SO_4^{2-} (*kosmotropic* ions) and NH_4^+ , SCN^- (*chaotropic* ions) on the diffusion of sodium hyaluronate (NaHy) in aqueous solutions. To do this, electrolytes with characteristic properties were selected, by combining of these ions, as follows: 1) two *kosmotropic* ions (MgSO_4 and Na_2SO_4), 2) two *chaotropic* ions (NH_4SCN), 3) a *chaotropic* cation plus a *kosmotropic* anion ($(\text{NH}_4)_2\text{SO}_4$), and 4) a *kosmotropic* cation plus a *chaotropic* anion (NaSCN). Thus, diffusion coefficients of systems containing NaHy and each one of the said electrolytes were carried out by using the Taylor dispersion technique [1-2], at 298.15 K.

The analysis of the results found was performed by assuming that, under the experimental conditions selected, these systems can be considered as pseudo-binary ones [3]. This analysis shows that the diffusion of this polysaccharide is strongly affected by both the occurrence and nature of the electrolyte present, as a consequence of *salting-in* and/or *salting-out* effects, resulting in the formation of new species from the different aggregation equilibria occurred. Since the determined pseudo-diffusion coefficient values, D , are not identical to the binary diffusion coefficients for either aqueous NaHy [4] or those for the electrolytes, it is possible to conclude that there must be interacting solutes. Despite the limitations of the model used, the results indicate the presence of eventual aggregates in these solutions, which play a no-negligible role on the diffusion behaviour of these systems.

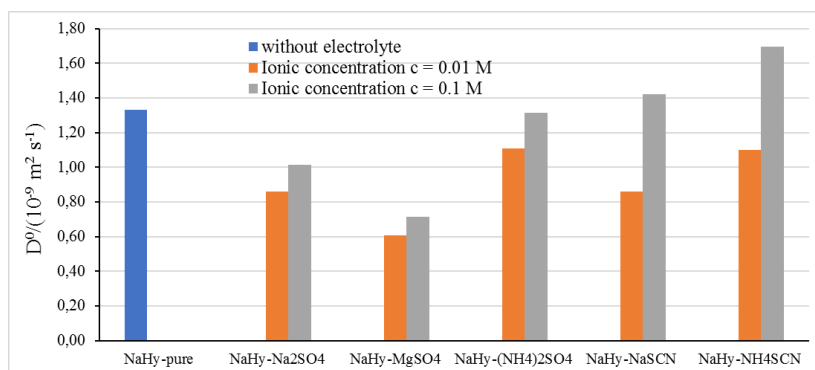


Figure 1. Limiting diffusion coefficient values for aqueous solutions of sodium hyaluronate in the presence of different electrolytes.

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Interplay of magnetic-dipol and PDMS-matrix forces between magnetic nickel-particles and well-ordered paramagnetic chains

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Hybrid materials offer a high potential for future applications due to combining the properties of two or more materials. We focused on the investigation of the interaction between magnetic particles with the surrounding matrix in 3D magnetic hybrid materials systems in applied magnetic fields [1-3].

To witness the interplay between matrix deformation and shifting of particles we adjusted the elastic modulus of the material to be below 10 Pa. While crosslinking the polymer under an external magnetic field chain formation of the super paramagnetic particles occurs. The particle chains differ in size and spacing, depending mostly on the strength of the magnetic field.

In recent studies, focus lay on the behaviour of well separate particles and single particle chains [2-3]. We observed antisymmetric buckling of nearest neighbour chains. Thus, while the distribution of the chains is momentarily random in space, main focus of current research is on various strategies to get an adjustable chain spacing. Adapting the magnetic field strength influences chain length and spacing. However, the reproducibility has to be improved, e.g., by carefully adjusting the magnetic field. An alternative, promising route, is the capillary assisted self-assembling of the particles on structured substrates [4].

In contrast, for well separated particle systems, nickel particles with bigger magnetic moments are used, which allows the use of matrices with much higher elastic modulus in the range of 100 to 1000 Pa. When an external magnetic field of 170 mT is rotated respectively to the particle axes, a nicely reproducible jumping apart (gap opening) and closing of nickel-particles (Fig. 1 b),c)) is observed. These jumps strongly depend on the initial particle distance. The detailed mechanism is yet not completely clarified but evaluated data strongly indicates interplay between magnetic dipol-dipol-interaction and forces due to the elastic deformation of the matrix. To clarify this question, we will extract the deformation field of the matrix around the particles to get an overall picture of the actually influencing forces.

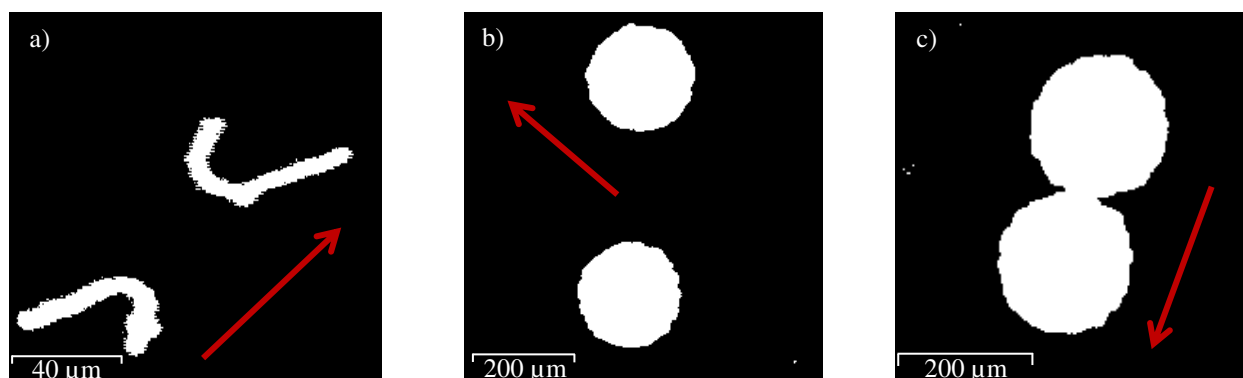


Figure 1. a) In white the super paramagnetic particle chains. Buckling of two neighbour chains. Distance is $\approx 55 \mu\text{m}$. Antisymmetric deformation of chains. In white the nickel-particles gaped b) or closed c). In red the orientation of the external magnetic field.

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Electric and dielectric properties for biopolyimide films

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The development of biobased polymers is indispensable for the establishment of a sustainable low-carbon society. A number of aliphatic biobased polymers such as polyesters; poly(lactic acid) [1], poly(hydroxyalkanoate)s [2], and poly(butylenes succinate) [3], and polyamides (polyamide 11 and polyamide 66) have been developed, but their low glass transition temperature, T_g , and only a small percentage of their substitutes limited their use for various applications as superengineering plastic. We have developed so far biobased PIs from bioavailable aromatic diamines, which were photodimers of 4-aminocinnamic acid (4ACA) derived from genetically manipulated *Escherichia coli* [4-6]. These biobased PI films showed ultrahigh thermal resistance with the temperature at 10 % of mass loss, T_{10} , values over 425 °C and no T_g values under 350 °C, which is the highest value of all biobased plastics reported thus far. This advanced thermal property can be useful for electric devices such as flexible polymeric electrodes that can be annealed at high temperature. On the application for electric devices, the electric properties such as resistivity, dielectric constant or dielectric breakdown voltage are very important. However, the electric properties for these films are not fully understood.

In this paper, we prepared biobased PI copolymer films (ATA/CBDA) of 4,4'-diamino- α -truxillic acid (4ATA) and 1,2,3,4-tetracarboxycyclobutane dianhydride (CBDA) and measured the electric resistance (volume resistivity) and dielectric constant for these films. We discuss the relationship between the electric properties and the molecular structure for biobased PIs. The electric properties for water soluble BPIs are also presented.

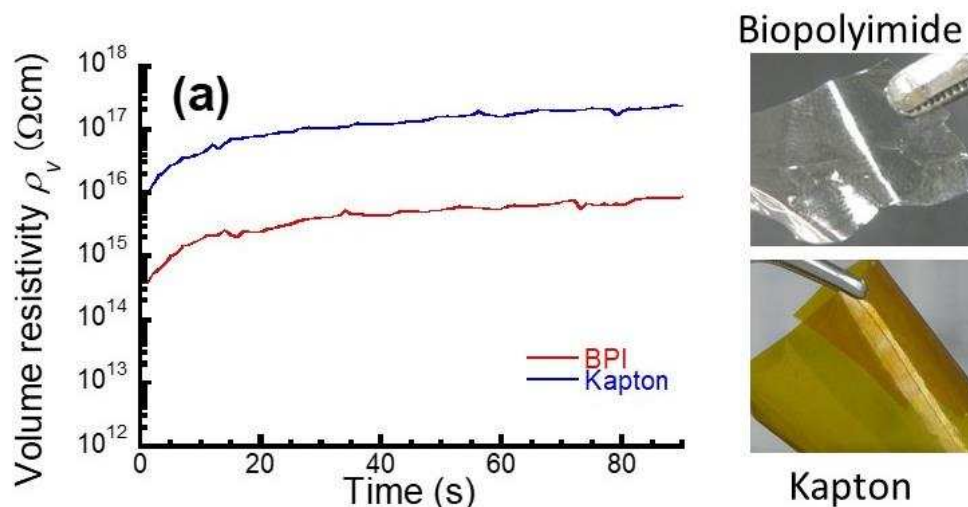


Figure 1. Volume resistivity and appearance for biopolyimide and Kapton films.

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Magnetorheological effect for carrageenan magnetic hydrogels

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Biological tissue, such as dermis of sea cucumbers, exhibits stimuli-responsive properties that the elasticity alters in response to a physical stimulus. Materials that physical property changes responding to a stimulus have been extensively investigated, particularly in the field of soft materials such as polymer gels, rubbers, or elastomers. Polymer gel containing magnetic particles is a stimuli-responsive gel that viscoelastic properties can be controlled by applying magnetic fields. We have fabricated magnetoelastic soft materials with various polymer matrices [1-6]. The elastic modulus of magnetic gels is enhanced by forming a chain structure of magnetic particles, similarly to magnetic fluids. Few years before, we have succeeded to fabricate a new class of magnetoelastic gel that demonstrates drastic and reversible changes in dynamic modulus without using strong magnetic fields [7,8]. At zero magnetic field, the storage modulus of the magnetic gel is low with $\sim 10^4$ Pa although the gel contains large amount of particles as much as $\phi \sim 0.30$, resulting from random dispersion of the magnetic particle in the gel. The magnetic particle, under magnetic field, aligns to the magnetic lines of force and forms a chain structure contributing to high storage modulus exceeding 4 MPa. Followed to the magnetic gel mentioned above, it was also succeeded to synthesize polyurethane elastomers showing drastic change in dynamic modulus by a factor of 277 [9].

In this paper, we present the magnetoelastic response and morphological properties of carrageenan magnetic hydrogel that underwent wide modulation of dynamic modulus (500 times higher than off-field modulus). In addition, we show new evidence that the relationship between carrageenan-concentration dependent particle morphology and the increase in the storage modulus. The origin of the giant magnetoelastic behaviour for carrageenan magnetic gels is discussed.

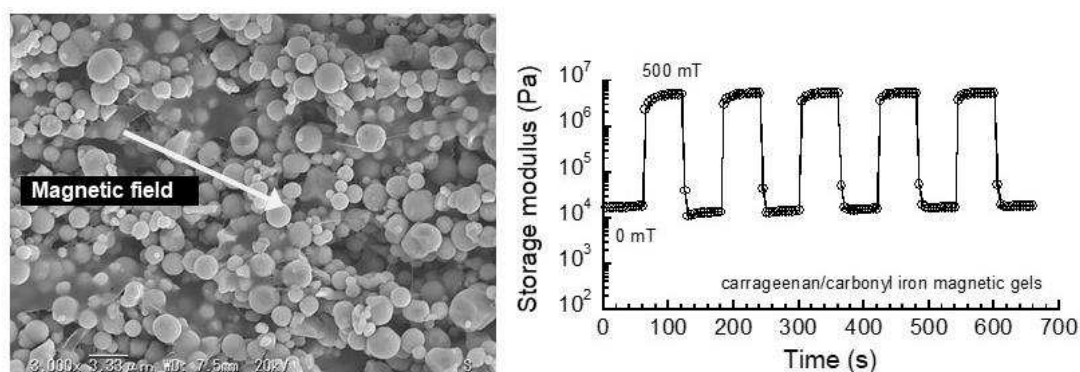


Figure 1. SEM photograph (left) under a magnetic field and magnetic response of storage modulus (right) against a pulsatile magnetic field for carrageenan magnetic hydrogels.

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Hydrogel-functionalized polyester fabrics

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Surface modification of textile-based materials is a promising technology that has attracted much attention in recent years due to its applicability in many interesting fields, including filtration, absorption, biomedical textiles, thermal and UV insulation, smart and intelligent textiles, flame retardant fabrics and textile catalysts [1]. In this context, polyethylene terephthalate (PET) fabrics, also known as polyester fabric, is most commonly used. One of the main advantages of using PET as carrier is the cost-effectiveness, which is a key feature for large-scale productions. Further important characteristics of such technical textiles are the physical and mechanical properties of the textile fibers such as, flexibility, stability, lightness, elasticity, anti-wrinkling [2].

Highly hydrated surfaces that exhibit special wettability properties were found to be highly effective for many applications including antifouling coating and oil/water separation [3]. Such surfaces can be performed using polymeric hydrogels. Hydrogels are cross-linked, 3D hydrophilic polymer network, which swell when brought into contact with water but do not dissolve.

In this work, we address a novel strategy for the grafting of hydrogels onto functionalized PET fabrics using different acrylates-based monomers. The hydrogel-modified PET textiles have been prepared by two steps modification, as shown in Figure 1. To this end, double and triple functional groups were firstly introduced onto the PET surface *via* an aminolysis reaction involving either allylamine or propargylamine. The final grafted polymer networks were then obtained after UV-induced radical photopolymerization with varying acrylate monomers in the presence of cross-linker. The resulting modified textiles were characterized by SEM, AFM, FTIR and contact angle measurements.

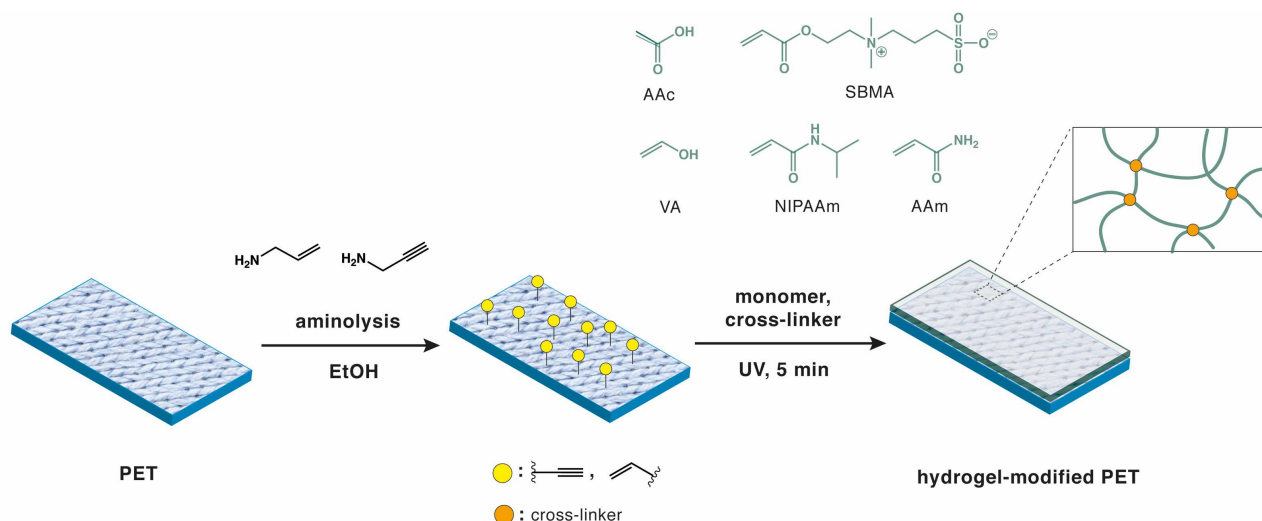


Figure 1. Schematic illustration of the novel strategy for the formation of hydrogel-modified PET fabrics.

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Multicolour tunable emission of Eu,Tb(PSA)Phen composite

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Lanthanide ions have excellent spectroscopic properties such as sharp emission lines, long lifetime, large Stokes shift and emission range from ultraviolet to near-infrared. These properties encouraged many studies, and the development of new lanthanide complexes have received great attention in the last years because of their large application range, which includes sensors, light-emitting diodes (LEDs), lasers or solar cells [1]. They possess low molar extinction coefficients, because of the Laporte forbidden F-F transitions and, thus, in order to obtain an enhancement of the characteristic emission of the lanthanide, an appropriate organic ligand can be used as an “antenna” to absorb light and then transfer the excitation energy to the central ion [2]. In this work new composites containing Eu^{3+} and Tb^{3+} with poly(sodium acrylate) (PSA) and phenanthroline (Phen) have been studied. The composites were obtained by addition of appropriate amounts of the reagents in ethanol/water 1:5.

Figure 1 (a) shows the emission spectra of Eu,Tb(PSA)Phen with different concentrations of lanthanides. It can be noted that the presence of simultaneous emissions of Tb^{3+} at 490 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$) and 545 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) and Eu^{3+} emissions at 592 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 650 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) and 690 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$). In addition, tunable emission colors were achieved by adjusting the Eu/Tb molar ratio. The corresponding CIE coordinates on CIE chromaticity diagram are shown in panel (b). When the Tb concentration begins to increase and that of Eu decreases, the emitting colors of the complex shift from red to orange, to yellow, and then to green. The characterization of the binuclear composites are complemented with the analysis of FTIR, UV-Vis, SEM and EDX mapping data. Based on the results obtained, we can conclude that the composites allow a systematic color-tuning in the emission as a function of the Eu/Tb molar ratio. This material can be promising for light emitting materials in the region from red to green or as sensors.

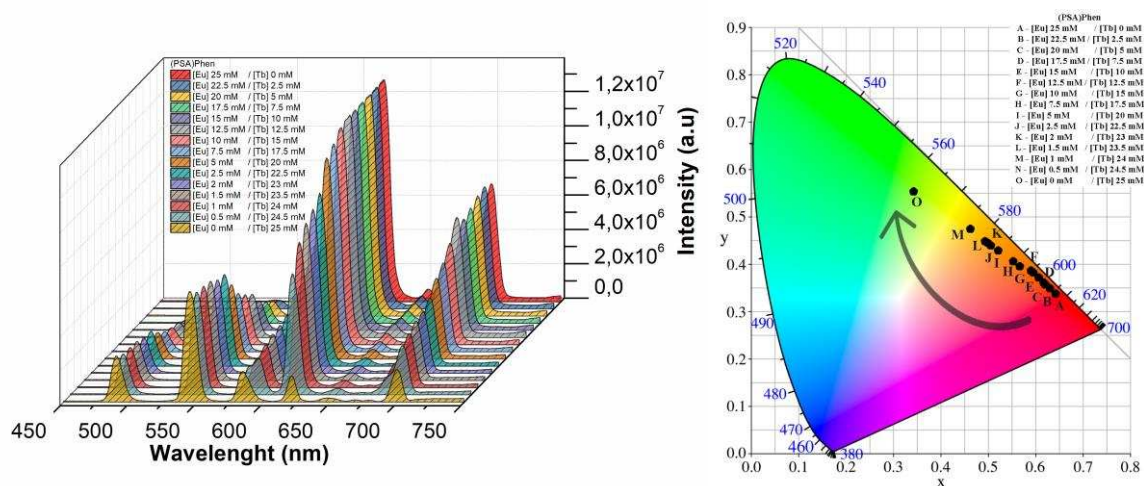


Figure 1. (a) Emission spectra of (PSA)/Phen composites with different molar ratios of Eu/Tb and (b) CIE coordinates of this composites.

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Zipper brushes from interfacial coacervation: Structure and interactions

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Conjectured to be related to “the origin of life on Earth” by Oparin [1], coacervation refers to association of oppositely charged macro-ions, an electrostatically-driven liquid-liquid phase separation process that is extensively found in nature. Coacervation of polyelectrolytes, nanoparticles, and surfactants is actively being exploited for the rational design of bio-inspired functional nanomaterials and new interfacial structures in a wide range of applications such as biomedical adhesives, coatings, microencapsulation technologies, gene delivery, anti-fouling, and as emulsion and foam stabilization [2]. We are exploring interfacial coacervation to design, fabricate, characterise and evaluate pH-responsive zipper polymer brushes, which can be replenished by switching the solution pH [3]. Such zipper brushes are formed by adsorbing an amphoteric block copolymer brush (ABC) to a surface-anchored polyanionic di-block copolymer (PAD) at pH ~ 7 . The complexation (or coacervation) between the positively charged ABC and the negatively charged polymer block in PAD can be reversed at pH < 4.5 , leading to the zipping-on and zipping-off of the ABC brush, making it pH responsive. As such, a solid and surface-highly grafted carpet of PAD is prepared using the Langmuir-Blodgett method with control of brush density (**Fig.1a**), and subsequently characterised at both the air-liquid (via tensiometry, Brewster Angle microscopy, XRR), air-solid (via ellipsometry, water contact angle and XRR) and solid-water interfaces (via XRR) [4] (**Fig.1b**). Consequently, the adsorption of a second layer of a cationic polymer will be studied, varying the polymer molecular architecture and the pH condition. X-Ray Reflectivity, Neutron scattering, and Surface Force Apparatus will be mainly used to give precise and unprecedented insights into zipper brush inner structure, properties and interactions, and the brush scaling behavior will be determined.

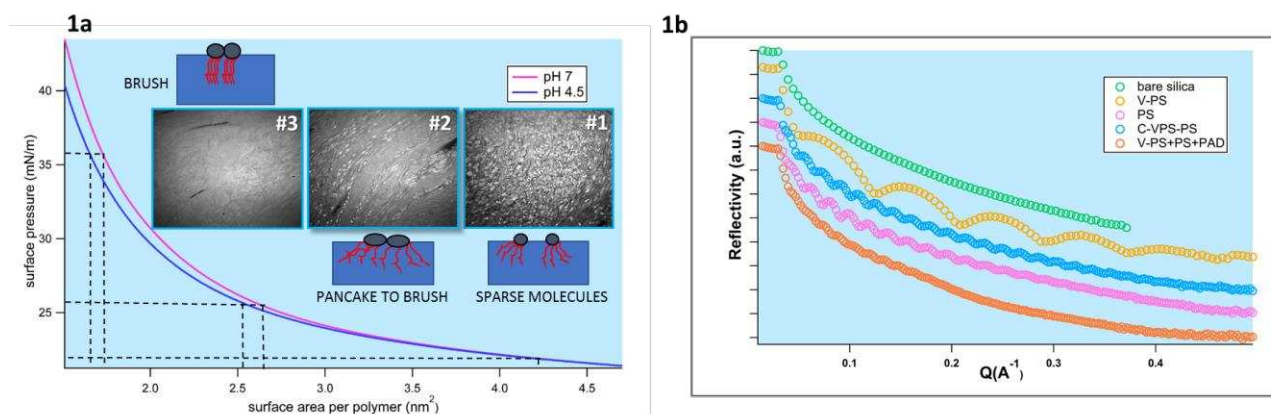


Fig.1a Surface pressure (n) as a function of the surface area per polymer (1/ σ) for PAD using a solution concentration of 1 mg/mL with microBAM images of PAD at surface pressure of 21.80 mNm⁻¹ (1), at surface pressure of 27.50 mNm⁻¹ where the negatively charged polymer block in PAD possibly undergo the “pancake-to-brush” transition (2), and surface pressure of 27.50 mNm⁻¹ during the formation of a solid polymeric brush monolayer (3). **Fig.1b** Reflectivity curves for bare silica (red curve), silica coated with grafted vinyl-polystyrene (yellow curve), silica coated with spin-coated polystyrene (violet curve), silica coated with vinyl-polystyrene and spin-coated polystyrene (light blue), silica coated with vinyl-polystyrene, spin-coated polystyrene and PAD monolayer deposited at surface pressure of 40 mNm⁻¹

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Synthesis of Anisometric Polyhedral Homopolymer Particles

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Non-spherical, aka anisometric particles are currently receiving increasing attention in the field of colloid science. In contrast to spherical particles, which mostly form close-packed structures, anisometric particles can assemble into intriguing superstructures, such as liquid and plastic crystals or superlattices. Moreover, they are able to generate different flow profiles at interfaces, which is highly interesting for technological applications, *e.g.* in paints, varnishes or composites. To date, polyhedral anisometric particles are mostly limited to inorganic compounds, *e.g.* metals or metal oxides [1]. Organic polymer-based particles would represent an excellent addition to inorganic particles for several reasons. First, they are composed of abundant elements, *i.e.* C, H, N, O, S. Second, they provide different density ranges, *i.e.* lower specific volumes, compared to inorganic substances, therefore raising interest for applications in composites where weight plays a crucial role. And third, they are much cheaper than *e.g.* heavy metal nanoparticles. However, the vast majority of synthetic approaches for the generation of organic homopolymers typically lead to spherical objects. Most of the techniques towards non-spherical homopolymer particles rely on deforming spherical latex particles, therefore such methods are mostly limited to the generation of roundish objects derived from spheres.

Recently, our group introduced a novel method for the synthesis of angular polyimide (PI) particles [3]. Combining light-weight with high thermal (>500 °C) and chemical stability, PIs belong to the class of high-performance polymers. To generate anisometric PI particles, we first synthesize single crystals of defined precursors containing both co-monomers (a diamine and a tetracarboxylic acid), so-called monomer salts (MS). These MS particles can be converted to PI particles by simple heating: the MS particles undergo a solid-state polymerization to the PI particles, with retention of the initial MS crystal shape (Fig. 1A). This shape retention potentially allows for accessing a plethora of PI particle shapes by altering the MS shapes. To date, MS crystals have been limited to big particles in the range of 200 to 300 μm . [3] With this contribution, we present a study on decreasing the size already down to $\approx 5 \mu\text{m}$ (Fig. 1B), and modifying the shape of MS crystals to expand the range of PI particle shapes, with the aim of generating a large set of different anisotropic particles at same chemical composition.

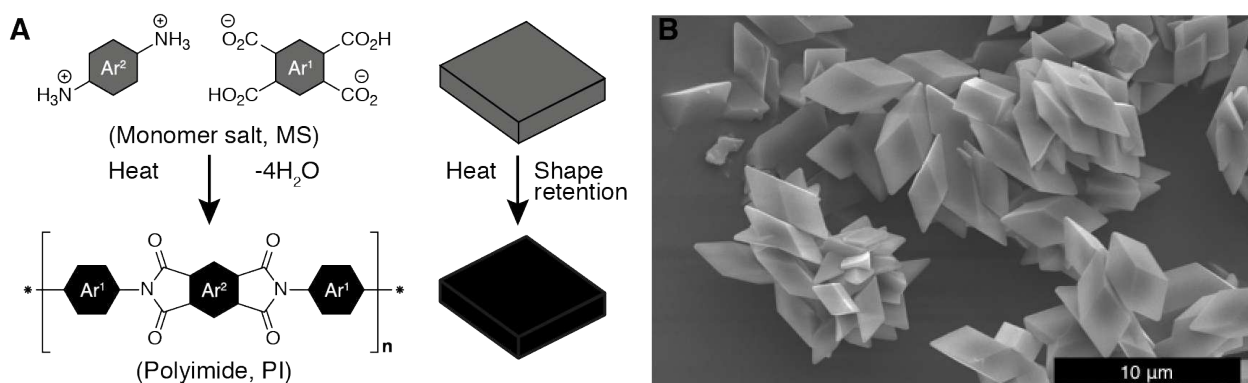


Figure 1. A. Solid-state conversion scheme of MS to PI. By solid-state polymerization, MS particles are converted to PI particles *via* shape retention, by simply heating the monomer salt particles to increased temperatures. B. SEM picture of rhombohedral-shaped MS crystals.

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Electrostatic Effects in Mixtures of Polyethylene Glycol and Poly(Sodium Methacrylate)

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Mixtures of charged and neutral polymers are often present in experimental and biological systems. In living cells, approximately 20-40% of the space is occupied by various species, meaning that macromolecules have to function in a crowded environment [1]. In order to mimic such an environment, polyethylene glycol, PEG, is often used as a crowding agent because it is highly water soluble and believed not to interact with other species in a solution.

In this contribution, the behavior of an anionic polyelectrolyte poly(sodium methacrylate), NaPMA, was studied in crowded environment provided by a high amount of PEG using dynamic and static light scattering techniques. 0.2 M NaCl was used as solvent and experiments were performed at a fixed NaPMA concentration of 2.5 g/L, while PEG concentration was varied from 0 to 150 g/L. A NaPMA standard with a high molecular weight, M_w , and narrow M_w distribution was used for the study, whereas PEG chains were much smaller.

The so called slow-mode behavior [2], characteristic for salt-free NaPMA solutions, vanishes as simple salt, e.g. NaCl, is added in sufficient amount. However, in NaPMA-NaCl-PEG mixtures the slow-mode signal is observed again. This is explained by the fact that PEG significantly lowers the dielectric constant of the aqueous medium [3], which leads to reinforced electrostatic interactions between NaPMA polyions and thus causes the reappearance of the slow-mode signal.

Experimental results were confirmed by Monte Carlo simulations. A coarse-grained model of the system also reveals stronger correlations between NaPMA molecules when the dielectric constant of the medium is lower, and thus qualitatively agrees with experimental results.

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Investigating the Behaviour of Different pNIPAM Architectures

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Poly(N-isopropylacrylamide) (pNIPAM) is the most widely studied temperature sensitive polymer in the literature. pNIPAM has a lower critical solution temperature (LCST) around 32°C, which is the temperature at which the polymer becomes immiscible in water [1]. pNIPAM can be synthesized to preferentially form several architectures including linear chains, hyperbranched polymer chains and microgels. pNIPAM can also be used as a co-monomer with other responsive polymers to make highly tunable, selective polymer materials with properties that are sensitive to multiple stimuli [2].

pNIPAM microgels are temperature sensitive materials that undergo a volume phase transition, where rather than becoming insoluble in water like the linear polymer analogue the microgel shrinks, due to the increased hydrophobicity of the material with temperature. At temperatures above the volume phase transition temperature (VPTT) the microgels significantly shrink in size, up to 100 times in volume, this is accompanied by a large reduction in the volume fraction of water inside the particle [3]. pNIPAM has attracted much interest since its discovery due to the VPPT being close to physiological conditions, resulting in applications in drug delivery, sensors and protein precipitation applications [2].

This work aims to investigate the effect changing the pNIPAM architecture has on the behaviour of the polymer system, and investigates how altering synthetic conditions affects what pNIPAM architecture is favoured. Several varieties of linear, hyperbranched, cross linked and fluorescent pNIPAM polymers have been synthesized during this work, with the phase behaviour and structure of these polymers characterized. The properties under investigation are the swelling versus deswelling behaviour as a function of temperature, the interaction with electrolytes and the optical properties of the polymers. Properties such as molecular weight, cross link density and particle size have been varied in order to understand the effect these properties have on the phase behaviour of pNIPAM. The properties of the prepared samples were characterized using confocal microscopy, direct contrast image microscopy, dynamic light scattering and SAXS.

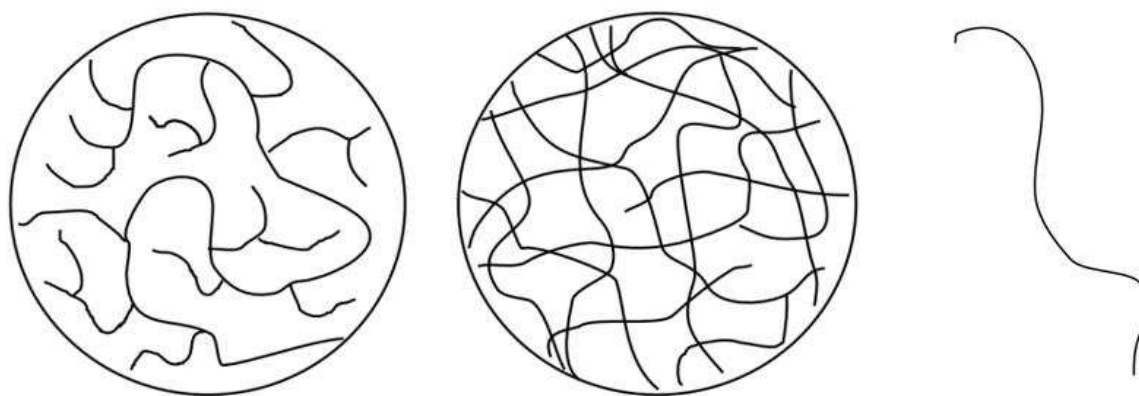


Figure 1. Examples of the different pNIPAM architectures synthesised and investigated as part of this project.

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Determination of antimicrobial activity of polyelectrolyte-surfactant hydrogels

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Polyelectrolytes can interact with oppositely charged surfactants and under the special conditions can form hydrogels. These hydrogels contain hydrophobic cores which are formed from the micelle-like nanostructures. Due to the presence of these hydrophobic core, hydrogels are able to solubilize hydrophobic substances (such as fluorescent probes, drugs) and therefore are the subject of research in several medical applications.

Hydrogels combine the behaviour of liquids and solids in a soft matter and their final attributes depends on the density of its network or the density of crosslinks connecting the network [1]. Network density and porous microstructure of hydrogels is extremely important since it affects the diffusion characteristics of hydrogels. This research was focused on testing the antimicrobial activity of the hydrogels which is based on diffusion methods. For this study hydrogels prepared from cationized dextran (DEAE) and negatively charged surfactant sodium dodecyl sulphate (SDS) were used. Another type of tested hydrogels were ones prepared from hyaluronic acid and positively charged surfactant carbethopendecinium bromide (Septonex).

Two methods were used for determination of the antimicrobial effect of prepared hydrogels: agar disc/well diffusion method and broth dilution method (which is more sensitive). Antimicrobial activity was tested against a gram-negative bacterium *Serratia marcescens* (SM), gram-positive bacterium *Micrococcus luteus* (ML) and against yeast *Candida glabrata* (CG) as well. Antimicrobial tests were focused on testing the antimicrobial activity of the hydrogels after preparation and subsequently after the washing process. Supernatants were also subjected to testing.

All hydrogels showed antimicrobial effect against all of the microbial strains after preparation. After the washing process antimicrobial activity in dextran hydrogels was weakened. Supernatants from dextran hydrogels showed no antimicrobial activity against all of the microbial strains. On the other hand supernatants from hyaluronic hydrogels showed antimicrobial effect against gram-positive and gram-negative bacterial strains only and against yeast they showed no antimicrobial activity as well.

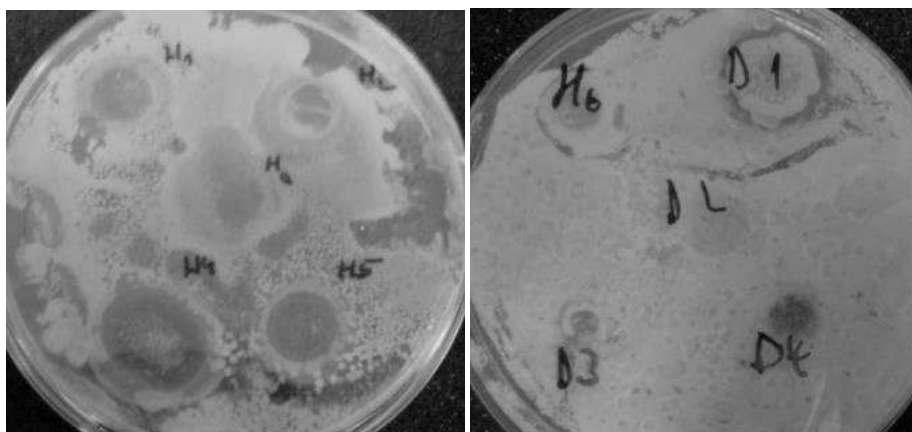


Figure 1. Resulting inhibitions zones in hydrogels. Test of the antimicrobial activity of hydrogels against gram-positive bacterium *Micrococcus luteus*.

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Phase behavior and solution structure of new UCST- and LCST-type polymers

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Thermoresponsive polymers are an interesting class of material for industrial and medical applications and also for fundamental research. Lower critical solution temperature (LCST) polymers, such as poly(N-isopropylacrylamide), are common and well-studied, whereas materials with an upper critical solution temperature (UCST) still are rare and not well examined. Depending on the material used, the transition temperature can be varied by different parameters, which can enlarge the potential field of applications. Here, not only it is interesting to tailor the temperature, at which the phase transition occurs, also it is interesting to control the type of transition, i.e. from LCST to UCST or vice versa. We synthesized acrylamide based copolymers that, depending on the composition, display either a LCST behavior, or a UCST-like phase behavior. We used turbidity measurements, static and dynamic light scattering as well as small angle neutron scattering (SANS) to study the phase behavior of our polymers on global and local length scales. In particular, from SANS important information on the polymer structure is accessible.

Application of gold nanostructures for the improvement of electrochromic and optical properties of conducting polymers composite

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Conducting polymers are being used for the development of chemical and electrochemical sensors and arrays, which can be applied in various fields such as biomedical, environmental and industrial sciences due to their attractive properties. These polymers are characterized by the ease of synthesis, high sensitivity and electrical conductivity, the stability of the material and low cost [1-3]. Scientific and industrial impact of nanoscience and nanotechnology in analytical chemistry, medicine and pharmacy has been growing in recent years. Gold nanoparticles are the most widely used metal nanoparticles due to their unique physical and optical properties [4-5]. Combining nanotechnology with conducting polymers can be a way to improve desired properties of the materials, as metal nanoparticles are known as excellent chromophores in the visible and near-infrared ranges due to an excitation of surface plasmons [6-7]. The aim of this work was to investigate the effects of incorporated gold nanostructures (AuNS) and gold nanoparticles (AuNP) in electrodeposited layer of poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) on the electrochromic and optical properties of conducting polymers composite.

Gold nanostructures were electrochemically deposited onto indium tin oxide (ITO) coated glass slide using different constant potentials. PANI/PEDOT polymers layer was electrodeposited onto AuNS/ITO and ITO substrate. The influence of AuNS and AuNP on electrochromic properties and on pH sensitivity of formed polymers composite was explored. Absorption spectra of modified polymer layers at different potentials were determined using UV/Vis spectroscopy. Furthermore, conductivity and stability of polymers composite layers were studied using cyclic voltammetry.

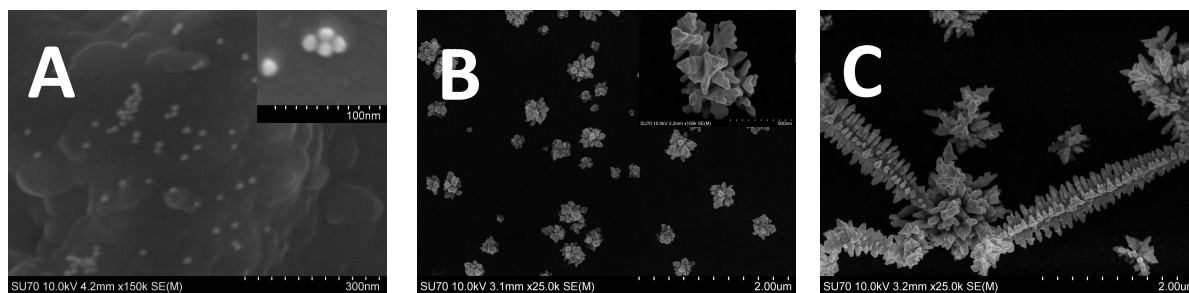


Figure 1. A – 13 nm gold nanoparticles on PANI/PEDOT layer; B-C – electrochemically synthesized gold nanostructures on ITO coated glass slide using different electrode potentials

Acknowledgements: This research was funded by a grant (No. S-LAT-17-1) from the Research Council of Lithuania.

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Bio-inspired Selenium Modified Microgels

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Glutathione peroxidase 1 (GPX1), the most abundant GPX enzyme found in many mammals is well known for its biological role in protecting the organism from oxidative damage. The selenocysteine residue in the protein's structure serves as the main engine in the biochemical function to reduce lipid hydroperoxides to their corresponding alcohols and to reduce free hydrogen peroxide to water [1]. GPX1, even at low concentration, allows highly effective anti-oxidation reaction to be carried out inside a physiological body. Therefore, one can speculate the redox properties of this enzyme being beneficial in technical applications such as a catalyst. However, GPX1 is unable to withstand the harsh environment conditions in technical applications such as high temperature, organic solvents, etc.

Materials mimicking the macroscopic structure of enzyme: glutathione peroxidase (GPX) has attracted great interest. The strategy is to incorporate catalytic active selenium (Se) moieties into 3D macrostructure. Provided with cavities within the macrostructure, redox reactions can be triggered by the selenium groups during the diffusion of small molecules through the pores [2]. Microgels are 3D crosslinked polymer network that are sensitive to environmental changes such as temperature, light, pH, etc. Poly(*N*-vinylcaprolactam) (PVCL) microgels were chosen to be the 3D scaffold. The synthesized thermoresponsive PVCL microgels were crosslinked by the diselenide as well as with bisacrylamide as the permanent crosslinker. Upon oxidation of the microgels by H₂O₂, diselenide were cleaved and converted to seleninic acid. Catalytic study was then carried out with the oxidized microgels in a model reaction; oxidation of acrolein to acrylic acid and methacrylate. The aim of this project is to produce catalytic active microgels with the ability to disperse them in the interface of solvent/non-solvent. Due to the solvation ability of the microgels in both solvents, the oxidation and reduction reactions can be conducted *in-situ* which could lead to product separation in the corresponding solvents after the redox reactions.

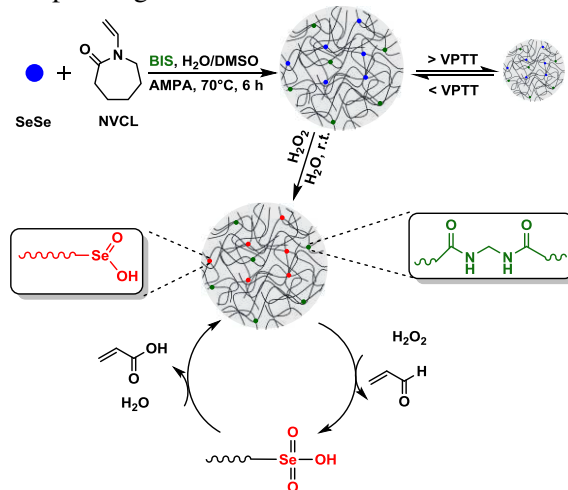


Figure 1. The synthesis of diselenide containing thermo-responsive PVCL microgels, diselenide (SeSe) converted to seleninic acid groups after oxidation by H₂O₂ that allow the oxidation reaction of acrolein to be carried out.

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Toward Electrochromic Detection of Gases: Conducting Polymer Layer on Transparent Substrate

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Electrochromic materials and devices can be used in various fields such as architecture, aeronautical engineering and manufacturing of sensors [1-3]. Many classes of materials possess electrochromic properties, however conductive polymers and their derivatives attracted considerable attention due to their low cost, environmental stability, high coloration efficiency and rapid switching ability [3,4]. Polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT) are often used for construction of electrochromic devices due to their unique electrochromic and optical properties [5]. The main aim of this work was the development of optical/electrochromic sensor sensitive to pH changes using conducting polymer layers.

PANI, PEDOT and PANI/PEDOT layers were electrodeposited on glass substrate coated indium tin oxide (ITO). Influence of monomers ratio on durability, stability and thickness of polymer layers were evaluated. Thickness and morphology of polymer layers were determined by atomic force microscopy in contact mod and by scanning electron microscopy. Raman spectroscopy and Fourier transform infrared spectroscopy were used for characterization of polymer layer structure. Conductivity of various polymer layers was evaluated by cyclic voltammetry measurements at different potential sweep rates. Absorption spectra of polymer layers on ITO-coated glass were registered using UV/Vis spectrophotometer. Obtained results showed that electrodeposited PANI/PEDOT layer on ITO-coated glass can be advantageously used for determination of solution pH. In addition, produced optical sensor further can be used for determination of gases such as carbon dioxide and ammonia.

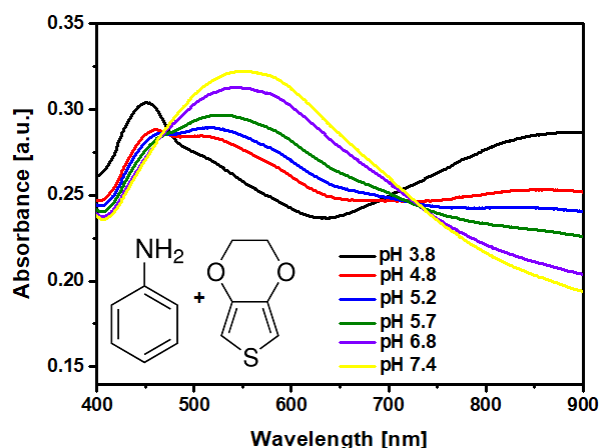


Figure 1. The UV/Vis spectra of PANI/PEDOT film in various pH buffer solutions.

Acknowledgement: This research was funded by a grant (No. S-LAT-17-1) from the Research Council of Lithuania.

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Surfactant – polyelectrolyte interactions studied by microcalorimetry and light scattering methods

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This study presents the formation of polyelectrolyte complexes from hyaluronan of three different molecular weights with oppositely charged surfactants CTAB and septonex. The aggregation behavior was observed from the microcalorimetric (isothermal titration calorimetry, ITC) and light scattering point of view (DLS, SEC-MALS). The experiments were performed in water at 25°C. The aim was to determine the aggregation concentrations of the surfactants (CAC).

The aggregation of hyaluronan was studied previously by Krouská et al. [1] but the published data for septonex are still limited. The results from a DSL method (particle size measurement, Zetasizer Nano ZS, Malvern Instruments) showed decreasing critical aggregation concentrations of both surfactants with increasing molecular weight of hyaluronan and vice versa. The microcalorimetric experiments (TAM III, TA Instruments) showed higher values of CAC mainly for lower molecular weight of hyaluronan. Furthermore, there is a slight shift of CAC between CTAB and septonex (from 3 to 2 mmol·dm⁻³) as presented in Figure 1.

The samples of hyaluronan were measured using SEC-MALS (Agilent Technologies, Wyatt Technology, USA) method before and after the aggregation with surfactants. The rapid decrease of sample molecular weight proved that almost all polyelectrolyte molecules formed the aggregates with surfactants – the aggregates remained on the filter (0,45 µm) while filtering the sample before measurement.

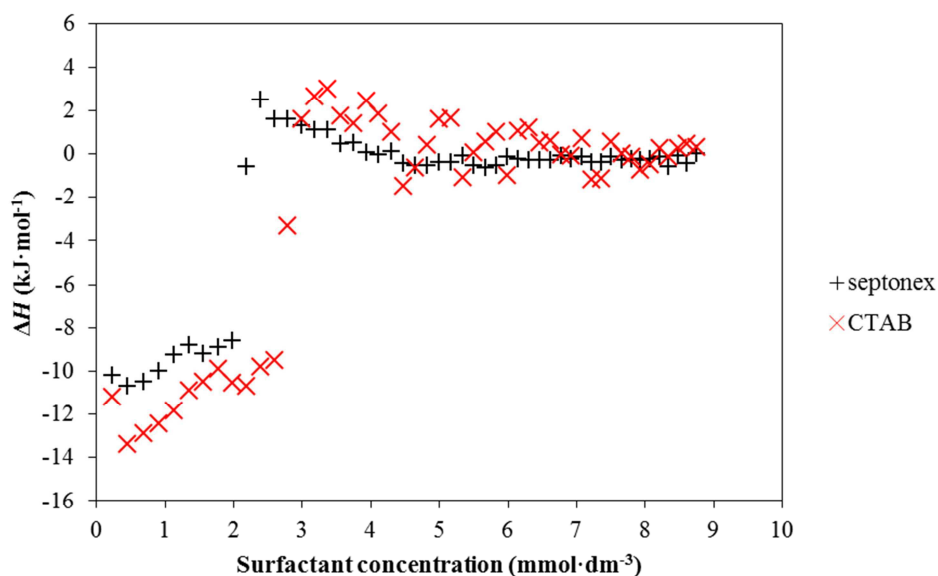


Figure 1. Effect of high molecular weight hyaluronan on aggregation behavior of CTAB and septonex.

Acknowledgements: This work has been supported by project “Materials Research Centre at FCH BUT – Sustainability and Development” No. LO1211 of the Ministry of Education, Youth and Sports of the Czech Republic and by the Czech Science Foundation (Project No. 16-12477S).

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Chemical 3D mapping of polymer composite fillers

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Particulate-polymer composites are used for a wide range of applications including paints, coatings, conductive materials and adhesives. Such composites commonly consist of two key components: (I) a polymer matrix and (II) fillers/particles. The matrix keeps the geometrical shape of the composite and may be adhesive, while the particles give the material application specific properties depending on the filler type. Filler types include pigments for coloring, solid particles for rigidity, conductive particles and hydrocolloids (HC) for viscosity modification or moisture absorption [1].

The particle dispersion, during material processing e.g. mixing and pressing, is important for the final material functionality. Specific applications require a percolated network of particles as well as a well-defined number of particles locally distributed near the composite surface [2]. Methods to investigate local particle dispersion and distribution are therefore needed for rational material formulation and processing. The bulk dispersion can conveniently be investigated using dynamic mechanical analysis (DMA). However, local differences in particle distribution e.g. at the composite surface cannot be distinguished from the bulk properties using DMA [3].

Here, we demonstrate a non-destructive, label-free method to map fillers dispersed in a polymeric matrix using coherent anti-Stokes Raman scattering (CARS) microscopy. CARS microscopy provides high resolution, video-rate imaging with chemical contrast obtained by detection of specific intrinsic molecular vibrational frequencies [4]. We specifically studied systems consisting of hydrocolloids dispersed in a hydrophobic polymer matrix, which are relevant for skin adhesives. We successfully obtained high filler-matrix contrast using vibrational frequencies characteristic for chemical differences in the system. Video-rate sequences were subsequently acquired during water exposure to probe real-time structural changes during composite aging.

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The structural, thermal and dynamic behavior of the thermoresponsive polymer poly(N-isopropylmethacrylamide)

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Poly(N-isopropylmethacrylamide) (PNIPMAM) is a thermoresponsive polymer, exhibiting lower critical solution temperature (LCST) behavior in aqueous solution. Compared to the well-investigated poly(N-isopropylacrylamide) (PNIPAM), which has similar chemical structure, PNIPMAM has a higher transition temperature (43 °C [1] instead of 32 °C). This may be due to the presence of the additional methyl groups on the vinyl backbone, which lead to steric hindrance and weaken the intramolecular interactions [2,3]. In order to understand how these effects along with the hydrophobic interactions influence the phase behavior of aqueous solutions of PNIPMAM, we investigate the temperature-dependent phase behavior of PNIPMAM in D₂O using turbidimetry, differential scanning calorimetry (DSC), small-angle neutron scattering (SANS) and dynamic light scattering (DLS), covering a large concentration range. We find that the phase transition consists of two steps, namely (i) hydrophobic aggregation at ~39 °C, as evident from turbidimetry and SANS, and (ii) the chain collapse and water release at ~44 °C, as evident from DSC, DLS and SANS.

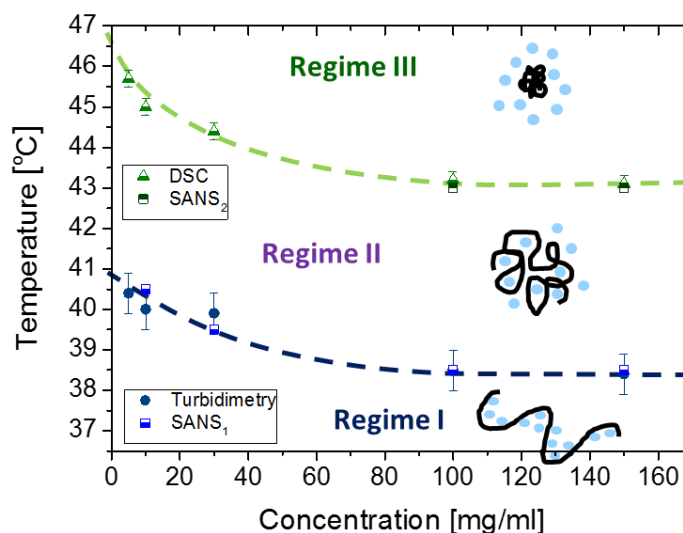


Figure 1. Transition temperatures from different methods in dependence on concentrations, as indicated.

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Morphology of Thermoresponsive Molecular Brushes With Copolymer Side Arms in Dilute Aqueous Solutions

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Molecular brushes are densely grafted polymers composed of a polymeric backbone and side arms. Their complex architecture can easily be adjusted by changing the side arm architecture. A series of amphiphilic molecular brushes with diblock or random copolymer side arms is investigated, where the side arms contain both poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) segments [1,2], both having lower critical solution behavior in aqueous solution, leading to a conformational transformation of the side arms, and thus the entire molecular brushes.

In the present work, the temperature-dependent conformation of the molecular brushes with PPO-*r*-PEO and PPO-*b*-PEO side arms, having the same PPO weight fraction, is studied in dilute aqueous solution. Figure 1 shows the experimental results from dynamic light scattering. As temperature is increased, the brush with random copolymer side arms shows a strong increase in hydrodynamic radius, R_h , at a temperature of 41 °C, where the molecular brushes aggregate due to the collapse of PPO. In contrast, for the molecular brush with block copolymer side arms, R_h increases gradually, starting at 58 °C, before the aggregation sets in at 68 °C. Small-angle neutron scattering gives further detailed information of the underlying temperature-dependent conformational changes. This model system provides insight into the effects caused by the thermoresponsive behavior of the PPO and PEO segments under the different steric constraints.

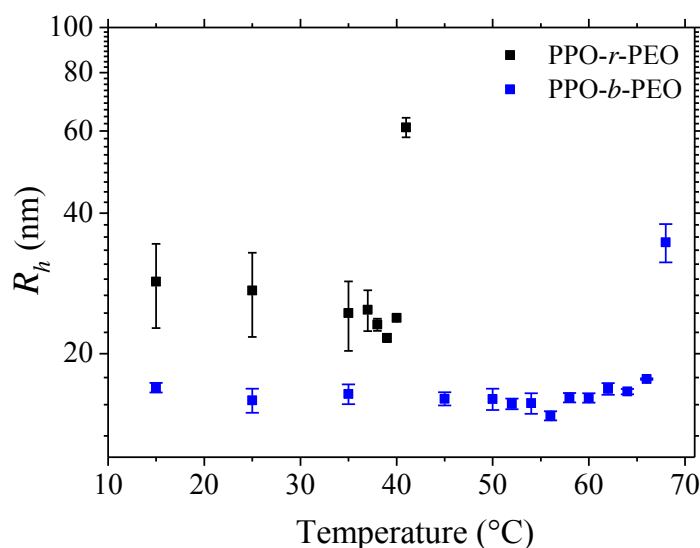


Figure 1. Dependence of hydrodynamic radius, R_h , on temperature of molecular brushes with PPO-*r*-PEO side arms (black squares) and PPO-*b*-PEO side arms (blue squares).

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Design, preparation and coloration approaches with new anthraquinone dyes in supercritical carbon dioxide

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When dyeings in super critical CO₂, non-polar dyes are used to enable dissolution. Polyester (polyethylene terephthalate or PET) is also non-polar and during the dyeing process, the dye molecules can diffuse into the polymer matrix, where they are physically bonded. Because of its non-polarity, polyester can be dyed in super critical CO₂ with non-reactive, so-called disperse dyes.

Anthraquinone disperse dyes play a vital role in the dyestuffs industry. These molecules are more stable under the experimental conditions and as well as in various organic solvents when during the calibrations. Molar absorption coefficients of anthraquinone dyes are considered to spectroscopic determination even at very low concentrations.

Herein, we have synthesized novel anthraquinone dyes from readily available starting materials by using simple and convenient methods. All the synthesized compounds were characterized by ¹HNMR, ¹³CNMR, UV and HRMS. Dyeing of polyester fabric with anthraquinone blue dyes performed under supercritical carbon dioxide conditions. Most of the anthraquinone dye derivatives exhibited excellent blue color property under supercritical CO₂ conditions.

The mechanism involved in the disperse dyeing of polyester fabric is the CO₂ penetrates and swells the polymer matrix, thereby facilitating the diffusion of dye molecules through the polymer. Upon supercritical state, CO₂ molecules exit the shrinking polymer fibers and the dye molecules are retained in the matrix medium.

Acknowledgements:

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Effects of nitroaromatic pollutant integration on the structure of plant lignin

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Lignin is a complex and second most abundant natural polymer. It presents a potential source of useful aromatic compounds. Lignin is synthesized in plant cell walls from 3 monolignols: p-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S). Its synthesis proceeds through radical-coupled reactions mediated by enzymes such as peroxidases and laccases. Lignin is important for providing structural integrity of the plant cell wall, rigidity of the stem and enabling transport of water through the plant vascular system [1].

One of the compounds released during the pyrolysis of wood lignin is guaiacol (GUA). Secondary transformations of GUA in polluted air result in the formation of its nitrated derivatives (NGs, such as 4-nitroguaiacol (4NG) and 4,6-dinitroguaiacol (DNG)). These compounds share their core structure with lignin monomers (i.e. aromatic ring with hydroxyl and methoxy moieties, Figure 1). By precipitation, GUA and NGs are deposited onto the Earth's surface, where they can be uptaken by plants.

Our research on the effects of GUA and NG pollutants on plants showed that DNG influences plant growth most severely. GUA has only a minor impact on plant growth. We also observed that plant uptake of DNG proceeds at the slowest rate, whereas GUA uptake is the fastest. These results indicate that the more nitro moieties the compound possesses the greater threat it poses to plants.

Given the similarities between GUA, NGs and biological monolignols (Figure 1), it is reasonable to assume that GUA and NGs can be integrated into the lignin polymer. This would lead to a weakening of the polymer's integrity because these compounds cannot form the same types of bonds as monolignols due to the absence of the hydroxypropene side chain (or the presence of nitro moieties), preventing the crosslinking.

Due to the complex and relatively unknown structure of lignin, simulations and molecular dynamics can be useful tools for predicting certain properties of the complex polymer [2]. Using these tools allows insight into the lignin structure and characteristics after GUA and NGs were integrated into the polymer [3]. Since DNG possesses two nitro moieties at positions necessary for bond formation, it is anticipated to have the greatest impact on the integrity of plant lignin. GUA and mononitrated NGs are expected to have less of an impact on the polymer than DNG.

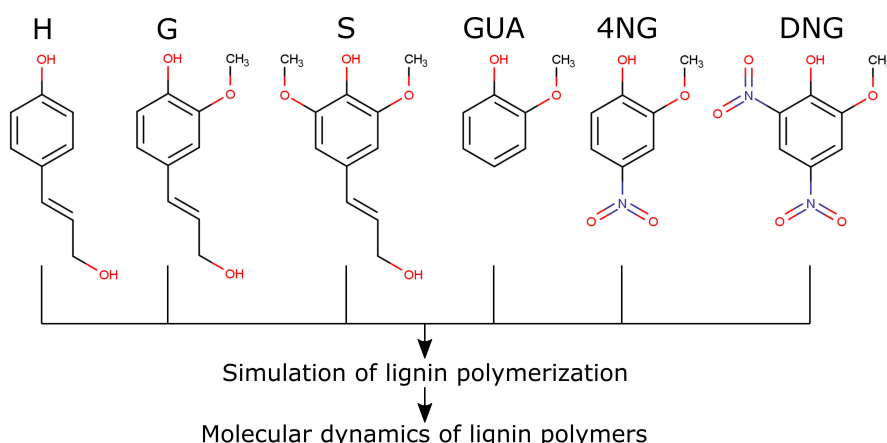


Figure 1. A short diagram of simulations involving lignin structure and properties. Compound acronyms are explained in the text.

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Transport of organic dyes in biopolymeric hydrogels

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Biopolymeric hydrogels based on oppositely charged polyelectrolytes and surfactants can contain micelle-like nanostructures potentially usable for medical applications. Integration of the nanocontainers for pharmaceutically active substances into hydrogel matrix can solve problems with their hydrophobic nature. Interactions of biopolymeric electrolytes with oppositely charged surfactants which can result in dissolving hydrophobes in micelle-like nanocontainers formed by surfactants. In this study, hydrogels were prepared either from hyaluronan and cationic surfactant septonex (carbethoxypendecinium bromide) or from diethylaminoethyl dextrane and sodium dodecylsulphate as described previously [1]. Nile red was used as a model diffusion probe in order to investigate the release of active substances from hydrogel. The probe was incorporated into hydrogel structures in their preparations and its release was monitored in time by UV/VIS spectrometry. It was found that the equilibrium between the formed hydrogel and supernatant can be established after several days or weeks. A re-arrangement of diffusion probe in the hydrogel structure was connected with the decrease in concentration of supernatant. Therefore, some molecules of dye were incorporated into the hydrogel after its preparation. If the supernatant was replaced by pure solution without dye, a new equilibrium was established and the diffusion of dye from the hydrogel was observed. Diffusivity of dye in hydrogels was determined on the basis of mathematical model described our previous work [2].

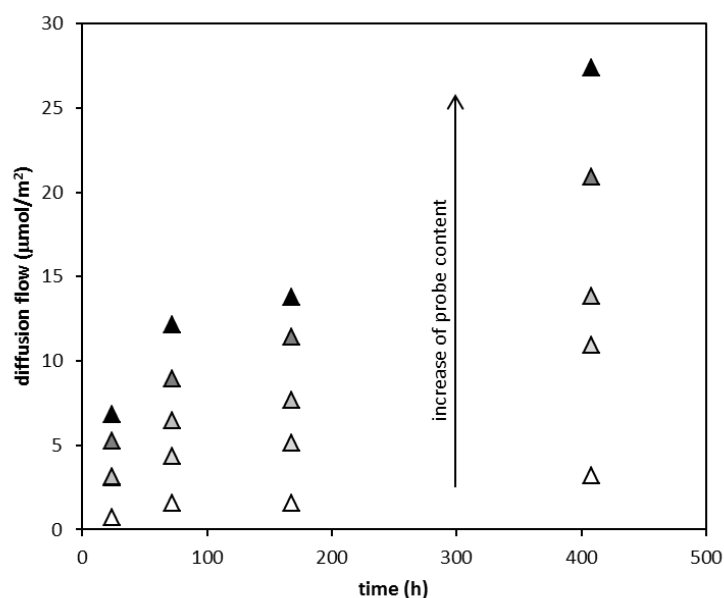


Figure 1. Time development of diffusion flow from supernatant into diethylaminoethyl dextrane-SDS hydrogel

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Influence of polymer coatings on biological soil removal for hard surfaces

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The removal of biological soils from hard surfaces is usually been achieved by using detergents on already deposited soils. Another possible approach consists on developing materials that are resistant to soil deposition, thereby maintaining the surface to always be clean. A popular attempt is to use an anti-attachment strategy wherein a surface is pre-treated with a polymer coating. In order for this strategy to be effective, it is necessary to develop a deep understanding of the physical interaction forces at play. Biological soils can be extremely complex since they may contain multiple molecules with different hydrophobicity and charges [1]. Colloidal particle deposition on homogeneous surfaces has been widely described in the classical DLVO (Derjaguin, Landau, Verwey, Overbeek) theory of colloidal stability [2,3], in which the total interaction is described as the total sum of van der Waals attractive forces and electrostatic double layer interactions (can be either repulsive or attractive). However, the DLVO theory does not take into consideration short-range interactions that are important for adhesion like polar interactions or Brownian motion movement forces. A deep mechanistic understanding is therefore necessary in order to design polymer coatings for household surfaces that will yield the best performance against biological soil deposition at common cleaning conditions.

Here, a range of structurally and chemically different polymers have been chosen to study deposition kinetics and interactions on three representative household surfaces, being glass, polycarbonate and stainless steel. The experiments have also been carried out at two common cleaning pH values, 3 and 11. The deposition kinetics and the surface coverage of the polymer coatings was determined by means of surface plasmon resonance (SPR), while streaming potential and laser Doppler electrophoresis (LDE) measurements were performed to evaluate surface charge and colloidal charge, respectively. This information was combined with scanning electron microscopy (SEM) images of the deposited polymers.

The biological soil deposition on the treated surfaces was followed by means of SPR, combined with fluorescent measurements where adsorption isotherms were generated by indirectly measuring residual organic soil concentration in solution after equilibration with treated surfaces. The influence of the soil deposition on the surface charge has also been studied by means of streaming potential measurements.

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Temperature-programmed synthesis of responsive micron-sized poly(*N*-Vinylcaprolactam) microgels

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Microgels or nanogels are cross-linked polymer networks that can respond to environmental change like temperature or pH. When triggered, they collapse or swell in solvents, while preserving their 3D structure. Micron-sized microgels can have plenty of interesting applications in crystallization studies, microlensing or mimicking cells. Microgels with the size above 10 μm can be synthesized using microfluidics [1]. However, very low yields and specific equipment requirements lead to high demand on synthesis of microgels via dispersion polymerization approaches. Moreover, the typical size of such gels synthesized using standard batch polymerization reactions is in nanometer scale. Thus, particles ranging from 1 to 10 μm are hardly accessible, and means to obtain them need further investigation. Micron-sized poly(*N*-Isopropylacrylamide) (pNIPAm) microgels have been obtained previously [2]; however, known toxicity and suspected cancerogenicity of pNIPAm disqualifies the usage of these gels in medical applications.

In contrast to pNIPAm, poly(*N*-Vinylcaprolactam) (pVCL) is non-toxic and biocompatible [3], making it a great candidate in medical and biomaterial fields. Here, for the first time, we have synthesized temperature-responsive pVCL microgels with large diameter (1–5 μm) via aqueous, surfactant-free precipitation polymerization. The size control was achieved by employing programmed temperature ramp during the nucleation stage of polymerization. In this work, the influence of various parameters such as monomer, cross-linker and initiator concentration, rate of temperature ramp, start and end temperature as well as dosing of the reagents was investigated. We were able to obtain microgels in different size ranges, depending on parameters altered. To best characterize such big but soft particles confocal microscopy was utilized. *In-situ* dynamic light scattering measurements as well as in-line reaction calorimetry, where heat flow of the reaction can be monitored, were carried out. Consequently this study hopes to give more insight and understanding about the formation mechanism of larger pVCL microgels.

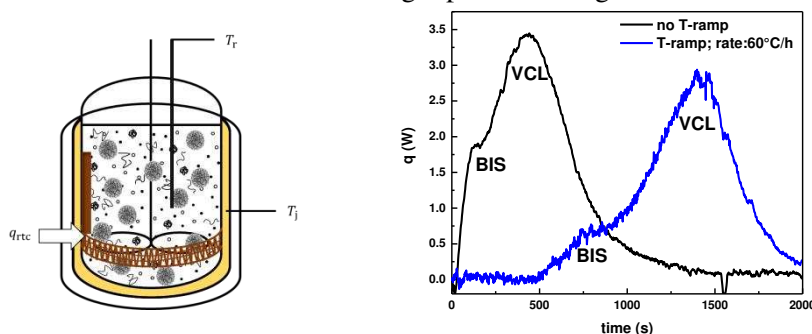


Figure 1. Right: Heat profile of VCL microgel synthesis from in-line reaction calorimetry with and without temperature ramp (T-ramp), VCL as the monomer and BIS (*N,N'*-Methylenebis(acrylamide)) as the cross-linker; left: schematic illustration of reaction calorimeter setup.

Acknowledgements: This work was performed as part of Collaborative Research Center 985 “Functional Microgels and Microgel Systems”.

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New approach to native cellulose aqueous solutions characterization

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Many important cellulose applications involve, at some stage, dissolution and, for different reasons, this task is typically complicated. The development of inexpensive and environmentally friendly alternatives, with less harmful compounds, to the solvents used nowadays is thus of great interest in the industrial circle. Cellulose dissolution is a challenging process which is often very sensitive to the solvent characteristics such as pH, temperature or presence of additives [1,2].

How well dissolved cellulose is in solution and how it organizes are fundamental questions far from being totally understood. Additionally, the typical low pH required for dissolving cellulose in acidic solvents limits the use of typical characterization techniques. In this respect, Polarization Transfer Solid State NMR (PT ssNMR) and cryo-TEM emerge as reliable alternatives. In this work, combining PT ssNMR, microscopic techniques (cryo-TEM) and rheology, different acidic systems based in aqueous phosphoric acid with and without other additives are investigated. The studied solvent systems are capable to efficiently dissolve cellulose, although degradation occurs to some extent. PT ssNMR is capable to identify the liquid and solid fractions of cellulose, the degradation products and it is also sensitive to gelation. A transition from solid to liquid is observed, in solutions containing 10wt% cellulose, as the temperature rises from 25° to 60°C and can be followed both with rheology and PT ssNMR.

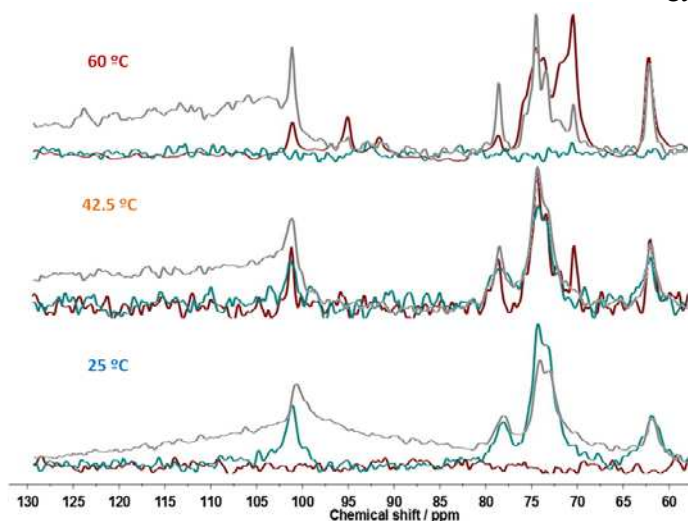


Figure 1. PT ssNMR of 10wt% cellulose in aqueous phosphoric acid solution at different temperatures.

Acknowledgements: The Coimbra Chemistry Centre, CQC, supported by FCT, through the project PEstOE/UI0313/2013 is acknowledged. The authors also acknowledge to ESMI (European Soft Matter Infrastructure) by the financial support (Proposal E E160700746).

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IR spectroscopy characterization of water in polyelectrolyte-surfactant hydrogels

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Oppositely charged polyelectrolytes and surfactants can form, at specific conditions, hydrogels containing micelle-like nanostructures. Due to the hydrophobic core of the micelles, these materials are capable of solubilizing hydrophobic substances within hydrophilic soft solid matrix. Such hybrid materials can be subject of interest for medical applications. Their structure is not fully resolved but the micelles are believed to form the (electrostatic) crosslinks of the gel network and to connect the long polymer chains. Water in these hydrogels forms not only the dispersion medium but also creates hydration shell around micelles and polymer chains. The state of water in the hydrogels and its role in their structure is also an interesting and important issue. In this study we report on the characterization of water as reflected in infrared spectra.

Hydrogels were prepared either from hyaluronan and cationic surfactant septonex (carbethoxypendecinium bromide) or from diethylaminoethyl dextrane and sodium dodecylsulphate as described previously [1]. FTIR spectra were obtained by means of an Attenuated Total Reflection (ATR) technique using a Nicolet iS50 spectrometer. The IR-Series spectra were recorded over the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} and were the average of 8 scans with total collection time 600 min to see the release of water from hydrogel. The broad and intense O–H stretching absorbance band of bulk water in polyelectrolyte-surfactant hydrogels is the result of overlapping components [2]. The frequencies of each component were determined using Fourier self-deconvolution method (FSD). The measured spectra were deconvoluted in the wavenumber range of 3700–3000 cm^{-1} .

The IR-Series and FSD spectra of bulk water in polyelectrolyte-surfactant hydrogel are shown in Figure 1. The FSD spectra contain a sharp and intensive peak at 3242–3228 cm^{-1} corresponding to subpopulation of water pentamers which are characterized strong intermolecular interactions via linear hydrogen bonds. The peaks observed at 3404–3392 cm^{-1} are ascribed to subpopulations which are more coupled in a tetrahedral structure and contain some non-linear and/or absent hydrogen bonds between them. The appearance of water molecules in a highly disturbed hydrogen bond network is revealed in the 3568–3550 cm^{-1} frequency zone.

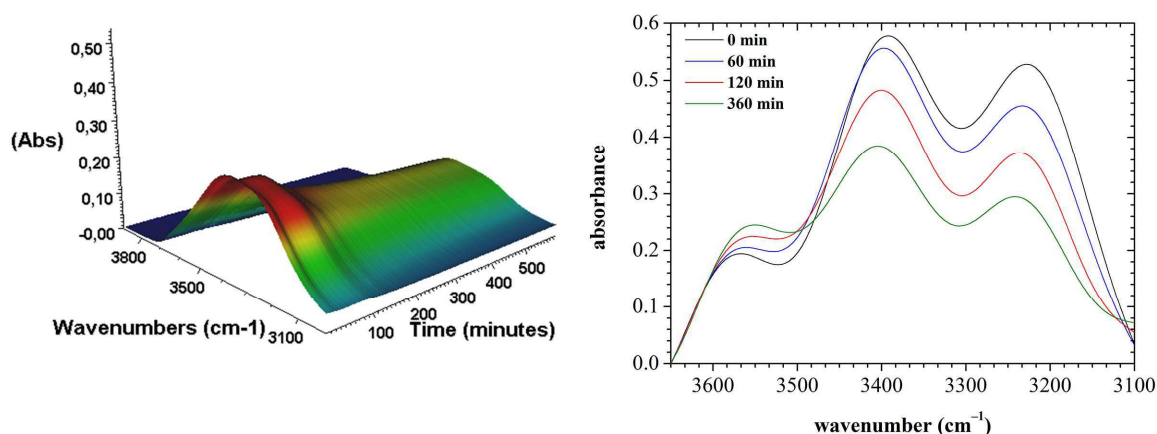


Figure 1. IR-Series (left) and FSD (right) spectrum of diethylaminoethyl dextrane-SDS hydrogel

Acknowledgements: This work was supported by the Czech Science Foundation, project No. 16-12477S and by the project LO1211 from National Programme for Sustainability I (Ministry of Education, Youth and Sports, Czech Republic).

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Effect of Magnetic Nanoparticle Distribution in PNIPAM Microgels on their Magnetic Response

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A magnetic field as a trigger allows a fast switching of properties of magnetic materials. Embedding for instance magnetic nanoparticles (MNP) into polymeric microgels (ferrogels) allows fast changes in shape of the ferrogels. This offers future application as sensors and actuators and in drug delivery systems, using the magnetic nanoparticles as guidance and triggers.

Here, a thermosensitive poly-N-isopropylacrylamide (PNIPAM) microgel was chosen as matrix for the CoFeO₄ nanoparticles [1]. In order to understand and to control the magnetic properties of the ferrogel, the mutual effects of the internal structure of the microgel and the distribution of MNP have to be understood. Therefore it is of high interest to get a deeper insight into the distribution of the crosslinker (BIS) of the microgel and the MNP distribution.

To tailor the structure of the microgels, they were synthesized by two different methods: the batch method [2] which leads to an inhomogeneous distribution of the cross-linker and the feeding method [3] which produces homogeneously crosslinked microgels.

The bare microgels and the magnetic microgels were investigated with dynamic light scattering (DLS), atomic force microscopy (AFM), transmission electron microscopy (TEM) and Zetasizer. Beside the measurement of the microgel characteristics first measurements of the magnetic response of the magnetic microgels will be shown.

The results show that the homogeneity of the crosslinker distribution is the key factor for a homogenous distribution of CoFeO₄ nanoparticles inside the microgels. A homogeneous distribution in turn offers a higher response of the magnetic microgel to an externally applied magnetic field as previous experiments have shown [1]. Two systems are compared, one with a heterogeneous structure close to a core/shell structure and one with isotropic distribution of the MNP inside the microgels. As an example a magnetic microgel is shown in figure A detailed analysis of the 2D-TEM images allows a reconstruction of the 3D distribution of MNP.

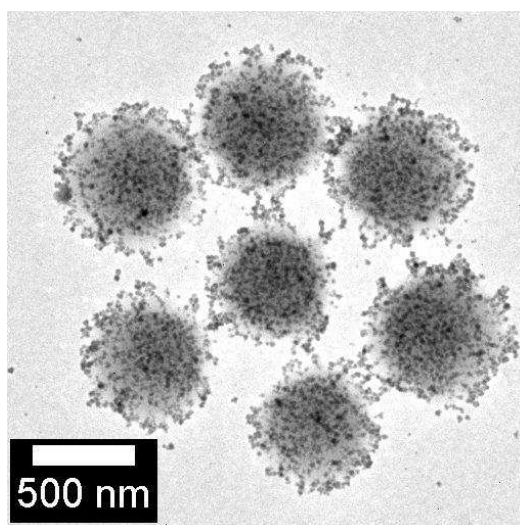


Figure 1. TEM picture of magnetic microgels.

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Streaming potential and UV VIS analyses of fabrics modified by surface modification polymers

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Polymers have become a necessary part of laundry detergent formulations because of the benefits that they could bring during the washing process. Anti-redeposition agents, dye transfer inhibitors and soil release polymers (SRP) are the most common and interest in understanding their deposition mechanism on different kind of fabrics is growing. [1] For instance, hydrophobic fabrics like polyester show a high affinity with hydrophobic soil. Surface modification, performed by SRPs, could increase their cleanability by providing soil repellency or improved soil release in the wash. [2] New generation polymers are gaining attention because of their ability to increase cleaning efficiency even at low dosage. Moreover, these polymers could deliver benefits even at low temperature and in short washing cycle.

In this poster, we use streaming potential to assess the effectiveness of polymer deposition and the subsequent surface modification of substrates. To measure this for irregular surfaces (fabric fibers for instance), we employ Surpass 3 to assess polymer adsorption. [3-4] The observed magnitude of changes in streaming potential was found to depend strongly on the polymer's chemical structure (e.g. charge) and concentration. Once deposited onto fabrics, the modification in surface charge affects its interaction with the soil. This poster will show how streaming potential values could predict cleaning benefits from the polymer's fabric surface modification.

Streaming potential has also been used to evaluate the impact of the interaction between the polymer and different types of surfactant (anionic, cationic, nonionic) ubiquitous in detergent formulations on the deposition of SRPs and the subsequent change in the fabric surface charge. Moreover, the surface charge changes detected via streaming potential could help in understanding the polymer-surfactant interaction occurring in the bulk solution. Consequently, these results could help in understanding preferential deposition of surface modifying agents even in a real wash condition.

Since it is extremely hard to measure directly the polymer deposit on surfaces, we use Cary 60 UV/Visible online spectrophotometer to generate the adsorption isotherm of the polymer by indirectly measuring the residual polymer concentration in solution before and after the interaction with fabrics. The percentage of polymers adsorbed is used to assess which polymer is more efficient for soil repellency at low dosage.

Acknowledgements: This project Bioclean has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 722871.

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Poly(sulfobetaine)/polycation complexation in water and on interfaces

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Aqueous solutions of the zwitterionic polymer, poly(sulfobetaine methacrylate) (PSBMA) exhibit upper critical solution temperature (UCST) that is modulated by salts and various other solutes. The polymer also forms stable complexes with charged molecules, such as surfactants and fluorophores, as inferred from isothermal titration calorimetry (ITC) and spectroscopic techniques.

We report here the preparation of macromolecular complexes between PSBMA and the polycation, poly(allylamine hydrochloride) (PAH), focusing on the interactions between the two polymers deposited on solid substrates by a layer-by-layer process. Surface plasmon resonance spectroscopy (SPR) and quartz crystal microbalance with dissipation (QCM-D) were used to determine the thickness, water content, and rheology of the multilayers. We observed that the polymers molar mass and the solution salinity affect the properties of the films. The PSBA/PAH films properties were compared to those of previously reported macromolecular complexes of polycations and polyzwitterions with phosphorylcholine repeat units.

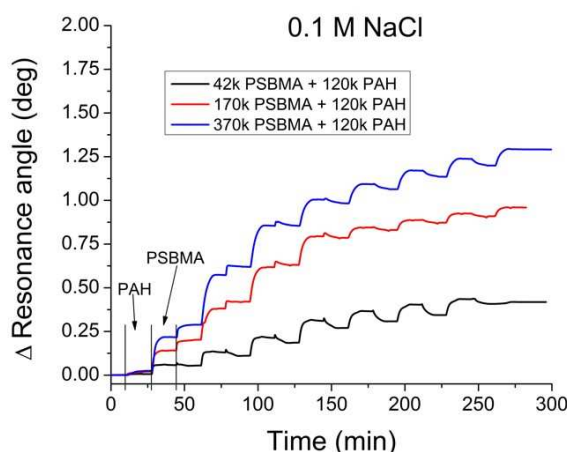


Figure 1: Molar mass dependent kinetics of the formation of PAH/PSBMA films monitored by SPR .

***In-situ* optoelectronic properties of a conducting polymer film studied by means of electrochemical spectroscopic ellipsometry**

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The dielectric function contains important information about the optical and electronic properties of conducting and semiconducting materials. In the focus of the presentation is the experimental dielectric function of a hydrated poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film, determined from the *in-situ* measured ellipsometric VIS/NIR spectra under varied conditions of electrochemical doping[1]. In the experiments, the electrochemical potential of the film was controlled by applying an external equilibrium potential equal to the electromotive force at the PEDOT:PSS thin film electrode in a three electrode cell. The main electronic transition (cf. Fig. 1) was resolved from the free electron absorption by fitting the Tauc-Lorentz-Drude dielectric function[2], and notably exhibits an isosbestic point around 1 eV. The electrical conductivity of the film was calculated from the Drude term, and was drawn into relationship with the main electronic transition by applying a redox isotherm under assumption of a constant density of states. The fitted Nernst slope of only 12 mV is an evidence of very strong electrostatic repulsions between the oxidized EDOT⁺ sites in doped PEDOT, which is in turn responsible for a low capacitance of the electrical double layer at the PEDOT "surface". The latter gives rise to an electrochemical potential range (about 0.5 V wide) in which PEDOT:PSS exhibits almost exclusively capacitive behavior. This result corroborates the hypothesis that within the above potential regime, the operating mechanism for the organic electrochemical transistors implementing a PEDOT:PSS channel invokes predominately the field effect rather than redox reactions.

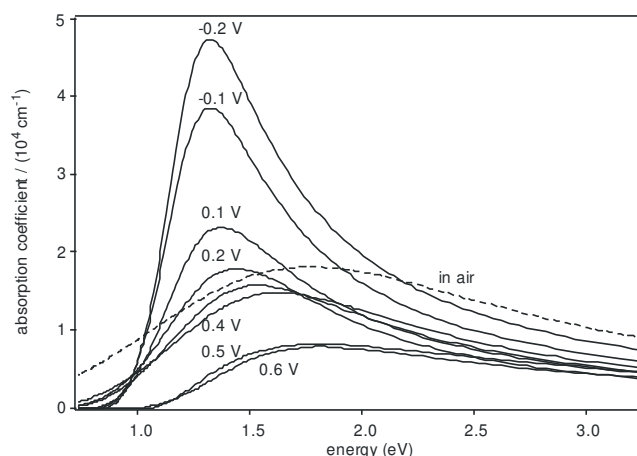


Figure 1. Ordinary absorption coefficient of the PEDOT:PSS thin film in 0.1 M KCl solution for varied electrochemical potential vs. Ag/AgCl electrode, calculated from the pure Tauc-Lorentz term (subtracted Drude) in the dielectric function. The latter was fitted from the experimental ellipsometric spectra.

Acknowledgements: This work was performed within the project Organic bioelectronics (FP7-PEOLPLE-ITN-2013 PITN-GA-2013-607896), and supported by the European Fund for Regional Development and the Ministry of Science, Education and Sports of the Republic of Croatia under the project Research Infrastructure for Campus-based Laboratories at the University of Rijeka (grant number RC.2.2.06-0001)

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Self-assembly properties and kinetics of Amphiphilic drug molecules in oppositely charged microgels

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Cationic-amphiphilic molecules are an important group of active substances which are commonly used in cancer therapy, as antidepressants and antihypertensive agents. These molecules are characterized by having both hydrophobic groups and cationic hydrophilic groups. They have the ability to aggregate in a solution in a surfactant-like manner. The aggregation pattern can be quite different depending on the structure of the molecule[1].

Microgels, on the other hand, are cross-linked polymer networks which are sensitive to environmental variables such as temperature, pH and ionic strength. The swelling/deswelling concept of the microgels is very important in drug release profile[2]. By this means, a large amount of drug of opposite charge can be loaded inside the microgels by ion exchange mechanism[3] to deliver it to the desired target inside the body[2,4].

In this project we want to improve the fundamental understanding of the drug-aggregation inside microgels. Micromanipulator-assisted light microscopy was used to investigate single microgels during loading, as in figure 1, and release of the drug. Small/Wide angle X-ray Scattering SAXS/WAXS was used to determine the shape of the aggregate inside the drug-loaded microgels, while the binding isotherm was determined by using μ diss profiler (pION). A single gel microscopy technique, a micromanipulator-assisted light/fluorescence and confocal microscopy, in a small liquid volume[5] will be used to investigate the spatial distribution of the drug inside microgels at intermediate levels. Results show differences in deswelling kinetics and in binding isotherm between Amitriptyline or Adiphenine (Cationic-amphiphilic drugs) and Cationic surfactant dodecyltrimethylammonium bromide (which was used earlier as a model molecule).

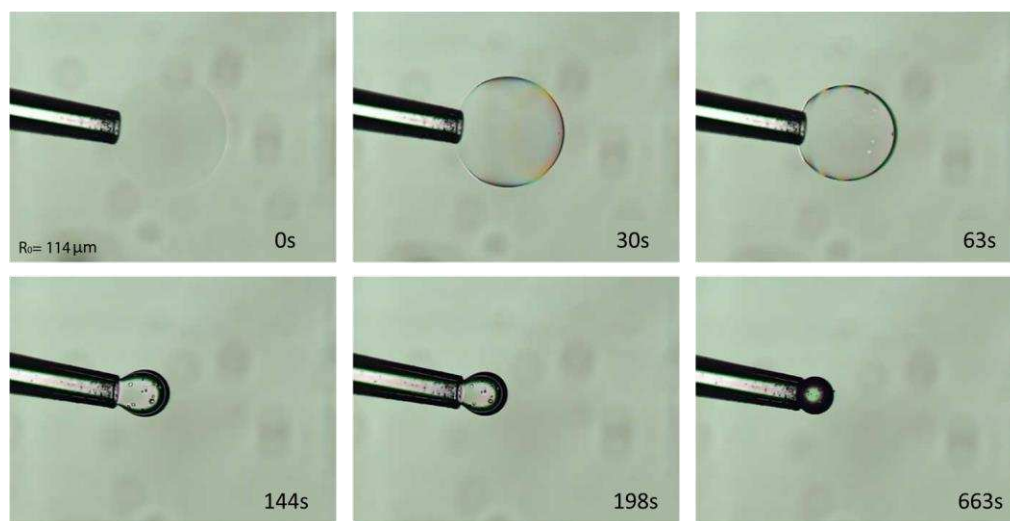


Figure 1. A single microgel with radius 114 μ m held by Micromanipulator, deswelling kinetics in a flow of Amitriptyline.

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Temperature induced conformational change and hydration of poly(methacrylic acid)

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Poly(methacrylic acid) (PMAA) is an interesting polyelectrolyte, the conformation of which may be tuned by pH and/or ionic strength but also by temperature.

PMAA have been reported a long time ago to form thermoreversible gels which are obtained at low pH when PMAA stands in its acidic conformation ($\alpha \sim 0$). This temperature induced phase separation of concentrated PMAA solutions has been poorly addressed in literature. Both intermolecular hydrogen bonds between carboxyl groups on neighboring chains and hydrophobic interactions induced by the methyl group lead to physical cross-links that are assumed to be responsible for the gelation process. Rheological measurements on concentrated solutions of PMAA have shown the formation of a gel while heating, (fig. 2.a).

This behavior is associated with a LCST observed in a simple transmittance experiment using the same temperature ramp of 1°C/min, (fig. 1.a). In order to assess the transition at a nanometric scale, SANS experiments were carried out on concentrated solutions at a temperature above the LCST (fig. 1.b). These results were also correlated with ²H NMR relaxation experiments performed on solvent molecules.

In this presentation, we will show that at the nanoscale, the phase transition of PMAA is quiet slow (figure 1.B) in comparison to other LCST behaviour polymers (more than 10 hours for PMAA versus around 15 minutes for PNIPAM for instance). The study of the kinetics of LCST transition will enable us to understand the structure of the gel formed at high temperature.

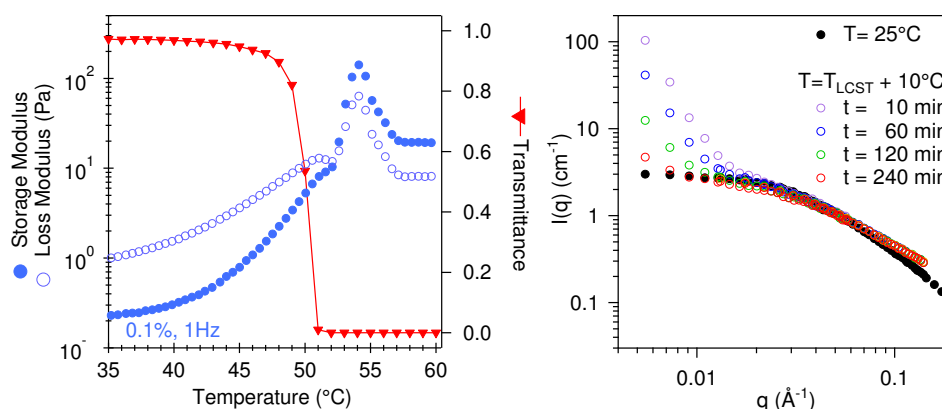


Figure 1. (a) Storage modulus and transmittance results of a 100g/l solution of PMAA in deuterated water at pH=3 as a function of temperature. (b) SANS curves during time of a 120 g/l solution of PMAA in deuterated water at pH=3 heating at 60°C.

Interactions of poly(L-arginine) and poly (L-lysine) with casein in LbL films

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We studied the interactions of poly(L-arginine) and poly (L-lysine) with α - and β -casein and their effect on the conformational changes of polyelectrolyte/casein complexes structure when casein is embedded in multilayer films. We used ATR FT-IR spectroscopy and selected region from 1800 to 800 cm^{-1} as the fingerprint region of the IR spectrum [1] with the most important vibration modes of amides: amide I vibration (measured in the range from 1700 to 1600 cm^{-1}), caused primarily by the stretching of the C=O bonds, and the amide II vibration (from 1600 to 1500 cm^{-1}), caused by deformation of the N-H bonds and stretching of the C-N bonds [2]. The exact frequencies of these bands depend on the secondary structure of the proteins or peptides [3]. Sequential adsorption of PLArg/ α -cas or β -cas and PLL/ α -cas or β -cas layers manifested in an increase of the absorbance of the amide I vibration band with the number of adsorbed layers. PLArg/cas films exhibited larger increase of absorbance at deposition of each consecutive layers (both PLArg and casein) and were thicker than (PLL/cas) films (as evidenced by ellipsometry), whereas, irrespectively of polycation type, thicker multilayers were built with α - than β -casein. Maximum of amide I vibration was at: 1649 cm^{-1} for α -cas, 1640 cm^{-1} for β -cas, 1650 cm^{-1} for PLArg and 1654 cm^{-1} for PLL respectively. For (PLArg/ α -cas)_n films the maximum of amide I vibration band was at 1647 cm^{-1} for 1 and 4 bilayers of the adsorbed film, whereas (PLArg/ β -cas)_n films, it was shifted from 1650 cm^{-1} for 1 bilayer to 1643 cm^{-1} for 4 bilayers. Similar effects were observed for (PLL/cas)_n films. The maximum of amide I band vibration was shifted from 1649 cm^{-1} for one bilayer to 1647 cm^{-1} for PLL/ α -cas bilayers and from 1645 cm^{-1} for one bilayer to 1644 cm^{-1} for four PLL/ β -cas bilayers, respectively.

To elucidate the differences in interactions between caseins and polycations we run the molecular dynamics simulations of the system consisting of short polyelectrolyte chain and polypeptide chains representing several aminoacid sequences – casein fragments. We found that the average interaction energy of PLArg with phosphoserine (PSE) containing polypeptide was significantly higher than of PLL and this difference increased with the number of PSE residues (up to c.a. 7 kcal/mol). Since α -casein contains more PSE than β -casein, it interacts stronger with poly-L-arginine and thicker films are formed.

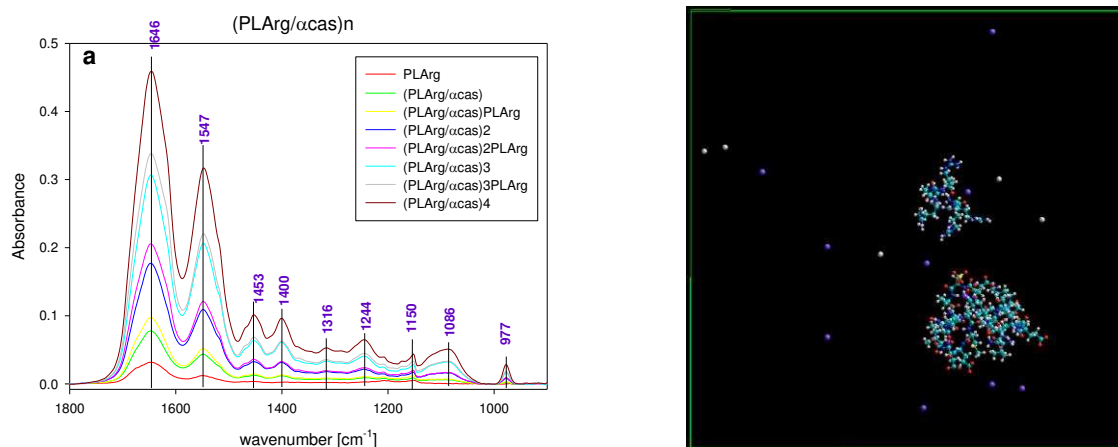


Figure 1. Left – IR spectra of PLArg/ α -cas multilayer films, Right – snapshot from MD simulations.

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The influence of surface properties of polyelectrolyte multilayers applied as support for amphiphilic membranes

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Polyelectrolyte multilayers (PEMs) formed by alternate deposition of polycations and polyanions from their solutions (LbL – Layer-by-Layer) provide a versatile and tunable, biomimetic soft cushion on which amphiphilic membranes, as lipid bilayers with tailored structural characteristics could be formed. However, the mechanistic details for the correlation between PEM properties and bilayer structures are yet to fully emerge. The understanding of the underlying interactions and coupling mechanism between supported lipid bilayer and the polyelectrolyte multilayers is important to biomedical and biosensing applications.

The main goal of presented studies was to examine the structural and chemical properties of selected PEMs and to correlate them with the kinetics of the formation and structure of lipid bilayers, formed by liposome fusion atop a positively charged PEM cushion. Polyelectrolyte films were formed from the following pairs of polycation/polyanion: PDADMAC/PSS, PLL/PGA and PEI/PSS. By combining the quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM), we have investigated the process of the formation of complete SLBs in dependence on underlying cushion formed from various polyelectrolytes. Further, the surface properties of PEMs were investigated in detail. The film thickness and swelling properties were characterized by ellipsometry. The wettability and surface free energy of the PEMs were determined by contact angle measurements using the sessile drop analysis. Additionally, electrokinetic characterization of the studied films was performed by streaming potential measurements and the structure of PEM was characterized by synchrotron X-ray reflectivity. Our results show, that the degree of hydrophobicity and swelling properties of PEMs play a crucial role in the kinetics and the quality of the obtained supported lipid bilayers. In particular, the polar component of the surface free energy is the main factor influencing the selective adhesion, fusion and rupture of the vesicles. Moreover, we have observed that, the highly hydrated polymer chains improved the quality of resulting lipid membrane.

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Determination of free energy and bias depending on tether length in single-molecule unbinding experiments

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Atomic Force Microscopy (AFM) has proven an excellent tool to probe bond attachment and rupture at a single-molecular level by applying Jarzynski's equality under non-equilibrium conditions. Here we probe an amine gold bond using a surface functionalized with polymeric tethers terminated in an amine head group that can interact with a gold-coated AFM tip. Pulling of the tip induces stretching of the polymeric linker and eventually the breaking of the gold amine bond. The integrated work of multiple repetitions of single rupture events allows to estimate the free energy related to the rupture of this well-studied system.

The interpretation of these results, however, shall be regarded with caution as we are in fact using a non-equilibrium process to calculate an equilibrium quantity. Here, we specifically probe how departure from equilibrium and finite sampling alter the estimated parameters. Therefore, we increased the length of the polymeric linker used to anchor our relevant head group (amine) for single-molecular detection. We observed a considerable broadening of the work distributions and a resulting significant bias of the calculated free energy estimates as function of the tether length. This gives place to a growing bias, especially for all probed linkers with a length above 20 nm, where the free energy estimates do not converge anymore because the conditions are further away from thermodynamic equilibrium. From our analysis [1] and that of Gore *et al.* [2], it is clear that far too many repetitions of these experiments (up to tens of millions) would be needed to reach convergence for the longest linkers used, suggesting important experimental design aspects of our method.

From the above figures we determine that theoretically a very extensive sampling would also allow to converge estimates for long linkers to an acceptable bias (below 10-15 %). Short linkers converge considerably more efficiently; however, shorter tethers pose other experimental challenges such as the difficulty to tell the pulling event from background adhesive interactions. As such, a compromise must be found between polymer length and sample size.

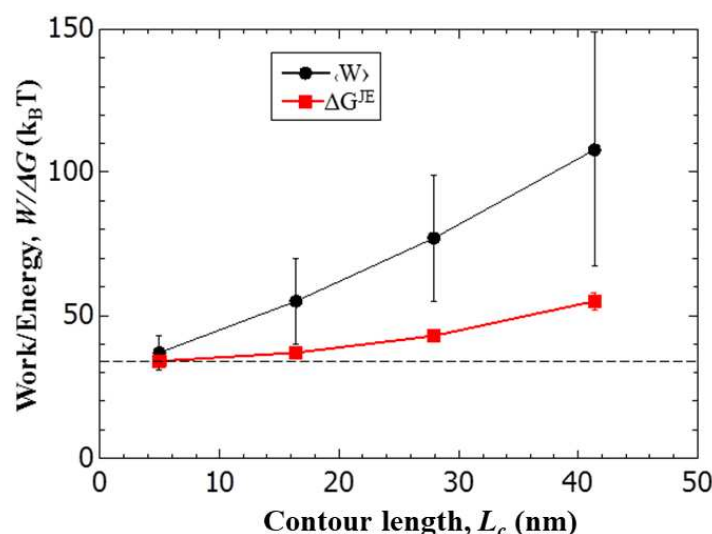


Figure 1. Shift in average work W and free energy estimate ΔG as a function of tether length.

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Polyvinyl alcohol micro/nano-gels prepared through salting out: rationalizing the aggregation process and tuning the microstructural properties

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Polyvinyl alcohol (PVA) is a biocompatible nonionic polymer used in several industrial and pharmaceutical applications [1]. PVA-water mixtures are known to undergo physical gelation, a property that makes PVA one of the most valuable polymer for the production of films and hydrogels with excellent mechanical properties [2]. Although there is an extensive fundamental research on PVA macroscopic hydrogels, the formation and characterization of PVA micro-aggregates in solution has been hardly explored. Related studies would potentially lead to the preparation of novel nanomaterials in which PVA aggregates act as scaffolds, with applications in the fields of catalysis, photonics and medicine. Interestingly, salts are known to modulate the aggregation properties of proteins and polymers in water [4]. In this report, conditions in which salts can be used to drive microscopic aggregation of PVA in water are discussed. Furthermore, an extensive study on kinetic evolution of PVA aggregation induced by NaCl, studied by means of dynamic and static light scattering as well as the microstructural characterization of the aggregates through small-angle neutron scattering and microscopy imaging are presented. The PVA nanogels are formed during an aggregation process that go through a conformational change of the free chains in solutions, which rearrange to form randomly oriented lamellae. These microgels show a "sponge-like" structure, with a chain density that increases with NaCl concentration.

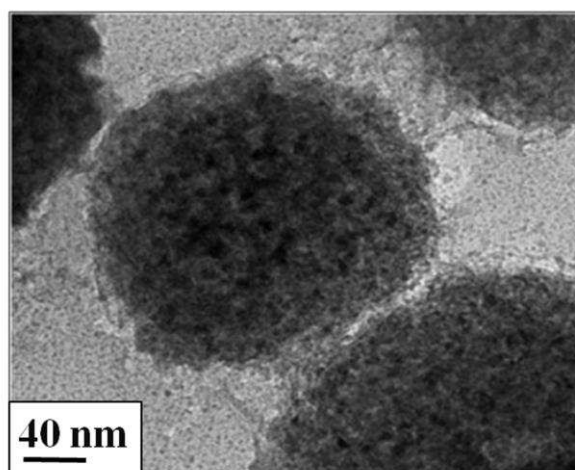


Figure 1. TEM image of PVA nanogels.

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Localisation of Polyelectrolyte and Surfactant at surfaces of aqueous mixture: A neutron reflectivity study

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The surface properties of oppositely charged polyelectrolyte/surfactant mixtures play an important role in colloidal dispersions (foams, emulsions) *e.g.* for cosmetics, cleaning products and in food technology [1]. The general problem is that the total adsorbed amount can be determined but not the amount of each component. We were able to detect polyelectrolytes and surfactants amount separately from each other. Therefore, a strategy with different contrast variations in neutron reflectometry experiments was developed [2]. In addition, we were also able for the first time to localize both components at the air/water interface [3].

Extensive research on such mixtures was already performed with the focus on different polyelectrolytes [2,3]. However, the influence of the ionic strength on the localization of polyelectrolytes and surfactants has not been clear, so far.

The presented work focuses on the impact of salt (LiBr) on the adsorption behavior of mixtures of the anionic polyelectrolyte SPSO2-S220 with the cationic C₁₄TAB. Neutron reflectometry experiments including extensive contrast matching were performed to get insight into the amount and composition of the adsorbed polyelectrolyte/surfactant complexes as well as the localization at the air/water interface.

The results indicate a non-linear relation between surface composition and bulk composition. The salt influences the surface composition and the formed structures at the surface in different manner than in the bulk.

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Super-Resolution Optical Microscopy resolves Network Morphology of Smart Colloidal Microgels

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We present a new method to resolve the network morphology of colloidal particles in an aqueous environment via super-resolution microscopy. By localization of freely diffusing fluorophores inside the particle network we can resolve the three dimensional structure of one species of colloidal particles (thermoresponsive microgels [1]) without altering their chemical composition through copolymerization with fluorescent monomers. Our approach utilizes the interaction of the fluorescent dye rhodamine 6G with the polymer network to achieve an indirect labeling. We calculate the 3D structure from the 2D images and compare the structure to previously published models for the microgel morphology, e.g. the fuzzy sphere model. To describe the differences in the data an extension of this model is suggested [2]. Our method enables the tailor-made fabrication of colloidal particles which are used in various applications, such as paints or cosmetics, and are promising candidates for drug delivery, smart surface coatings, and nanocatalysis. With the precise knowledge of the particle morphology an understanding of the underlying structure-property relationships for various colloidal systems is possible.

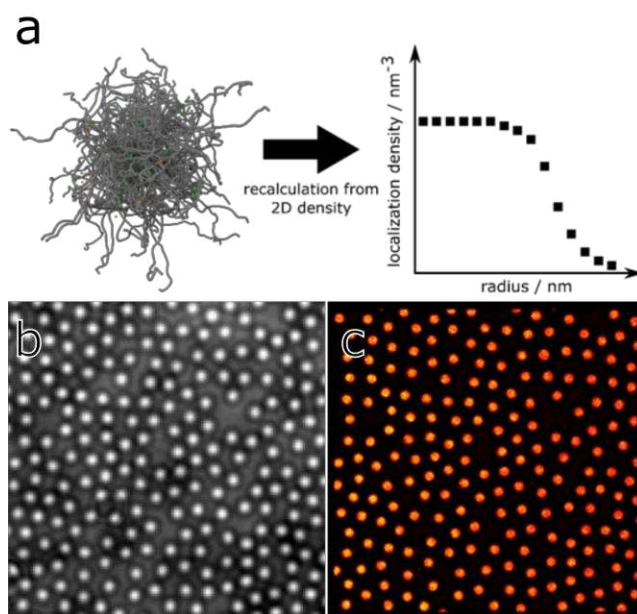


Figure 1. A schematic representation of a NIPAM based microgel saturated with rhodamine 6G molecules. Subsequent localization of single emitter fluorescence enables a direct 2D density calculation, which can be easily recalculated to a 3D localization density (a). Figure 1b shows the white light image and 1c the reconstructed image gained from single molecule localization microscopy.

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Internal structure of acrylamide based microgels: SANS determination of density profiles

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Microgels are colloidal gels smaller than 10 μm and can be used in a wide range of applications like drug delivery and smart surface coatings [1]. Microgels consisting of acrylamides like *N*-isopropylmethacrylamide (NIPMAM) or *N*-n-propylacrylamide (NNPAM) as network component, show a monomer-specific volume phase transition (VPT) at the volume phase transition temperature (VPTT). At this point, a change of temperature leads to abrupt reversible changes in size. To use microgels in sensors or for nanoactuators, the thermoresponse has to be precise and well known.

Co-monomer microgels synthesized in a two-step synthesis, with as first step a PNIPMAM core and as second step a PNNPAM shell around it show this property. Such particles display a **linear thermoresponse** between the two VPTTs of NNPAM (22 °C) and NIPMAM (43 °C) [2-3]. It is currently not known if the architecture is an interpenetration of the PNNPAM with the PNIPMAM core, or if it is a PNIPMAM-core- PNNPAM-shell system.

In order to investigate the architecture of these microgel systems, **we combined small angle neutron scattering (SANS) measurements with Monte-Carlo simulations** (Fig. 1, left). This combination results in a radial density profile of the polymer starting from the center of the particle. By extracting these profiles, we have evidenced how this profile changes with the content of the cross-linker (Fig. 1, right). Furthermore, we studied the change in this density profile during the collapse of the microgel, by changing the temperature.

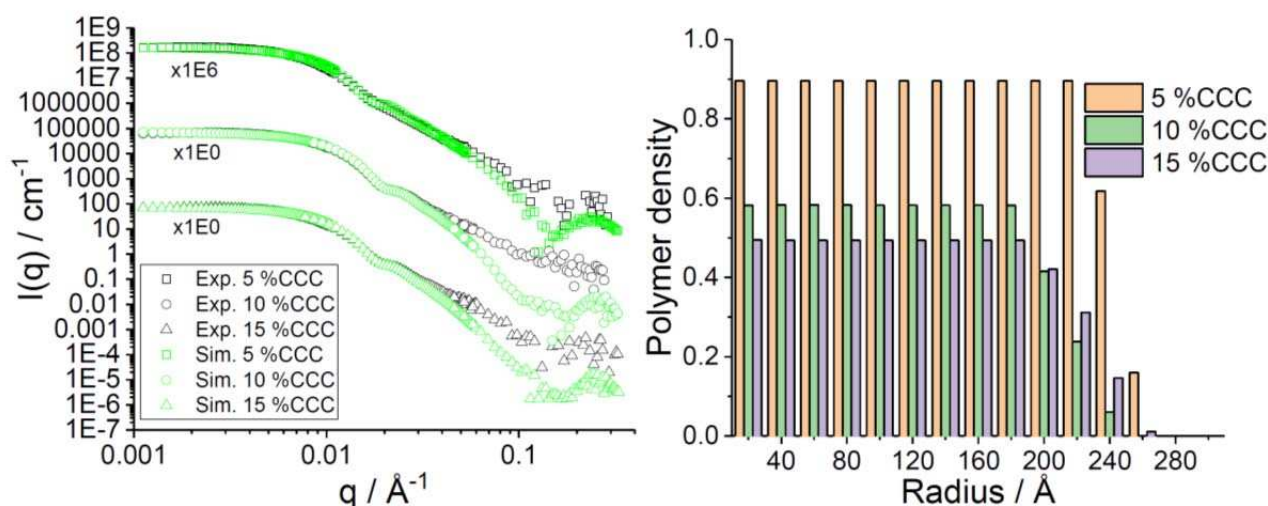


Figure 1. Left: $I(q)$ vs. q of SANS experiments (black) and Monte-Carlo simulations (green) of a PNIPMAM microgel with different cross-linker contents. Right: The extracted polymer density profile of the microgels.

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Core-shell microgels as smart carriers for silver nanoparticles

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Hybrid materials combining the interesting properties of nanoparticles with stimuli responsive microgels have obtained considerable attention during the last decade [1, 2]. Our contribution focuses on core-shell microgels based on the monomers *N*-isopropylacrylamide (NIPAM) as core material and *N*-*n*-propylacrylamide (NNPAM) as shell material. These microgels exhibit a very interesting linear phase transition region between the two volume phase transition temperatures (VPTTs) of the respective homopolymer microgels.

The particle architecture of the core-shell microgels is modified by copolymerization of the core with acrylic acid (AAc) and by a variation of the core cross-linker content. These modifications in the core region of the core-shell microgels are important steps to tailor the microgel properties towards an excellent ability to stabilize nanoparticles.

Silver nanoparticles are generated *in situ* inside the core-shell microgel templates and the temperature dependent catalytic activity of the hybrid system is studied by following the reduction of *p*-nitrophenole, a model reaction which is widely used [3], via UV/Vis spectroscopy. The results display, that the use of the core-shell microgels is a versatile approach towards catalytic particles with a switchable catalytic activity. Furthermore it is shown that tuning the mesh size of the core by means of the cross-linker content is an important parameter to achieve better switchability.

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Macroscopic DNA hydrogels that sense mechanical strain.

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Mechanosensitive materials can sense and respond to mechanical actuation. Such materials are ubiquitous in nature and control many biological processes from cell spreading and differentiation to senses of hear and touch [1]. These concepts inspired the design of artificial mechanochromic materials which respond optically to mechanical actuation. Current approaches are generally based on covalent bond rupture or chromophore aggregation which are irreversible and require large actuation forces [2,3]. Such systems are incompatible with hydrogels and soft materials. Weak and reversible force sensing require new mechanisms inspired from biological design based on dynamic supramolecular changes [4,5].

Here we present the design of fluorescent mechanochromic hydrogels based on DNA self-assembly. We prepared macroscopic all-DNA hydrogels using partially complementary multiblock single stranded DNA synthesized via enzymatic rolling circle amplification. These hydrogels are thermoplastic which allows for shaping and recycling by heating them above their melting temperature. We also designed these hydrogels to present large amounts of single stranded domains that we later use to anchor our fluorescent force sensors. The mechanochromic modules consist in a weak DNA duplex functionalized on one side with a fluorophore and on the other side with a quencher. As long as the duplex holds both in proximity non-radiative FRET prevents fluorescence. Mechanical stretching triggers the opening of the duplex which induces a decrease of FRET and an increase of fluorescence (Fig. 1A). We show quantitative strain-fluorescence measurements in homogeneous hydrogels (Fig. 1B, C) and control over the reversibility depending on the sequence and architecture of the module. We also present proof of concept applications for multiscale strain monitoring in composite materials (Fig. 1D), and visualization of freezing induced stress patterns (Fig. 1E).

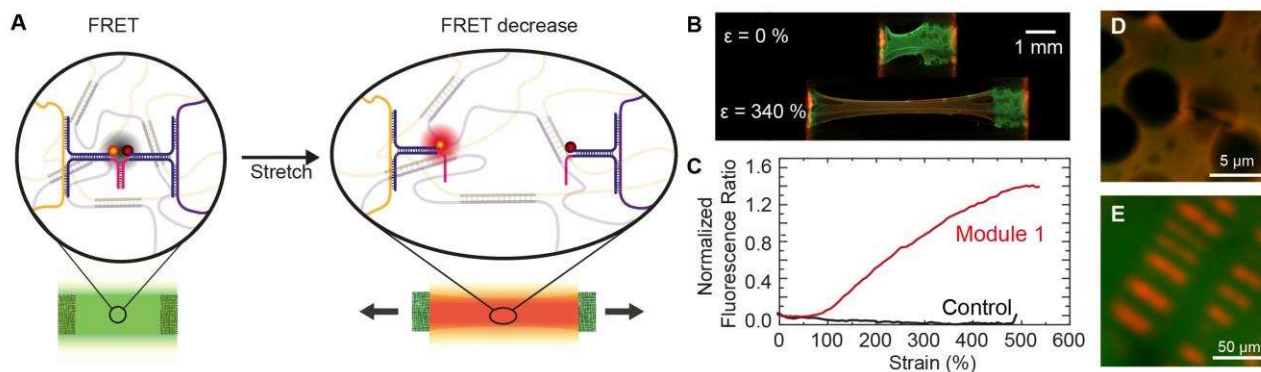


Figure 1. (A) Molecular mechanism of the DNA based mechanochromic module. (B) Widefield fluorescence imaging of the DNA hydrogel before and after stretching. (C) Quantitative strain-fluorescence curve ($\text{Fluo}_{488/510}/(\text{Fluo}_{530/580})$) for module 1 and a control module without force sensing duplex. (D) Confocal fluorescence imaging of microscale inhomogeneities in a model composite. (E) Widefield fluorescence imaging reveals freezing induced stress patterns.

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Thermodynamic properties of polyelectrolytes and associating electrolytes in solution

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The modeling of the thermodynamic properties of polyelectrolyte and complex ionic solutions is of interest in many areas, such as solution chemistry, chemical engineering, geochemistry and physics. In this work, we assume that polyelectrolyte and small charged complex can be described as a set of spherical subunits linked together by bonds so as to form chains, rings, star polymers, etc. Integral equations were developed to describe polymer chains from the interactions between their subunits. To solve these integral equations analytically, the mean spherical approximation (MSA) was used as a closure relationship to take into account the electrostatic interactions between the constituents. Explicit expressions were established for the electrostatic contributions to various thermodynamic properties.

For charged hard sphere chains, the pressure computed using these expressions was compared with those derived from simulation. Starting from expressions previously obtained for charged chains, suitable modifications have been made in order to describe also charged rings [1]. Furthermore, in solutions of complex electrolytes, clusters (like dimers, trimers, ...) must be taken into account to properly describe the structure and the thermodynamic properties. In our approach, the interplay between electrostatic and short-range attractive interactions between the subunits was taken into account with the same integral equations as those used for the charged chains. Analytic expressions were obtained for the speciation, and activity and osmotic coefficients in these solutions [2]. This is the first model that takes into account any number of sites on charged systems in the framework of integral equations. This description is an extension of previous works on the formation of charged dimers and trimers [3, 4]. The model is related to the SAFT theory. However, the effects of electrostatics and of the binding process are treated consistently in the thermodynamic integration leading up to the Helmholtz energy.

To illustrate, the speciation and the osmotic coefficient were computed for an electrolyte composed of a divalent cation possessing 4 binding sites and a monovalent anion with 1 site. This case is representative of chemical association in solutions of e.g., ZnCl_2 or CdI_2 . Finally this model could also be applied to describe the specific short-range attractions between counterions and nano-colloids whose charge comes from acid-base surface sites [5].

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Lipase encapsulation in cellulose derivative: structure and function

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The use of enzymes to catalyze organic synthesis has become an interesting alternative to conventional chemical methods. One of the most intensively studied method is the technique of solubilising lipases in water-in-oil microemulsions. Due to problems in product isolation and enzyme reuse in such systems, the use of microemulsion-based organogels (MBGs) has attracted attention [1]. MBGs were shown to be effective biocatalysts allowing the bioconversion of numerous substrates leading to the production of high added value products. Nevertheless, the structure of these organogels remains unknown. This work presents an attempt to elucidate the MBG structure in relation to the biocatalytic ability of therein immobilized lipase.

The enzyme was encapsulated in w/o microemulsions that were consequently gellified with hydroxy-propyl-methyl-cellulose (HPMC). The application of these lipase-containing gels for various biotransformations was carried out.

The structure of the MBGs was investigated using several techniques. Differential Scanning Calorimetry (DSC) was used to investigate the state of the incorporated water and indicated up to four different states of water, depending on the amount of the water in the gel [2]. The behaviour of the water/oil interface was further investigated by Electron Paramagnetic Resonance (EPR), to clarify the behaviour of polar and non-polar molecules in the organogels. It was revealed that after microemulsion incorporation there is no distinction between water in the biopolymer network and water in the microemulsion. Surfactants continue to form interfaces although they are dispersed. It was also revealed that lipophilic constituents of the organogel present high local concentration, probably by being restricted in channels. This result was also supported by Scanning Electron Microscopy (SEM) which was used to explore the surface of the organogels in relation to their composition.

The biocatalysts were further successfully used for the synthesis of various high added value products of industrial interest, such as phenolic and lipid acid esters, terpene alcohol esters, monoacyl glycerides and epoxides [3,4]. The effect of gel composition on the above applications is discussed, as well as the reusability and storage ability of the lipase-containing catalysts.

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Proteolytic degradation of gelatin-tannic acid multilayers

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Edible films are of high interest for a wide range of applications. They do not only possess an extraordinary potential for use in the food industry but also, because of their guaranteed biodegradability, they stand out as ideal substitutes of the highly contaminant synthetic films. Gelatin is one of the most common constituents of biodegradable/edible films [1]. Because of its poor mechanical properties, the formation of gelatin films usually requires of structural modifications. A strategy that has attracted interest recently is its cross-linking by means of tannic acid [2]. However, whereas the biodegradability of gelatin is well established, this is not the case for most of the films where this protein has been cross-linked, including those where tannic acid was used for this purpose. In this work, we addressed this gap in knowledge. Specifically, we built at different ionic strength gelatin-tannic acid multilayers by means of the layer-by-layer self-assembly technique, and studied by means of Electrochemical Impedance Spectroscopy and Quartz Crystal Microbalance with Dissipation their structure and resistance to proteolytic degradation. Results indicated that films formed at physiological ionic strength exhibited a compact structure, which limited their proteolytic degradation. On the contrary, gelatin-tannic acid films formed at low ionic strength exhibited a swollen structure that resulted in the fact that they were almost immediately degraded when exposed to proteases. Overall, this work shows that by controlling the ionic strength at which proteinaceous films are grown it is possible to tune the access to relevant cleavage sites by proteases and, therefore, their biodegradability. These results are of relevance for different applied research fields. On the one hand, the reported resistance to proteolytic degradation by gelatin-tannic acid films grown at physiological ionic strength indicate that they are better suited for applications, such as edible packaging, where the ability to resist proteolytic degradation is desirable. On the other hand, the low resistance to proteolytic degradation of gelatin-tannic acid films formed at low ionic strength and the fact that this process could be easily monitored by means of electrochemical impedance spectroscopy opens the possibility of using this degradation as a mechanism for electrochemically based sensors for e.g., bacteria/biofilms.

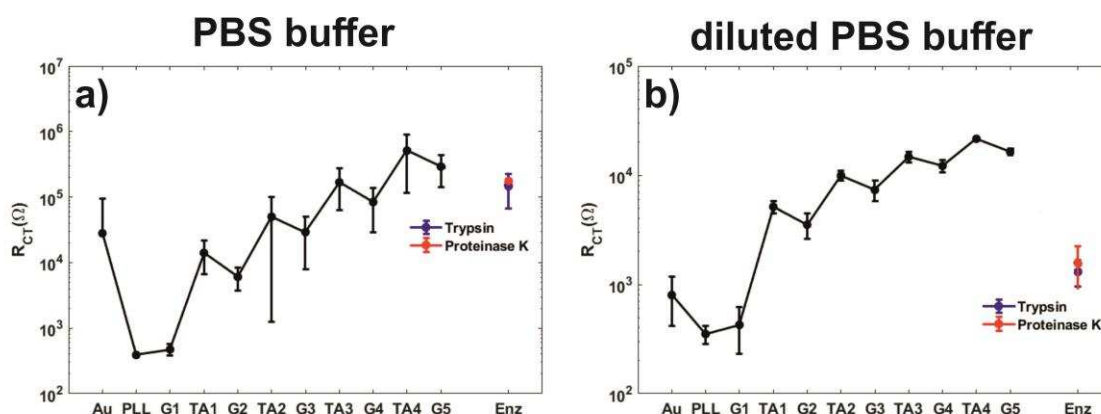


Figure 1. Effective charge transfer resistance (R_{CT}) values calculated from EIS experiments where the growth of gelatin-tannic acid multilayers in physiological PBS buffer (a) and in diluted PBS buffer (b) were monitored followed by treatment with the proteases trypsin and proteinase K.

Acknowledgements: Financial support from the Knowledge Foundation (grant number 20150207) is gratefully acknowledged.

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Glass Transition and Interfacial Dynamics of Poly(vinyl alcohol)-Silica Nanocomposite Systems - A Molecular Dynamics Simulation Study.

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In the proximity of a particle, polymer glass transition behaviour deviates from its bulk counterpart. This behaviour is also known as the nanoconfinement effect [1]. The change in the local dynamics of polymer segments at polymer-particle interface can lead to a shift in the glass transition temperature [1-4]. In addition to that, the interplay of the substrate surface chemistry and the polymer structure plays crucial role in determining the nature of interfacial interaction that affects the glass transition temperature (T_g).

In this work, all atom molecular dynamics simulation has been performed to study the glass transition behaviour of poly(vinyl alcohol) (PVA) confined by the silica substrate to resemble a PVA-silica nanoparticle composite system. The chemical structure of the silica surface is varied by the extent of hydroxyl functionalization (0%, 25%, 50%, 75%, 100%) that corresponds to silica nanoparticles prepared under different pH conditions. The interactions between the PVA and the hydroxylated silica lead to the change in the segmental relaxation of the polymer chains under confinement and consequently result in a shift in T_g . We have found that the amount of T_g change depends on the extent of hydrogen bonding interaction between PVA and silica surface. T_g of the composite systems was determined from temperature-dependent α -relaxation time using the Williams-Landel-Ferry (WLF) theory, in which the relaxation times were calculated from the intermediate scattering function via the Kohlrausch-Williams-Watts (KWW) theory. Free energy of adhesion determined from umbrella sampling simulations of the composite system sheds lights to the thermodynamics of interfacial interactions. Our results suggest strong attractive interactions between PVA and silica nanoparticles with higher OH coverage originated from hydrogen bonding interactions that give rise to greater T_g increase, while bare silica nanoparticle surface led to a suppression of T_g .

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AFM Nanomechanical Characterization of Waterborne Coatings and the Effect of Relative Humidity

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Waterborne organic polymer dispersions are ubiquitous and can be found in a wide range of different applications such as paints and varnishes, pressure-sensitive adhesives, textiles, construction materials, paper coatings and inks. However, they also have weaknesses and how they are affected by moisture is one of them. They exhibit poorer water barrier properties than solvent borne coatings [1,2]. Moisture can also have a significant effect on their mechanical properties [2]. In fact, the characterization of the mechanical properties of organic coatings is essential for predicting their performance, a long-term goal of the coating industry. Various techniques are available for characterizing the mechanical properties of coatings. Hardness testing and dynamic mechanical analysis are among those that are well-established. However, these techniques operate in the macro-scale i.e., they are not suitable for very thin-coatings. For these cases, AFM offers unparalleled potential. The most common way to characterize the mechanical properties of polymer coatings by AFM is by pressing the tip against the sample and calculating the deformation as a function of the applied force i.e., by means of the so-called force curves. Then, the mechanical properties of the coatings such as the Young modulus are obtained by applying a suitable continuum elastic theory. Here we will show that by means of this method it is possible to monitor, in an extremely reproducible way if parameters such as the tip radius and cantilever force constant are well characterized, how the stiffness and adhesiveness of waterborne polyurethanes depends on relative humidity. Moreover, we will also show that this method is sensitive to characteristics of the coatings such as cross-linking of polyurethane chains. However, waterborne coatings, including polyurethanes, are not elastic but viscoelastic instead. This is evidenced e.g., from the hysteresis between the loading and unloading segments of the force curve and from the dependence of the effective Young modulus on the loading rate. So far, there is not a solid scheme to obtain viscoelastic parameters from force curves. Instead, this is possible by means of other approaches such as thermal noise contact resonance spectroscopy, where the thermal noise of the cantilever when in contact with the coating is monitored [3]. We will discuss here the dependence with relative humidity of the viscoelastic properties of waterborne polyurethane coatings obtained by means of this method.

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Nano- and micro- particles as drug delivery carriers and constituents of coatings

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Drug delivery carriers and biomedical coatings greatly benefit from versatile nanometer sized biocolloids and micrometer sized particles. In drug delivery applications biocolloids can be used either directly or serve as templates for polymeric carriers.

In this talk, different calcium carbonate particles will be discussed used as delivery carriers or serving as versatile, porous templates for polymeric drug delivery carriers. Application of porous particles for protection and delivery of enzymes is one of the growing application areas. Polymeric carriers are attractive due to a variety of different stimuli, which can be used for controlling the encapsulation and release, including physical, chemical and biological ones [1]. Intracellular delivery by means of particles is seen as one of their important applications, with further progress toward delivery into such organisms as worms [2].

On the other hand, biomedical coatings stand to benefit from application of particles for enhancement of mechanical properties and from providing ingredients for controlling their physico-chemical properties. In addition, incorporation of particles into the coatings brings additional drug delivery capabilities. The above mentioned functionalities will be analysed on an example of application of calcium carbonate particles in hydrogel coatings [3].

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Combining DNA phase transition and hybridization to form all-DNA colloids and superstructures.

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Inspired by biological soft-tissues, the fabrication of addressable, biocompatible and hierarchically structured materials is a key challenge for material science, nanotechnology and medicine [1]. DNA provides synthetic materials with the highest level of molecular structural control and nanoscale complexity (DNA origami...). Yet processes to create micro and macro-structured DNA architectures are scarce.

Here we present a new method at the interface of biochemistry and macromolecular physics to prepare various all DNA microstructures. We use long “multiblock” single stranded DNA synthesized by rolling circle amplification as primary elements. The key for fast and efficient structuration rely on two antagonistic processes. A new sequence dependent LCST-type phase-transition that promotes self-assembly at high temperature; and canonical DNA hybridisation which prevails at low temperature (Fig. 1A). We developed multiple strategies to navigate these complex self-assembly landscapes and freeze the assembly upon cooling to obtain homogeneous (Fig. 1B) or core-shell particles (Fig. 1C) (with a solid or liquid core), and capsules (Fig. 1D). Since the particles consist mostly of single stranded DNA they can be addressed for functionalization, self-assembly and hierarchical superstructure formation. As examples we prepared multiparticles assemblies (Fig. 1E), continuous cellular hydrogels (Fig. 1F), and light responsive hybrid DNA/gold- nanoparticles structures (Fig. 1G).

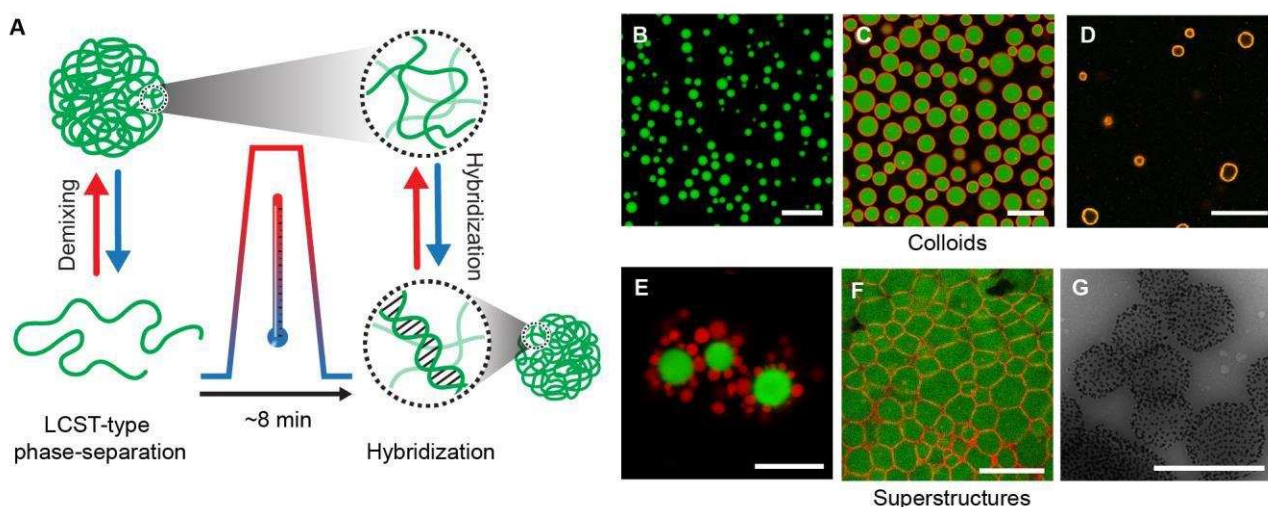


Figure 1. (A) Schematic representation of the two temperature dependent process driving the formation of all-DNA colloids. (B-F) Confocal microscopy imaging of various colloids and superstructures. The primary structures consist of (B) homogeneous particles, (C) core-shell particles and (D) capsules. DNA driven assembly and controlled heating allow the formation of (E) core-satellites aggregates and (F) continuous cellular hydrogels. (G) Transmission electron microscopy of light responsive DNA colloids decorated with gold nanoparticles. Scale bars: (B-F) 10 μm, (G) 500 nm

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Polyurethane based patchy colloidal particles mimicking the mesoscopic structural organization of the antimicrobial peptides to induce a selective disruption of the bacterial cytoplasmic membrane

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Antimicrobial peptides (AMPs) are essential components of the host innate immune response as a first line of defense to combat pathogenic microbes [1]. AMPs have a complex hierarchical structure formed by the self-assembly of simple building blocks like amino acids mediated by supramolecular interactions. The fundamental structural principle underlying all classes of AMPs is the ability of the molecule to adopt a shape in which clusters of hydrophobic and cationic amino acids are spatially organized in discrete sectors of the molecule, enabling them to induce a selective disruption of the bacterial cytoplasmic membrane [1]. In this context, we developed colloidal particles based on a novel polyurethane functionalised with a polyionic liquid. These particles mimic the patchy mesoscopic structural organization of AMPs. A cationic hydrophobic liquid monomer (HDIL) was grafted from the amphiphilic polyurethane (NHP407) by a redox initiated aqueous heterophase polymerization where NHP407 acts as a reductant and ceric ammonium nitrate as an oxidant. A cationic hydrophilic monomer (HIL) was sequentially added and polymerized (HPIL) to a hydrophobic polyionic liquid block (HDPIL). The chemical structure of the synthesized colloidal particles was elucidated from the recorded ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra. The morphological characterization was analysed by cryo-TEM. It is clearly observed that the patchy colloidal particles of self-organized mesophases were formed by discrete nanodomains of charged ionic liquid moieties (Figure 1). The dark areas in the cryo-TEM image can be ascribed to the ion pairs of cations and anions, resulting in a higher electron density compared to non-ionic polyurethane blocks. The aqueous dispersion of NHP407-g-(HDPIL-b-HPIL) has a ζ eta potential of magnitude + 55 mV stemming from the quaternary ammonium moieties of the respective HDPIL and HPIL blocks. The minimum bactericidal concentration (MBC) determined by the broth microdilution method was as low as 3.9 μ g/mL and 31.25 μ g/mL against *S. epidermidis* and *S. aureus* respectively. The colloidal dispersion at ~15 μ g/mL, reduced 99% of *S. aureus* viability within 30 minutes. The IC₅₀ of the designed colloids on L929 fibroblasts was higher than the minimal inhibitory concentration determined on susceptible *S. aureus* and *S. epidermidis*, showing a selectivity index of 7.06 and 14.12 respectively. The focus of the future experiments is to have a precise control over the individual block length, which would pave a pathway for reaching a higher selectivity index.

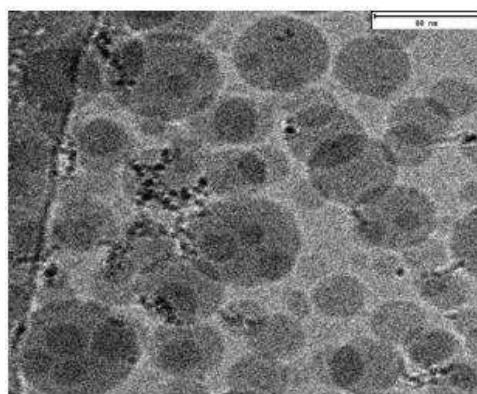


Figure 1. Cryo-TEM image of aqueous dispersion of NHP407-g-(HDPIL-b-HPIL). The image shows a scale bar corresponding to 80 nm, acquired at magnification of 5E4 \times which corresponds a pixel size of 0.331 nm.

Acknowledgements: HyMedPoly received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 643050

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Structural and transport properties of a hydrogel mimicking the subcutaneous tissue

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In drug delivery, the subcutaneous (SC) route increasingly supersedes the oral and intravenous route of drug administration. Contrary to the latter two ways of delivery, there is still lack of a standardized *in vitro* model to predict *in vivo* absorption and bioavailability of drugs administered by SC-injection [1]. In order to improve the release of biotherapeutics, it is crucial to understand the fate of a drug formulation from the site of injection to the uptake by the blood capillaries and the lymphatic system [2,3]. We aim to identify the biophysical factors which affect the transport through the interstitial space and to study to which extent the interactions are related to molecule size- or charge.

To get a deeper mechanistic understanding of SC drug delivery, we synthesized a hydrogel consisting three - chemically functionalized - major components of the SC-tissue: Collagen *type I*, to provide structural rigidity, Hyaluronic acid and Chondroitin sulfate, to represent the negatively charged polyelectrolyte backbone of proteoglycans. The precursor components were crosslinked by *Thiol-Michael addition click reaction* to yield a hydrogel, where variations in composition show different microporosities and mechanical strengths.

We investigated the properties of the synthesized hydrogels in an interstitial-fluid-like environment, focusing on changes of the microstructure upon swelling and mass transfer of selected molecules. Structural information obtained by electron microscopy is correlated with data from light- and small angle x-ray scattering, the different mesh sizes of the network are derived from rheometry. Diffusion of model proteins of different molecular weight through the hydrogel matrix is captured by confocal microscopy to complete a first picture of a novel synthetic model of the subcutaneous tissue.

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Need for colloid biology: Are bacterial cells really just particles?

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The surface of the bacterial cells is negatively charged mainly due to the excess of negatively charged moieties of bio-macromolecules incorporated in their membrane and cell wall. If we regard bacterial cells as colloid particles, we can predict the zeta potential of approximately -40mV using the Smoluchowski equation. According to the DLVO theory this potential should be high enough for the cells to form a stable suspension. The theory predictions do not account for the unusual colloidal properties of cells and their constant adaptation to the environment, which enable them to aggregate and form biofilms on surfaces even at conditions of the electrostatic repulsions between particles. (**Figure 1**). By using the principles of colloid physics we are demonstrating how the electrostatically deposited oppositely charged polyelectrolytes on the surface of bacterial cells cause diverse biological effects, such as, controlling their metabolism and growth as well as their spatial distribution and intercellular interactions. Accordingly, polyelectrolyte layers induce the formation of enlarged cells, up to 2-times the original size, with highly induced constitutively expressed genes. On other hand, by modifying the surface charge of bacterial cells we showed that the cells adhere to the oppositely charged surfaces. Exploiting this property, we developed a top-down approach of the controlled aggregation of bacterial cells to form simple aggregates or multi-layered heterocellular structures involving different types of cells. In 3D- aggregates we showed that the cells interact through exchange of metabolites and in planar cellular structures, namely the artificial biofilms, we showed their effects on the succession of the communities forming the biofilms in the environmental conditions.

Based on our insights and emergent behaviour of the system composed of colloids and the living microbial cells, in contrast to the system composed only of the non-living colloidal particles or macromolecules, we propose a new field of colloid biology, which includes, besides the chemical and physical aspects, also the incorporation of biological principles, which determine the behaviour of the “live colloid system”. All the emergent effects attribute to the unusual behaviour of cells with the ability to actively modify their surface and metabolism according to the extracellular conditions in the colloid systems.

Knowing the principles of the colloid biology is not only interesting for basic studies of the interactions of bacterial cells within the colloidal environment, but also extremely important for applications such as vaccination, biocorrosion protection, drug delivery and anticancer treatment, as well as tissue engineering with live or attenuated bacterial or other sorts of cells.

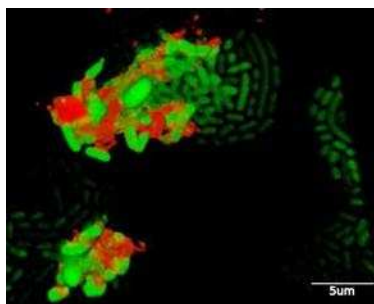


Figure 1. Bacterial cells (green) are responding to the environment when aggregated or entrapped within the colloids, here polyelectrolytes (red). Cells are interacting with each others, resulting in enormous expression rate of the green fluorescent protein without previous induction.

Biomimetic Folding Particle Chains

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We show how microfluidics can be used in combination with AC electric fields to assemble flexible chains of colloids [1] with full control over the sequence of particles on the single particle level. Our goal is to experimentally observe and control the self-folding of colloidal chains [2]. In analogy to how the sequence of amino acids determines the folded 3-D structure of proteins, we aim to control the folding of our colloidal polymers by the sequence of particles in the string [2, 3]. These colloidal strings simulate biological polymers, but can be observed in real-time by optical microscopy. The interactions between the particles are determined by the individual surface modifications and by the solvent composition. Since simulations suggest that the prerequisites to determine a specific folded structure are different isotropic interactions plus an attractive directional interaction between the colloids [2], we synthesize particles with both isotropic and patchy interactions. Using confocal microscopy and holographic microscopy these interaction potentials between the different species as well as the resulting folding behaviour are studied.

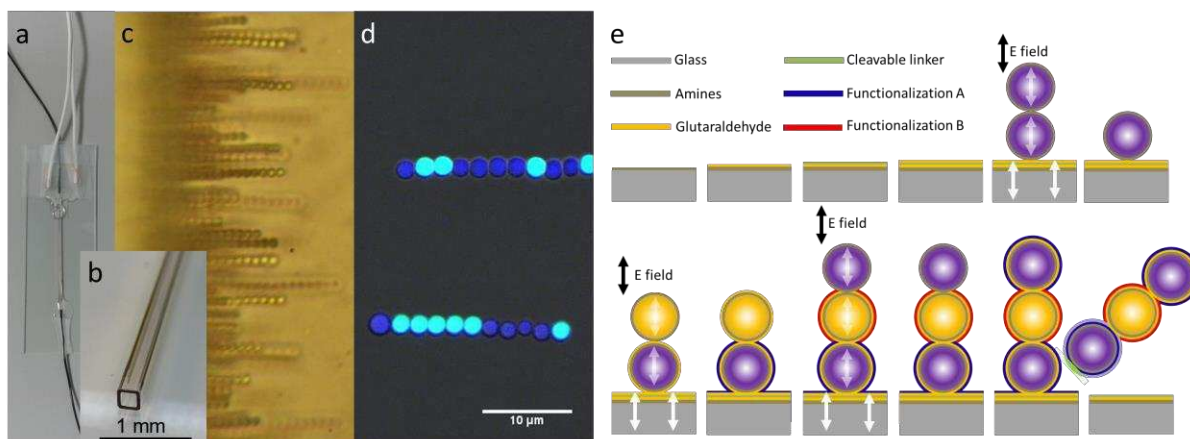


Figure 1. **a.** capillary with external electrodes, **b.** zoomed capillary, **c.** brightfield micrograph of induced dipole driven string formation at the capillary wall, **d.** confocal micrograph of fluorescent polystyrene particles aligned in arbitrary sequences, **e.** strategy to make multiple strings with identical sequences in parallel: subsequently render the wall sticky for aminated particles, applying an AC field to stick at most one particle on one spot, remove excess particles, make the first generation of particles sticky and stick at most one second particle to the first particles, neutralize the wall and determine the interaction type of the first generation of particles with a functionalizing compound, making the second generation sticking and add a third generation, neutralize and determine the interaction type of the second generation and so forth.

Acknowledgements: We are grateful for the financial support of FWF Stand-alone project P 27544 “Selbstfaltende Partikelketten”.

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Directional insertion of cone-shaped channel protein in model membranes by neutron reflectometry and electrophysiology

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Insertion of a small potassium (K^+) channel protein (KcV_{MA-1D} and KcV_{NTS}) [1,2] in model membranes has been investigated by neutron reflectometry. The profitable small size of the investigated channel allows to perform measurements on macroscopic single supported bilayers of DPPC and DMPC. Reflectometry was also performed on bilayer of DPPC floating over a DSPC supported one, thus on a physically decoupled bilayer system, dynamically free. Fully deuterated lipids were used in order to highlight the contribution of the naturally hydrogenated protein to the reflected spectrum. In this perspective also substitution of the hydrogenated chaperon molecules with deuterated phospholipids, was performed. The insertion of the overall asymmetric, truncated cone-shaped channel tetramer into membranes, was studied by following the change in the contrast profile of the membranes after protein incubation in solution, representing the transverse structure of the bilayer. Results underscore an asymmetry of the contrast profile, demonstrating a favorable directional insertion.

Parallel electrophysiology experiments on the electrical activity of the channel reconstituted in planar lipid bilayers with the same composition also demonstrate a preferential orientation of the channel. We can speculate that when functional read-outs by electrophysiology are not possible, reflectometry can be a useful technique for assessing the transmembrane orientation. Moreover, matching the two techniques on reconstituted single membrane, highlights a route to structure-function connection on channel-protein biophysics.

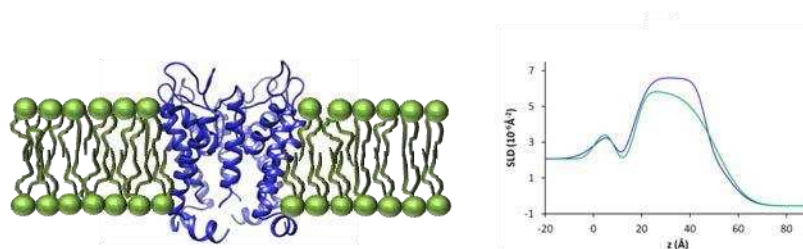


Figure 1. Protein insertion in model phospholipid bilayer (left) and transverse SLD profile (right).

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Non-Equilibrium States of Sticky Colloidal Particles: Phase Separation and Dynamical Arrest

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Soft materials can form amorphous solids, e.g. gels and glasses, which are relevant for such diverse fields as food engineering, pharmaceutical industry and materials science. To analyze the non-equilibrium states of colloidal particles interacting via short-ranged attractions, we use a perfectly monodisperse suspension of nearly spherical particles, namely globular proteins (lysozyme). The metastable gas-liquid binodal, the attractive glass line and the second virial coefficient B_2 for various solution conditions, i.e. salt concentrations, have been determined by optical microscopy, centrifugation experiments and light scattering. If the temperature axis of the binodals is expressed in terms of B_2 , data obtained under various conditions fall onto a master curve, as suggested by the corresponding states law [1]. For colloids with short-ranged attractions, gelation has previously been related to gas-liquid phase separation and a universal state diagram has been proposed if scaled by B_2 . However, this is in contrast to our findings. Arrest lines for different salt concentrations overlap within experimental errors, whereas they do not overlap if the temperature axis is replaced by B_2 . This indicates that the binodals are not sensitive to the details of the potential, but can be described by one integral parameter, i.e. B_2 , whereas the arrest line appears governed by its attractive part.

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Is a single layer of polyelectrolytes covering bacterial cells poisonous as Tunic of Nessus or protective as a warm coat?

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Physiological capabilities of bacterial cells and inter- intraspecies interactions can be significantly increased by modification of the external structure of bacterial cells. Since cells resemble negative surface charge mainly due to the composition of a cell envelope it has been shown to be convenient for consequent polyelectrolyte adsorption on the cell surfaces. This approach for bacterial cell modification is very convenient since variety of parameters (e.g. surface charge, polymer composition as well as thickness of adsorbed layers and strength of the interaction of polymers with cells) can be much more under the control than the cells are genetically modified.

In the process the first layer deposited over the cell surface must be positively charged. However, it is well known from literature that cationic polymers exposed to bacterial cells can notably reduce amount of alive cells. Many parameters as size of the polymer, its structure, charge density or type of charged groups play crucial role in the cell activity. In addition, complexity of the cell surface structure, and activity of bacterial membrane and cell wall, which are involved in bacterial cell respiration and the transporting of different molecules complicate straightforward approach of the covering of the cells. To modify bacterial surface by polyelectrolyte deposition with the lowest possible toxic effect, on one hand it is important to cover cells efficiently and on other hand, it is needed to have in mind the physiology of particular bacteria and differences in the polymers properties.

Therefore, our aims were to determine: (i) the cells physiological properties on the efficiency of deposition of polyelectrolytes on cell surface, (ii) physiology of bacteria after deposition and (iii) toxic level of different types and sizes of polymers including primary and tertiary amines against several bacterial strains.

According to our results using growth experiments, time-lapse confocal (see Figure 1.) microscopy and STED, the prediction of toxic effect of polymers on bacteria is not straightforward when different strains are used. Here, we determined two main reasons to be acting as growth restrictors: (i) mechanical interference of individual cells with polyelectrolyte shells and (ii) reduction in survivability interfering with the respiration of cells.

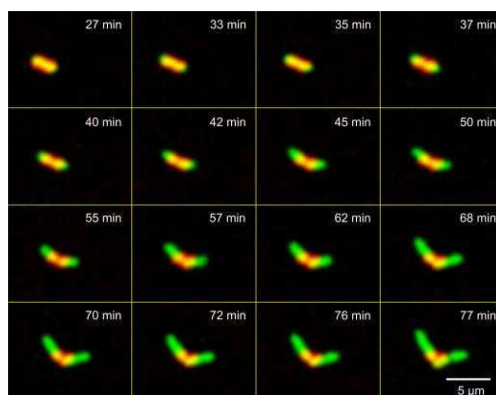


Figure 1. Escape of *E. coli* cells from deposited polyelectrolyte shell, (green is GFP producing cells, overlap regions are yellowish).

Antioxidant inorganic-organic hybrids of high functional and colloid stability

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Natural antioxidant enzymes are the primary defence systems against reactive oxygen species (ROS). Enzyme supplementation is a promising way to deal with increased ROS concentrations, however, their high sensitivities to the environmental conditions make this impossible either in parenteral or oral administration. Therefore, various nanoparticle systems are being developed to deliver enzymes in immobilized forms. The main requirements of the nanoparticulate supports are to defend the enzyme, carry it into the targeted cells and to be resistant against aggregation in the delivery process. The present results were obtained in systems containing nanoparticles (titania nanosheets (TNS) [1] and layered double hydroxides (LDH) [2]) and enzymes (superoxide dismutase (SOD) and horseradish peroxidase (HRP)) or mimicking compounds.

The TNS and LDH were prepared hydrothermally first and functionalized with charged polymeric compounds (so-called polyelectrolytes) to improve their colloidal stability and to promote immobilization of the biocatalysts. The aggregation processes were suppressed by adsorbing a saturated layer of the polyelectrolytes on the particles, the suitable doses were determined in electrophoretic and light scattering measurements [3]. SOD and HRP enzymes strongly adsorbed on the particle surfaces. Their structural integrities were kept during the immobilization and the enzymatic activities were very similar to the bare enzymes and they possessed the advantages of the heterogeneous catalysts.

Besides, an enzyme mimicking metal complex, namely copper(II)-histamine ($\text{Cu}(\text{Hsm})_2$) was immobilized on poly(4-vinylpyridine-co-methyl methacrylate) (PVPMAA) functionalized LDH platelets (Figure 1). As revealed in electron paramagnetic resonance spectroscopy measurements, the complex was attached to the copolymer via coordinative bonds between the copper(II) ions and the nitrogen of the pyridine groups. The obtained hybrid material showed good SOD-like activity. More importantly, its superoxide radical scavenging ability was kept even at higher temperatures, where the native SOD lost its function after a few minutes. Summarily, the above discussed antioxidant systems showed great activity in ROS decomposition and formed highly stable dispersions. They are promising candidates in applications either in biomedical treatment or industrial processes, wherever the aim is to reduce ROS concentration.

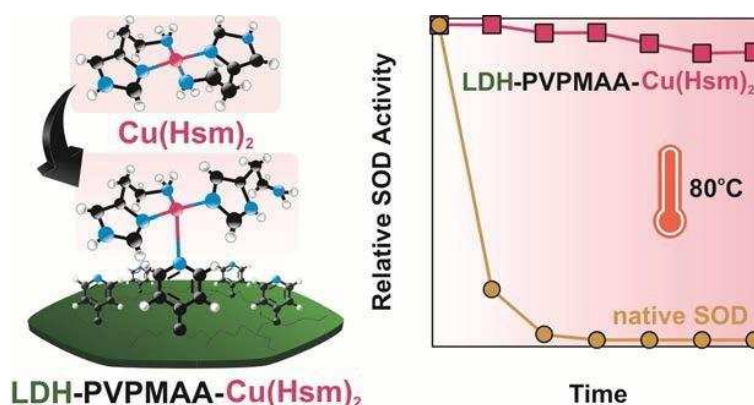


Figure 1. Scheme of immobilization of $\text{Cu}(\text{Hsm})_2$ complex on copolymer functionalized LDH particles (left) and superoxide radical scavenging activity of the bare SOD and its mimic at elevated temperature (right).

Acknowledgements: Financial support by the Lendület program of the Hungarian Academy of Sciences (96130) is gratefully acknowledged.

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Bactericidal behaviour of self-assembled fatty acid crystals on highly ordered pyrolytic graphite

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The wings of cicadae and dragonflies have been found to possess a surface nanostructure comprised of arrays assembled from fatty acids. These nano-arrays can physically interact with any bacterial cells membranes coming into contact with the surface, killing the cells. Mechano-bactericidal surfaces such as these are of significant interest because they do not necessitate the use of antibiotics, to which the bacteria can become resistant. This paper reports the bactericidal effect of two of the main lipid components of the insect wing epicuticle, namely palmitic (C16) and stearic (C18) fatty acids.

Films of these fatty acids were crystallised on the surface of highly ordered pyrolytic graphite (HOPG). It was apparent that the presence of two additional CH₂ groups in the alkyl chain resulted in the formation of quite different surface structures. Scanning electron microscopic (SEM) and atomic force microscopic analyses showed that the palmitic acid microcrystallites were more asymmetric than those of the stearic acid, where the palmitic acid microcrystallites were observed to be an angular abutment in the scanning electron micrographs. The principal differences between the two types of long-chain saturated fatty acid crystallites were the larger density of peaks in the upper contact plane of the palmitic acid crystallites, as well as their greater proportion of asymmetrical shapes, in comparison to that of the stearic acid film.

These two parameters may be an important contributing factor to the higher bactericidal activity on surfaces derived from palmitic acid. Both the palmitic and stearic acid crystallite surfaces displayed activity against Gram-negative, rod-shaped *Pseudomonas aeruginosa* and Gram-positive, spherical *Staphylococcus aureus* cells.

The simplicity of the production of these microcrystallite interfaces suggests that a fabrication technique, based on solution deposition, could be an effective technique for the application of bactericidal nanocoatings.

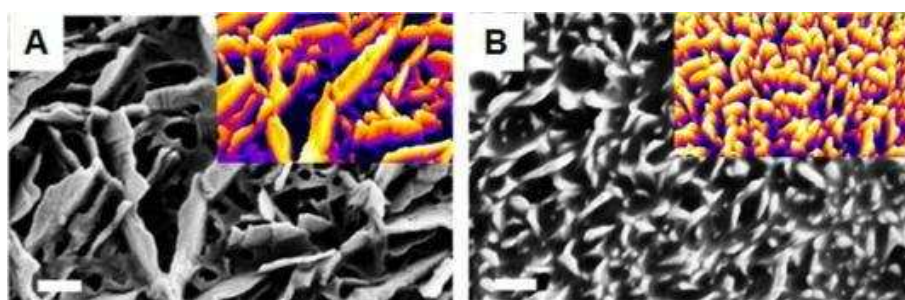


Figure 1. Fatty acid microcrystallites of palmitic and stearic acids assembled on HOPG substrata with a surface concentration of 30 $\mu\text{g}/\text{cm}^2$. (A) Palmitic acid and (B) stearic acid analysed using SEM shown in 2-dimensional images (greyscale) and 3-dimensional (colour) images. The scale bars are 1 μm for both the main and inset images.

Catanionic vesicles based on amino acid-derived surfactants: developing biocompatible and versatile molecular nanocarriers

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There has been a continuous challenge to develop nanostructured systems, such as vesicles, polymers, dendrimers, nanotubes and nanoparticles, that efficiently protect and deliver biomolecules to target cells. Amphiphiles with low cytotoxicity are of special interest for the design of drug and gene delivery formulations. Vesicle-based systems built up from either synthetic surfactants, which typically have relatively high levels of cytotoxicity, or lipids, which suffer from poor chemical and colloidal stability, have been extensively studied. On the other hand, catanionic systems have widened our understanding of vesicle formation by introducing more complex systems.[1] In particular, catanionic vesicles based on amino acid have emerged as interesting alternatives, improving biocompatibility and biodegradability, and offering molecular and self-assembling versatility (sensitivity to pH, temperature and ionic strength, charge and size manipulation, etc).

Recently, we have explored the vesicle-forming ability of different catanionic systems based on serine [2,3] and threonine. In one system, through rational design and suitable blending of surfactants, we showed that it is possible to build up both negatively and positively charged vesicles based on surfactants derived from the same amino acid, serine (Figure 1).[3] The cationic 16Ser/8-8Ser vesicles have a polydisperse log-normal distribution with $\langle R \rangle = 100$ nm forming at pH = 3.5 – 5.0. In comparison, the anionic 16Ser/8-8Ser vesicles are more polydisperse, with $\langle R \rangle = 150$ –180 nm, forming at pH = 6.5–9.5. A system of stable and robust vesicles with tailored features is at hand for drug delivery exploitation (doxorubicin is currently being tested).

The threonine derivatives have simple monomeric configuration and different alkyl chain length, and are designated by n ThrNa, where n is the number of carbon atoms in the hydrocarbon chain, ranging from 8 to 16. Phase behavior studies and microstructural characterization of several mixtures based on 12ThrNa as the anionic surfactant, and on gemini serine-based[2] and gemini conventional surfactants as the cationic surfactants have been carried out. Results from polarized light microscopy, cryo-SEM, DLS and zeta potential measurements will be presented and discussed.

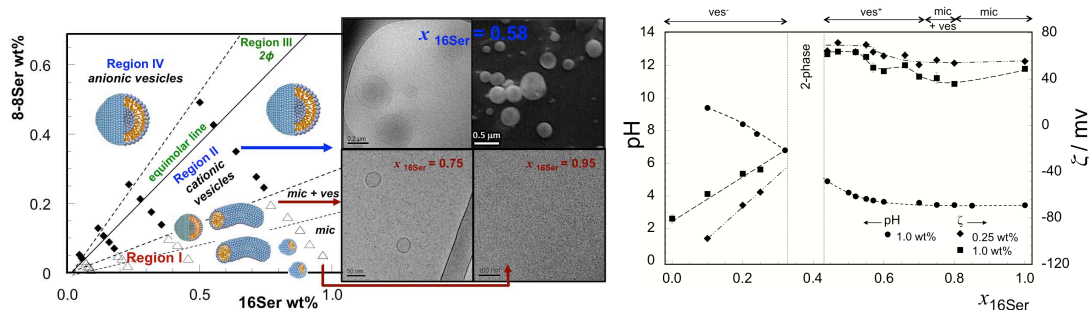


Figure 1. The 16Ser/8-8Ser catanionic mixture, with vesicles of varying size, charge and pH.

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The interaction of bilirubin- and coumarin-6-loaded micellar coordination clusters with α -, β - and γ -cyclodextrins

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Among the wide choice of surfactants, the interesting characteristics possess nonionic non-denaturing ones of Triton group with practically useful properties, such as biosensing, encapsulation, and drug delivery. The surfactants themselves are used as constituents of vaccines, for hydrophobic substances solubilization, nanocontainers creation or membranes permeability increasing. Earlier, an approach to conjugate micelles Triton X-100 and X-114 surfactants by incorporating a hydrophobic chelator into their interface followed by cross-linking by double-charged metal ions has been developed. This allowed the creation of effective systems capable of encapsulating and solubilizing of new hydrophobic anticancer compounds, fluorophores, toxic compounds much better compared to pure surfactants.

Previously, it was shown that the study of the interactions between surfactants and cyclodextrins, promotes the expansion of the application scope of both compounds, especially for targeted drug delivery due to their ability to solubilize hydrophobic substances.

In this study, we have shown that β - and γ -CD can be successfully used to destroy the MCCs with the sequential extraction of the encapsulated coumarin-6 fluorophore as its CD complex to a solution; in the case of MCC-encapsulated bilirubin, all the cyclodextrins can be used to extract the pigment. These findings may have important practical aspects of the application for biomedical purposes or while studying the revealed regularities in the MCCs stability of from the point of controlled release.

At the initial stage, it was determined that the fluorescence of coumarin-6 is enhanced in the presence of β - and γ -CD as well as in the solution of pure surfactant and becomes comparable with its fluorescence in pure MeOH, while in water and in the presence of α -CD this fluorophore practically have no any fluorescence. An addition of β -CD to freshly prepared MCC with encapsulated coumarin-6 causes an increase in its fluorescence by ~6-fold. The similar effect is observed for γ -CD (fluorescence signal amplification is in 2 times). In contrast, the addition of α -CD does not cause practically any significant changes in the coumarin-6 fluorescence inside of the clusters. Taking into account the obtained data, the possible explanation of these regularities is that during the interaction of MCC with β -CD, their destruction occurs with the formation of stable rotaxane-based complexes of β -CD with Triton X-114, accompanied by the release of coumarin-6, which, in turn, also reacts with cyclodextrin excess to form a complex having strong fluorescence. A similar effect is observed for γ -CD, however, taking into account that its effect on clusters is less than that for β -CD, coumarin-6 is more difficult to release from the MCC. In the case of interaction with α -CD, coumarin-6 remains completely inside the MCCs, since this cyclodextrin has practically no effect on MCCs. Moreover, under these conditions, it is not possible to extract the dye from the MCCs, since its fluorescence does not change after the addition of α -CD. In the case of interactions of bilirubin-containing MCCs, their similar destruction under the action of cyclodextrins occurs, and bilirubin in all cases form complexes with cyclodextrins rather than crystalline aggregates. The work was supported by the Grant Council under the President of the Russian Federation, the state support program for young scientists and candidates of the science of the Russian Federation No MK-2124.2017.3.

Tracking Populations of Extracellular Vesicles by Dynamic Light Scattering: Changes in Size Distributions of Submicron Particles in Human Blood Plasma after Heart Surgeries Engaging Extracorporeal Blood Circulation

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Successful enrolment of extracorporeal blood circulation (ECC) in early 1950s outset the era of the modern heart surgery and is nowadays indispensable in majority of the open-heart procedures. However, ECC is still linked to various mild to serious adverse reactions, mainly induced by activation of haemostatic and immune system. In severe cases, the ECC provokes systemic inflammatory response syndrome (SIRS), which can be followed by compensatory anti-inflammatory response syndrome (CARS). SIRS and CARS are important causes of poor treatment outcome. Extracellular vesicles (EVs) produced by different blood cells were already confirmed to influence coagulation [1-3] and inflammation [4-8]. Therefore, monitoring of the circulating EVs status might be noteworthy for predicting and preventing post-surgery complications.

In our study blood plasma samples were analysed by dynamic light scattering, employing CONTIN analysis [9]. This light scattering technique is non-specific and non-destructive and allows analysis of size distributions of particles smaller than blood cells with minimal pre-analytical sample treatment.

In the samples studied here, populations with mean R_h below 10 nm were attributed to proteins. In the size range of EVs, there were one (smaller, $10 < R_{h,90} < 50$ nm) or two populations (smaller and larger, $50 < R_{h,90} < 200$ nm), as observed at 90° angle (Figure 1). The population of larger particles significantly increases in number during surgical procedures engaging extracorporeal blood circulation. Further studies of correlations of these changes with post-operative events and treatment evolution might represent some new foundations for therapy optimization and improvement of treatment outcome.

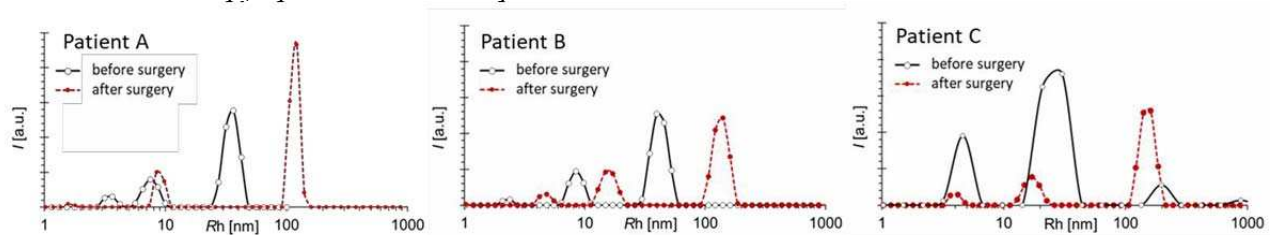


Figure 1. Three examples of representative changes in submicron particle size distributions in human blood plasma following heart surgery with extracorporeal blood circulation.

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Characterization of Extracellular Vesicles in Human Blood Plasma: Combination of Static and Dynamic Light Scattering

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Extracellular vesicles (EVs) have been studied extensively in the last few decades [1-5]. In this contribution, we have focused on methods for size and shape evaluation of particles in samples based on EVs, in particular on the combination of dynamic (DLS) and static light scattering (SLS). Although these two methods have already been used for the assessment of EVs isolates [6-8], a systematic analysis of their limitations for the analysis of EVs in human blood plasma has not yet been performed. We have tested the suitability of EVs characterization and suggested an approach for their analysis by DSL and SLS in human blood plasma.

DLS and SLS data yield two size parameters: the radius of gyration, R_g (a SLS result), and the hydrodynamic radius, R_h (a DLS result). The shape and architecture of the particles are then assessed through so-called shape parameter, ρ ($= R_g/R_h$). In the evaluation of R_h , viscosity is a crucial, but poorly understood and therefore often neglected parameter in particular in complex biological samples such as blood plasma. The value of R_h is derived from the scattered light fluctuations through diffusion coefficient, D , using the Stokes-Einstein equation. Accuracy of R_h obtained as a result of this analysis largely depends on the definition of the medium and on the correct viscosity assigned to it. In our approach, we determined the viscosity value for the DLS analysis of EVs in blood plasma samples, which reduced the divergence between the attributed R_h values of EVs populations in human plasma samples compared to EVs isolates from the same samples in buffer solutions. Size distributions of particles that were recognized to correspond to EVs were similar in all types of analysed samples, *i.e.* in blood plasma, in isolates of EVs obtained from it (in phosphate buffer saline) and in exosome standard (Lyophilized Exosome Standards; HansaBioMed LLC, Estonia) (Figure 1). The value of ρ (≈ 1) confirmed the hollow vesicular structure of EVs in all samples. The findings from LS were supported by the analysis of the same samples by atomic force microscopy, asymmetric flow field flow fractionation, flow cytometry and nanoparticle tracking analysis.

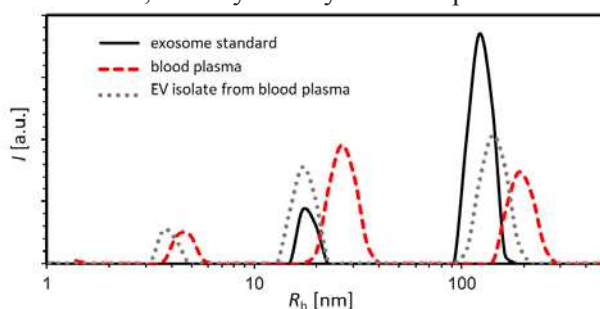


Figure 1. Particle size distribution (angle: 90°) in different samples when viscosity of water is accounted for in the calculation of R_h .

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How to build a defined synthetic shell on bacteria in a tailor-made manner?

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The engineering of the surface of the bacterial cell is extremely potent in forced attachment of cells to any sort of surfaces or the addition to cells new functions by attaching molecules such as enzymes, ligands, antibodies etc. These modified bacterial cells can increase the efficiency of biotechnological processes by decreasing lag phase, forming biofilms or flocs, or in medicine to induce specific immune response and increase vaccination efficiency [1]. Here we investigated a method of electrostatic interaction of cells with polyelectrolytes since cells can be assumed to act similar to negatively charged particles. Although, nonliving particles such as calcium carbonate, silicon dioxide and polystyrene beads were demonstrated as a suitable core for building capsules using layer-by-layer approach (LBL). The bacterial cells are different sort of particles due to the variable surface properties, constant modification of their envelopes and at the end of the procedures they need to be kept alive.

Hence, cells can rapidly form spatial random-sized uncontrollable aggregates after being exposed to polyelectrolytes [2], and to make controllable deposition of polyelectrolytes on their surfaces it is needed to have in mind the physiology of particular bacterial species and selected correct polyelectrolytes not showing toxicities or forming clumps.

Therefore, in prior of covering by LBL we determined the properties of the surface charge of bacterial cells at different distinct physiological stages using Ohshima's softness model. After the deposition, we determined efficiency of covering, aggregation level, and change in protein expression level as well as their survivability.

Our results showed that by using particular polyelectrolytes on cells at particular growth stage they can be well encapsulated in tailor-made shells under defined architecture and staying alive, resulting in increased cell weight till cracking the capsule wall and escape from it. Such capsules due to the enormous strength (up to 300MPa) caused interesting physiological effects such as delayed growth dependent on the number of layers due to mechanical constriction of individual cells and producing high amount of proteins in contrast to the control non-LBL modified cells.

The LBL approach developed here is very convenient since the architecture of the cell wall can be very well-defined in sense of charge densities, presence of active groups, strengths as well as thickness of layers after the deposition of a particular polyelectrolyte, the attachment of particular molecules and number of layers, respectively.

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Assembling of magnetic fluorescence engine for bacterial theranostics

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Bacterial strains such as *Salmonella* spp and *Listeria monocytogenes*, when trained to infect and destroy cancer cells, can be very successfully used in treatments of different sorts of tumors [1]. Moreover, the intrinsic property of bacteria to induce and modulate strong immune response via cell envelope producing endotoxins as well as by excreting variety of immunogenic molecules can increase therapeutic effect and better prognosis of the disease outcome [2]. However, the repertoire of type of bacterial cells used in such treatments is limited, since currently only above mentioned bacteria can be somehow trained to act relatively specific against the tumors. Moreover, it is important to trace bacterial cells, while they get introduced into the blood circulation system to evaluate efficiency of the targeting of tumors and not to harm the organism by causing sepsis. Since bacterial cells cannot be loaded with fluorescent dyes or their surface modified without the use of the methods of genetic modifications, here we showed a method of electrostatic modification of bacterial cells to make cells that can be remotely guided as well as visible through the tissues.

Our method is based on the exploitation of the electrostatic properties of the negatively charged bacterial cells. We used bacterial cells as a template for the polyelectrolyte adsorption starting with the deposition of the layer of positively charged polyelectrolytes, which were labelled with Cy7 dye, forming shells that produce fluorescent signal in the far red spectrum after excitation.

In addition, between the layers we introduced the magnetite nanoparticles in order to remotely guide bacteria using magnetic field. The bacterial cells were administered in the femoral artery of the mouse animal model where they were trapped at the particular body site using simple permanent magnet. The distribution of such bacteria within the body was monitored using luminograph.

According to our results, the procedure that we developed is very convenient and highly effective as a delivery mechanism for alive bacterial cells at a specific site (see Figure 1.), since we increased the local signal for more than 5 times and decreased the dissemination of the bacterial cells over all the body.

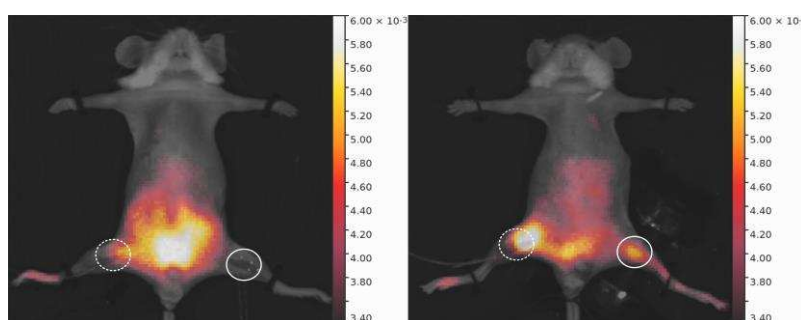


Figure 1. Distribution of bacterial cells modified with magnetite nanoparticles and Cy-7 stained PEI in the mice bodies. Control mouse (left) and exposed under magnet mouse (right) respectively, dash circles – place of injection, solid circles – place of the cell collection.

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Influence of the synthetic lipid-like pyridinium amphiphile structure on the formation of magnetic liposomes

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Magnetic iron oxide nanoparticles (NPs) due to their biocompatibility and functionality may find possible use in biomedicine for theranostic applications which combine therapy and diagnosis into one approach. In this work, we demonstrate how the produced ferromagnetic nanoparticles (γ -Fe₂O₃) functionalized using new self-assembling 1,4-dihydropyridine (1,4-DHP) amphiphiles with variations of the substituents at the cationic head-group of the molecule. The liposomes formed by these 1,4-DHPs are promising tool for the delivery of DNA into cells [1,2]. 1,4-DHP amphiphiles are also attractive molecules as they contain 1,4-DHP core, which is an intrinsic structural part of many pharmacologically active compounds and drugs [3].

The aim of this work is evaluation of influence of the 1,4-DHP structure and on the preparation method of magnetic liposomes. Spontaneous swelling (SpSw) [4] and reverse-phase evaporation (REV) [5] methods were applied. The structures of the investigated 1,4-DHP derivatives are shown in Fig. 1 (compounds 1–7).

The produced magnetic liposomes (MLs) were characterized by dynamic light scattering (DLS) technique (ZetaSizer Nano ZS), optical microscopy (OM) and electron microscopy (TEM and SEM). The results obtained for MLs prepared by the SpSw and REV methods were also compared.

It is shown that REV method along with the use of 1,4-DHP amphiphiles has proved its applicability for production of giant MLs size till 20 μ m (comps. 1 and 2). The non-polar alkyl chains extension leads to a reduction in size of the MLs. The vacuum and accordingly evaporation process' duration affect the MLs size.

It has to be admitted that preparation of liposomes with SpSw method is highly dependant on structure of 1,4-DHP and swelling temperature. In order to determine the temperature range when liposomes can be formed, the compounds in solid state were tested using thermogravimetric (TG) and differential thermal analysis (DTA) (Shimadzu DTG-60). SpSw method shows the best result at MLs production. The sizes of MLs obtained by SpSw observed by OM vary in the 1–18 μ m range for compounds 1, 2, 3 and 7. Comp. 6 has ability to form a homogeneous liposomal dispersion.

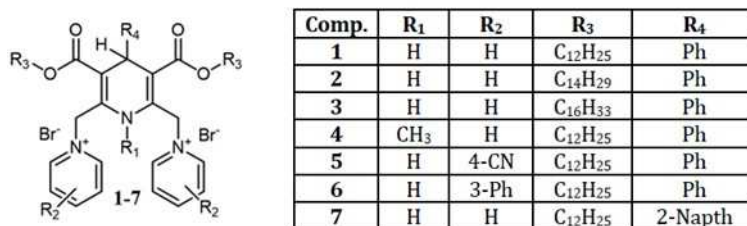


Figure 1. Structures of the studied 1,4-DHP derivatives 1–7.

Acknowledgements: Support from PostDocLatvia project No 1.1.1.2/VIAA/1/16/018 (for O. Petrichenko) is gratefully acknowledged.

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Human serum albumin adsorption at gold substrates

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Adsorption kinetics of human serum albumin (HSA) at a gold substrate was studied using the quartz microbalance (QCM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy. Measurements were performed at pH 3.5 for various bulk suspension concentrations and ionic strengths. The QCM experimental data were compared with the dry coverage of HSA derived from AFM and from the solution of the mass transfer equation acquired using a hybrid random sequential adsorption model. In this way, the water factor and the dynamic hydration function for HSA monolayers were quantitatively evaluated as a function of dry coverage for various ionic strengths. A comparison of these results with previously known for a silica sensor confirmed that the QCM kinetic measurements are sensitive to the roughness of the sensor, quantitatively characterized in terms of the *rms* parameter. For the rough gold sensor (*rms* = 2.5 nm, average surface feature size 6 nm) the QCM mass transfer rate constant was 2.6 times lower than for the silica sensor characterized by *rms* = 0.86 nm. This gives for the gold sensor the apparent water factor equal to one and zero hydration function. Moreover, the hydration function increased for larger HSA coverage and was dependent on ionic strength in contrast to the silica substrate (see fig. 1). This unexpected behavior was interpreted in terms of the buoyancy effect where the HSA molecules adsorbing in cavities existing at rough surfaces replace the stagnant (hydrodynamically bound) water. Hence, these results confirm that the sensor roughness of the size comparable with protein molecule dimensions exerts a decisive influence on their adsorption kinetic derived from QCM measurements.

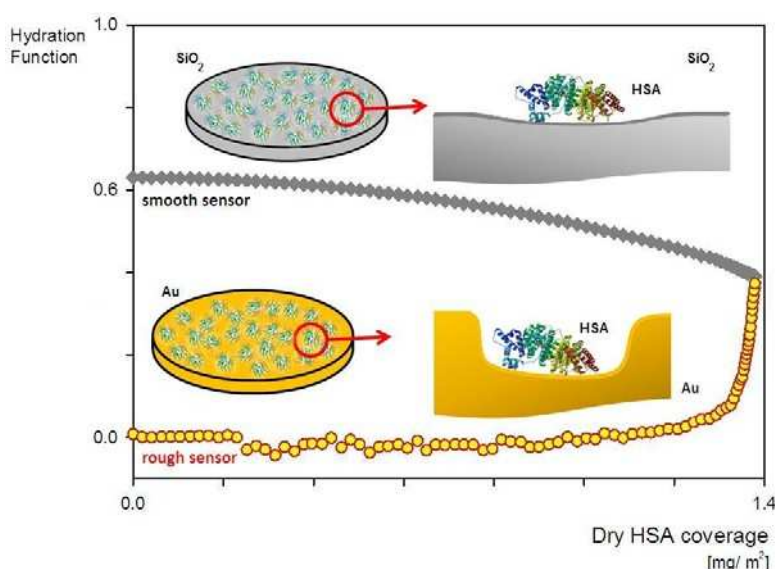


Figure 1. Adsorption of HSA on gold and silicon sensors.

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Determining mechanism of albumin and fibrinogen adsorption on mica

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Human albumin (HSA) and fibrinogen (Fb) monolayers on mica of controlled coverage were produced by controlled adsorption under diffusion transport. It was confirmed that these molecules irreversibly adsorb on mica with the rate governed by the bulk transport. The electrokinetic properties of proteins monolayers produced in this way were studied using the streaming potential method. The dependencies of the monolayer zeta potential on the coverage, pH and ionic strength were determined. Experimental data were interpreted in terms of the general electrokinetic model that allowed to determine the coverage of proteins under in situ conditions. The charge distribution and orientation of molecules in the monolayers was determined using the colloid deposition (CD) method where negatively charged polystyrene microparticles (820 nm in diameter) were used. In Fig. 1 the experimental results are plotted as the dependence of the normalized microparticle coverage Θ/Θ_{max} on their minimum approach distance obtained h_m [1]. It is seen that the normalized microparticle coverage decreases to 0.5 at $h_m = 5$ nm that agrees with the length of the shorter axis of the spheroid approximating the HSA molecule shape. Therefore, the results shown in Fig. 1 suggest that HSA adsorption at mica at pH 3.5 and ionic strength range of 0.15–0.01 M occurs under the side-on orientation. For comparison, the results obtained for fibrinogen adsorption at mica are also plotted in Fig. 1 [2]. It is observed that in this case the critical value of h_m is equal to 75 nm that agrees with the extended length of the fibrinogen molecule predicted at this pH [3]. Therefore, one can conclude that the colloid deposition method is an appropriate tool for determining in situ the thickness of protein monolayers and in consequence adsorbed molecule orientations.

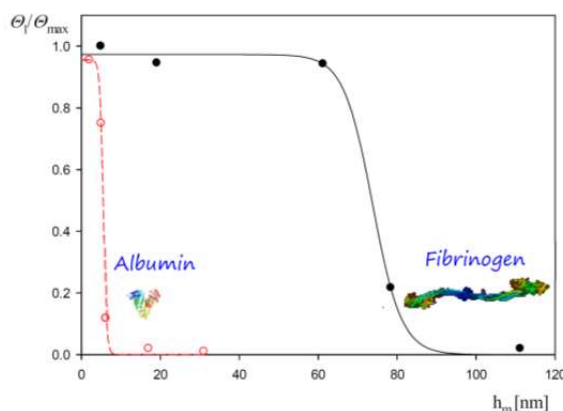


Figure 1. The normalized coverage of microparticles Θ/Θ_{max} at protein monolayers vs. the minimum approach distance h_m regulated by ionic strength varied between 0.15 and 0.01 M (pH 3.5). The dashed and solid lines show the results obtained for HSA and Fb, respectively.

Acknowledgements: This work was supported by the NCS Grant: UMO-015/19/B/ST5/00847 and the NCRD grant POIG 01-01.02-12-028/09.

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Human serum albumin (HSA) monolayers on positively charged polymer microparticles

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Human serum albumin (HSA) is used as biocompatible vector in drug delivery systems, for the formation of anti-adherent coatings against blood plasma proteins, platelets and bacteria in hemodialyzer membranes, catheters, pacemakers, titanium implants. It is also used as the blocking agent by preparing immunoglobulin covered microparticle suspensions (latexes) used in agglutination immunoassays [1-4].

Human serum albumin (HSA) adsorption on positively (see Fig. 1) and negatively charged polystyrene microparticles was studied at various pHs and NaCl concentrations. Thorough electrophoretic mobility measurements were carried out that enabled to monitor in situ the progress of protein adsorption. The maximum coverage of irreversibly adsorbed HSA on microparticles was determined by different concentration depletion methods, one of them involving AFM imaging of residual molecules. An anomalous adsorption of HSA on the positive microparticles was observed at pH 3.5 where the maximum coverage attained 1.0 mg m^{-2} for NaCl concentrations of 0.05 M despite that the molecules were on average positively charged. For comparison, the maximum coverage of HSA on negatively charged microparticles was equal to 1.3 mg m^{-2} for NaCl concentrations of 0.05 M and pH 3.5. At pH 7.4 the maximum coverage on positive microparticles was equal to 2.1 mg m^{-2} for 0.05 M NaCl concentration. On the other hand, for negative microparticles, negligible adsorption of HSA was observed at pH 7.4 [5]. These experimental data were adequately interpreted in terms of the random sequential adsorption approach exploiting the bead model of the HSA molecule. Different orientations of adsorbed molecules, in particular, the edge-on orientation prevailing for positively charged microparticles at pH 7.4, were confirmed. This was explained in terms of a heterogeneous charge distribution over the HSA molecule prevailing for a wide range of pHs.

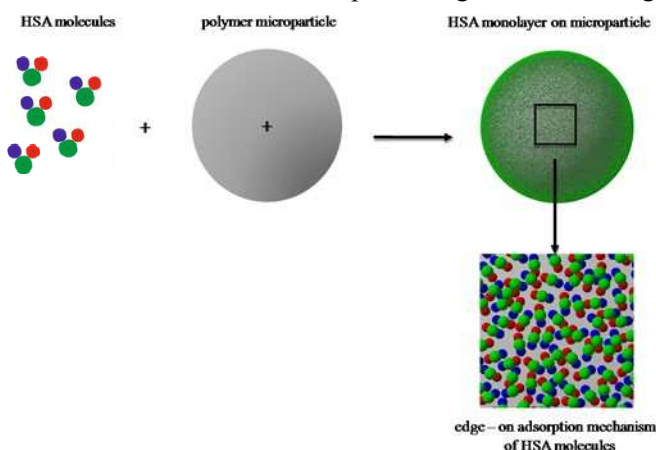


Figure 1. Adsorption of HSA on positively charge polymer microparticles predicted by random sequential adsorption modeling. Various color denote the three main domain of the HAS molecule.

Acknowledgements: This work was supported by the NCS Grant: UMO-015/19/B/ST5/00847 and the NCRD grant POIG 01-01.02-12-028/09.

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Not just a fluidizing effect: omega-3 phospholipids induce formation of non-lamellar phases in biomembranes

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DocosaHexaenoic Acid (DHA) belongs to omega-3 family, highly unsaturated fatty acids found in cell membranes as phospholipid acyl chains, which have been claimed to exert many beneficial effects, including neuroprotection and prevention of several diseases, including neurodegenerative disorders, such as Alzheimer and Parkinson diseases [1, 2].

However, molecular comprehension of these properties is still lacking [3]. Electron paramagnetic resonance (EPR), neutron reflectivity (NR) and cryo-TEM analyses show that incorporation of the DHA-di-phospholipid 1-2-docosahexaenoyl-sn-glycero-3-phosphocholine (22:6-22:6PC) in membranes formed by the naturally abundant 1-palmitoyl-2-oleyl-sn-glycero-3-phosphocholine (POPC) induces a decrease of acyl chains ordering in liquid disordered (L_d) membranes. Strikingly, beyond a threshold 22:6-22:6PC content, non-lamellar structures form, such as sponge-like and monodisperse spherical aggregates.

These peculiar 22:6-22:6PC features provide a reasonable key to interpret the effects of omega-3 fatty acids on biomembranes, opening to a comprehension of their biological role.

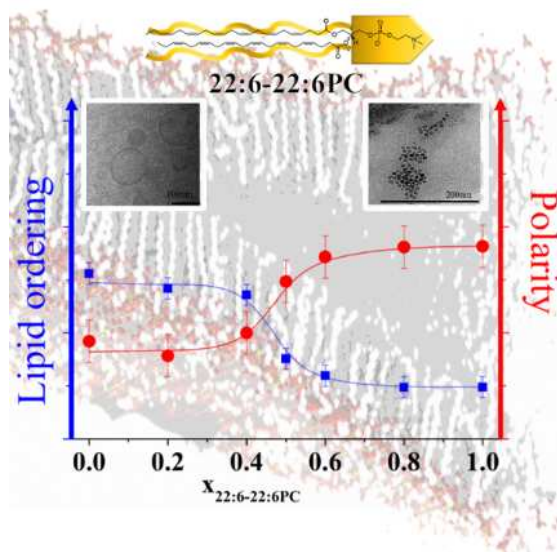


Figure 1. Evidences of 22:6-22:6PC-induced transition in POPC bilayers

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Conformation characteristics of DNA-based dendrimers in electrolyte solutions

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Dendrimers are synthetic macromolecules possessing a highly branched and regular internal structure. Charging these dendrimers leads to conformational responsiveness, i.e. one of the most important ingredients for their envisioned applications, which is essentially lacking for their neutral counterparts.

Recently, Luo and his co-workers at Cornell University synthesized dendrimer-like DNA (DL-DNA) via enzymatic ligation of Y-shaped DNA building blocks [1]. These charged DNA-based dendrimers are novel macromolecule aggregates, which hold high promise in bringing about targeted self-assembly of soft-matter systems in the bulk and at interfaces.

Inspired by these findings, we study systems of DL-DNA molecules in order to advance the theoretical analysis of novel self-assembled structures. First, we simulate a single DL-DNA molecule, whose base-pairs are modeled by charged monomers. Their interactions are chosen to mimic the equilibrium properties of DNA correctly. We then employ MD simulations to measure equilibrium properties, e.g., the tensor of gyration and form factors. The obtained results are compared to experiments. In order to simulate large ensembles of DL-DNA, we calculate a coarse-grained potential for the dendrimers by employing an approach based on the Widom particle-insertion method [2]. With this coarse-grained potential at hand, we investigate the phenomenon of cluster crystals of DL-DNA in the bulk [3], a novel form of solids with multiple site occupancy.

The study of these charged dendrimer systems is an important field of research in the area of soft matter due to their potential role for various interdisciplinary applications, ranging from molecular cages and carriers for drug delivery in a living organism [4] to the development of dendrimer- and dendron-based ultra-thin films in the area of nanotechnology [5].

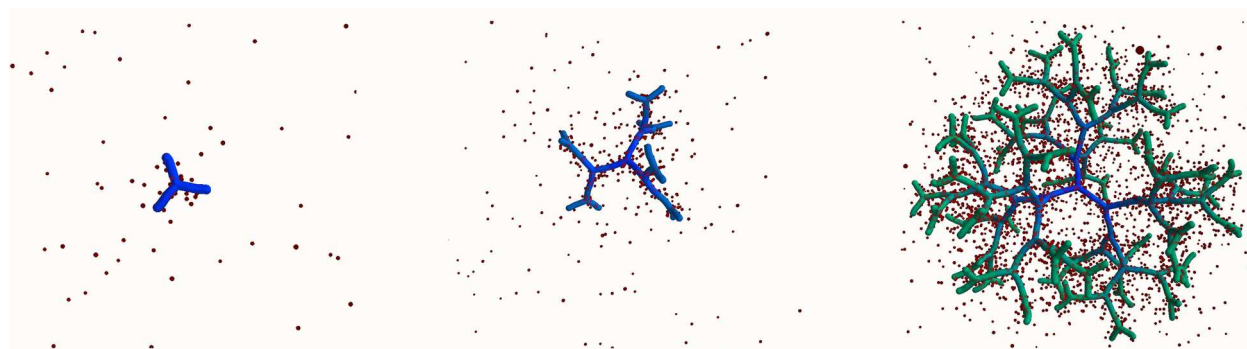


Figure 1. Simulation snapshots of G1, G3, and G6 DL-DNA (from left to right). Different generations of the dendrimers are indicated by different shades of blue, while counter-ions are colored red.

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Dynamic Hydration Function of Human Serum Albumin adsorbed at Silica Sensor

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In order to achieve efficient protein separation for biosensing and bioreactors, controlled adsorption of biomolecules at various surfaces is needed. The mechanism of protein adsorption still not completely understood, although the subject has been extensively studied [1,2]. Differences still exist concerning basic aspects such as: the driving forces, reversibility of adsorption, monolayer structure and stability, degree of conformational changes, maximum coverage and interpretation of isotherms [3].

In this work, attention is focused on human serum albumin (HSA- most abundant serum protein) in an attempt to unveil protein adsorption mechanisms. Adsorption kinetics of HSA at silica substrates was studied using the QCM-D, OWLS and AFM methods as a function of ionic strength at pH 3.5. The obtained experimental data were calibrated via the dry coverage of HSA derived from OWLS, AFM imaging and from the mass transfer equation solution. Thus, the dynamic hydration functions and water factors of HSA monolayers were quantitatively evaluated. The HSA adsorption runs were converted to the dry coverage vs. the time relationships, using the hydration function. It allowed to determine the maximum coverage of irreversibly bound HSA molecules. The parameter was equal to 0.4 and 1.4 mg m⁻² at pH 3.5 and for NaCl concentration of 0.001 and 0.15 M, respectively. These results confirm previous experimental data for mica derived by streaming potential measurements combined with theoretical modelling [4]. In this way, the side-on mechanism of HSA adsorption at silica sensor at pH 3.5 was confirmed. In addition, a quantitative analysis of the HSA desorption runs allowed to calculate the binding energy of reversibly adsorbed HSA molecules. These results enable one to develop a robust technique of preparing HSA monolayers at silica sensor of well-controlled coverage and molecule orientation.

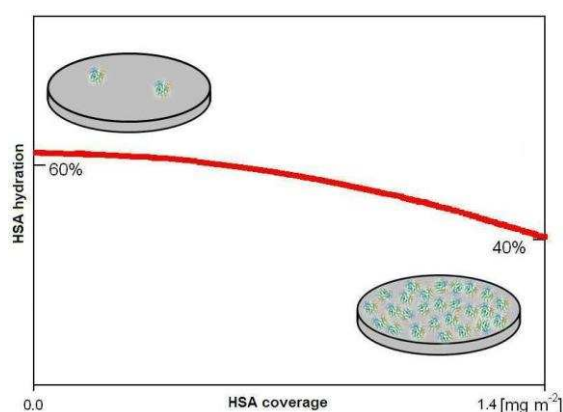


Figure 1. The dynamic hydration function for HSA at silica sensor.

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A computational and experimental investigation of the structural properties of the N-terminus MgtA peptide keif

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Many years ago, it was believed that proteins needed a clearly defined secondary and tertiary structure in order to have any biological activity. As research progressed, this was however proven to be wrong when it was discovered that many intrinsically disordered proteins and regions (IDPs and IDRs) are involved in an extensive number of biological functions [1]. Due to their intrinsic flexibility IDPs are generally more difficult to study, both experimentally and computationally. Nevertheless, the structure and function of IDPs are still widely studied through a variety of methods in order to understand how their lack of structure contributes to protein functions in the physiological environment.

Recent studies by Subramani et al. [2] have implied that the N-terminus of the magnesium transporter A (MgtA) protein (from hereon called keif) is intrinsically disordered, but the advantage of this disordered feature to the function of the protein is still unknown. Thus, in this study, the structure of the keif peptide part have been investigated by using both molecular dynamics (MD) and Monte Carlo (MC) simulations, as well as different experimental techniques such as circular dichroism (CD) and small-angle X-ray scattering (SAXS). Early predictions of the structure of keif suggested that even though it is disordered, its average shape should still be quite globular. However, it was quickly discovered through both simulations and experiments that keif in fact adopts extended conformations instead, see Figure 1. In addition to bulk studies at different ionic strengths, the effect of divalent ions has also been investigated.

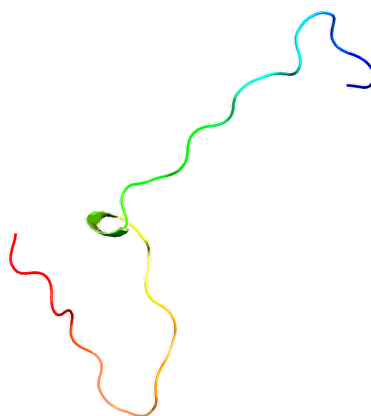


Figure 1. A snapshot of the representative structure of keif from molecular dynamics simulations.

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High throughput fabrication of cell spheroids by templating water-in-water Pickering emulsions

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Tissue engineering requires large amounts of cell spheroids [1-3]. Tissue spheroids have been actively used as 3D tumour models [4], tissue reconstruction and organ bioprinting [2]. Spheroids of adherent cells can be formed using different processes for cell clustering where they adhere to each other rather than to a substrate. The current processes of cell spheroid production involve spinner culture, NASA rotary culture and non-adhesive surfaces [5], the hanging-drop culture [6] and 3D culturing in microwells [7]. Although many techniques for tissue spheroids preparation have been reported, none of them are currently able to rapidly produce significant amounts of spheroids. Here we describe a simple and generic technique for high throughput generation of tissue spheroids based on encapsulation of dispersed adherent cells in a water-in-water Pickering emulsion stabilised by protein particles [8]. The emulsion is formed from a cell suspension in an aqueous solution of dextran (DEX), which is dispersed in an aqueous solution of polyethylene oxide (PEO) containing protein particles. The cells are trapped in the DEX drops of a stable DEX/PEO emulsion which they prefer compared with the continuous PEO phase. Further addition of more concentrated PEO phase leads to osmotically driven shrinking of the DEX drops and compresses the adherent cells into tissue spheroids which are isolated by breaking the emulsion by dilution with a culture media. We demonstrate the method by using HEK293 fibroblasts and show that the cells preserve their viability in the spheroid generation process. We also successfully prepared model membranes by growing HEK 293 cell spheroids in alginate films until they overlap and produce a tissue. This work will give researchers cheap and scalable technique for rapid preparation of similarly sized spheroids of adherent cells for bio-inks for 3D organ bioprinting applications and potentially for tumour models.

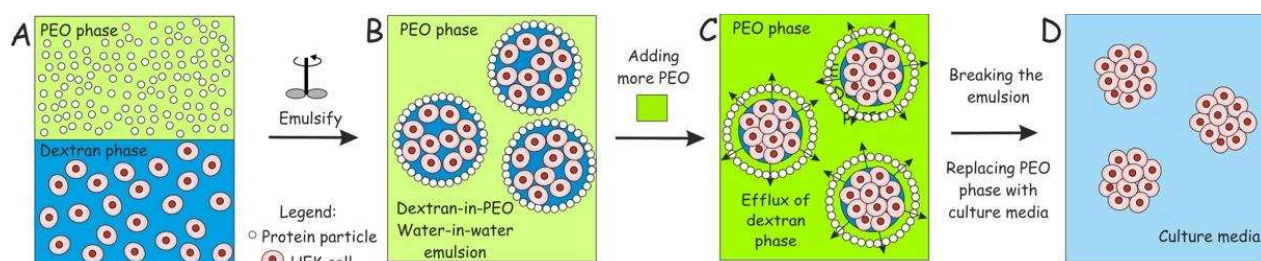


Figure 1. Schematics for our method for preparation of cell spheroids by templating DEX-in-PEO water-in-water Pickering emulsions.

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How Drops Start Sliding Over Solid Surfaces

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On a pivot window pane sessile drops of water start sliding when a critical tilt angle is reached, i.e. when the gravitational force acting on the drop overcomes the lateral adhesion force. The question may therefore be raised: How do drops start sliding over solid surfaces and how do the forces develop while the drops slide?

Therefore, we have investigated the lateral adhesion forces of liquids of different polarities and surface tensions on smooth, rough and structured surfaces [1]. The lateral adhesion forces were measured with a home build instrument [2], which is sketched in Figure 1. We found that the lateral adhesion force between a liquid drop and a solid can be divided into a static, a transition and a kinetic regime.

The forces upon drop sliding F_{LA} are associated with a contact angle difference between the rear θ_{Rear} and the front θ_{Front} of the drop, the liquid-air surface tension γ and the contact width L of the drop:

$$F_{LA} = k \cdot L \cdot \gamma \cdot (\cos \theta_{Rear} - \cos \theta_{Front})$$

The dimensionless factor k accounts for the precise shape of the solid–liquid–air three-phase contact line of the drop. A calculation of F_{LA} quantitatively agreed with the measured lateral adhesion forces. In particular, the calculation reproduced the transition between the static and kinetic regimes. Additional measurements with varying drop sizes and sliding velocities indicated that the lateral adhesion force is dominated by contact line friction and that interfacial friction only plays a minor role.

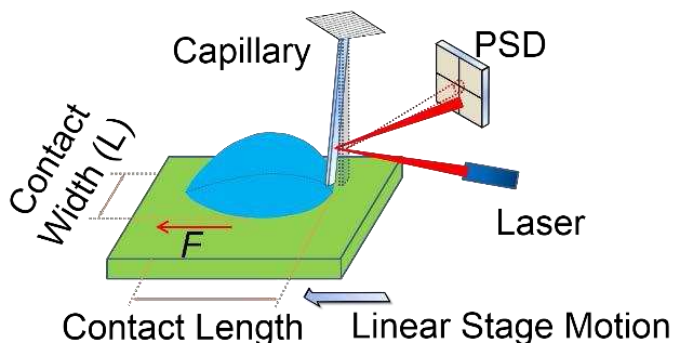


Figure 1. A drop of liquid is placed on a solid substrate mounted on a linear stage driven by a step motor. A laser beam is focused on a flexible capillary that acts as force sensor. The reflected light is focused on a position-sensitive detector (PSD). High-speed cameras simultaneously monitor the contact width, contact length and the contact angles at the rear and front side of the drop.

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Dynamic depletion force in wetting films due to surfactant micelles and its effect on the motion of bubbles in capillaries

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The mobility of fluid particles (bubbles and drops) in a capillary filled with nanofluid is governed by the friction in the wetting film intervening between the bubble/drop and the capillary wall. The quantitative modelling of this problem is important for various technological processes; microfluidics; transport in porous media and blood vessels. Bretherton's [1] analytical formula for the velocity of bubbles in vertical capillaries holds for fully mobile bubble surfaces, for Bond numbers in the range $0.842 < Bo < 1.03$, and for small Reynolds numbers. For $Bo < 0.842$, wetting films can be stabilized by the structural disjoining pressure due to nanoparticles or surfactant micelles, but in this case the bubble velocity is extremely low [2]. In our study [3], we investigated the rise of air bubbles in wider capillaries; the liquid phase was a micellar surfactant solution and the bubble rise was about 100 times faster than in [2]. Experiments were carried out with both ionic and nonionic surfactants at constant surface tension above the CMC. Interestingly, with the increase of micelle concentration, the bubble velocity also increases. This effect is counterintuitive, because the rise of micelle volume fraction leads to higher solution's viscosity, and one could expect slower bubble motion. To resolve this paradox, we developed a quantitative theoretical model, which is based on numerical solution of the hydrodynamic problem and takes into account (i) the variations in bubble shape; (ii) the exchange of surfactant molecules between the micelles and bubble surface and (iii) the related transport of adsorbed surfactant molecules along the bubble surface (Figure 1). At that, the effect of micelles is twofold: (i) They supply surfactant molecules to the bubble surface and render it mobile relative to the bubble profile, thus, accelerating the bubble motion. (ii) Because the micelles serve as sources of surfactant, their concentration inside the wetting film is lower than in the bulk, which gives rise to a dynamic depletion force [4] that decreases the film thickness and decelerates the bubble motion. The steady-state bubble velocity, which is influenced by the balance of these two effects, is predicted by the model in excellent agreement with the experiment [3].

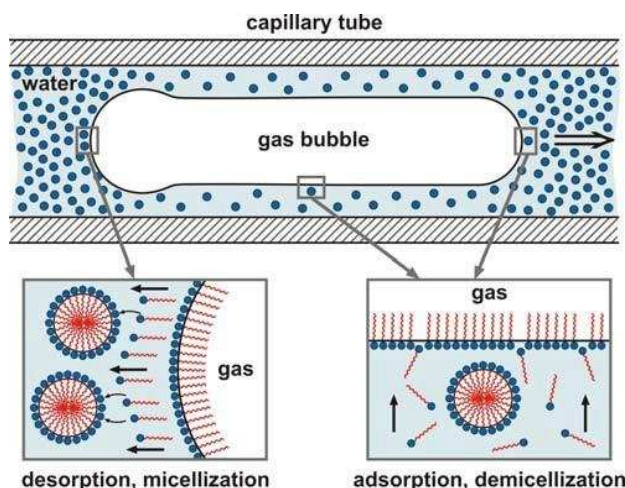


Figure 1. Sketch of bubble moving in a capillary with micellar solution and of the accompanying processes.

Acknowledgement: This work was funded by the ERC grant to S.K.S., EMATTER (# 280078).

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Wetting of milliscale step geometries with varying kinematic conditions

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Wettability research in the area of milliscale geometries is not so frequent [1-2], especially for dynamic quasi- steady and non-quasi-steady cases with Capillary numbers on the order of unity. To expand the understanding of wetting in this regime, experiments with varying kinematic conditions were performed. The geometric structure used for these experiments consists of two flat aluminium plates connected by a perpendicular step between them (see Fig. 1). This geometry allows examination of the coupling between the spreading across the faces of the structure and the interior and exterior corners. The height of the step was varied during the experiments from 0.05 to 15 millimeters with the fluid capillary length on the order of 1.7 to 2.7 mm.

The samples were vertically dipped into a liquid pool at different speeds and accelerations. As shown in figure 1 most of the experiments were performed with the dipping direction tangential to all faces of the geometry (marked primary in the figure). Additional experiments were performed with dipping in the directions labelled as secondary and tertiary in the figure and the behaviour of cyclic wetting and dewetting was analysed. Different liquids and liquid mixtures were used to perform the experiments.

In this presentation, the technique developed and used in this study to capture the contact line position of transparent liquids on metal surfaces will be briefly described. The results of the experiments, which will include the wetting time scales and geometric influences, will be shown, expressed with suitable dimensionless numbers. A wide range of values of these dimensionless numbers will be covered in this study to develop a clear picture of how the wetting behavior depends on the values and the different dimensionless numbers.

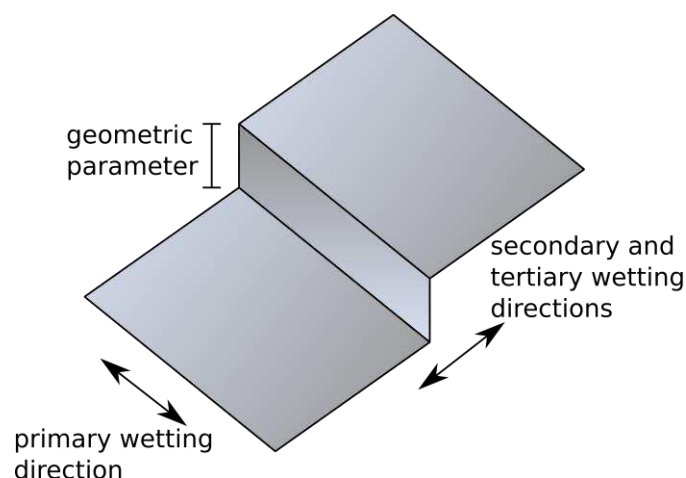


Figure 1. The step geometry used for the experiments.

Acknowledgements: We kindly acknowledge the financial support by the German Research Foundation (DFG) within the Collaborative Research Centre 1194 “Interaction of Transport and Wetting Processes”, Project A01a

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Emulsion-based Lubricant Replenishment Strategies for Lubricant-Impregnated Slippery Surfaces under Flow

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Lubricant-Impregnated Slippery Surfaces (LubISS) constitute of textured/porous substrates infiltrated with a chemically compatible lubricant [1]. The action of capillary forces establishes an immobilized liquid surface which keeps the lubricant in place within the texture.

As a consequence, they are liquid-repellent and non-sticking surfaces. Droplets immiscible with the lubricant slide off these surfaces very easily. A formidable challenge which needs to be addressed is the problem of lubricant depletion [2, 3]. Evaporation of the lubricant, cloaking, drainage due to gravity or flow conditions causes progressive loss of lubricant which in turn destroys the functionality of the coating [4, 5]. In this work, a proof of concept for a novel approach to the formation of LubISS is introduced. We rely on the flow of emulsions through a closed water-filled flow cell containing a regular and uniform micropillar array. We observe that oil droplets transported through the channel readily attach to the tops and walls of the micropillars. Subsequently, the droplets grow in size due to the coalescence with other arriving oil droplets. Eventually, the growing droplets spread onto the bottom substrate and hence gradually fill the channel, leading to the formation of a LubISS. The influences and effects of the texture and geometry of the solid substrate, the surface chemistry, the flow conditions, the oil viscosity, the chemical nature and the filling mechanism are investigated by Laser Scanning Confocal microscopy (LSCM) and advanced image processing. Central to the successful filling of a structure is the addition of a positively charged surfactant at a concentration within the range of the point of charge reversal in order to compensate for the negative charges present on the oil droplets preventing droplet coalescence. This approach can in principle facilitate a strategy for active lubricant replenishment preventing the detrimental depletion of lubricant since starting with the empty micropillar array represents the worst-case scenario of a porous structure completely depleted of lubricant.

Acknowledgements: The LubISS (Lubricant Impregnated Slippery Surfaces) project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722497.

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Scanning droplet adhesion microscopy for mapping wetting variations on water-repellent surfaces

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Superhydrophobic surfaces often contain microscopic irregularities in surface texture and chemical composition, which may affect or even govern macroscopic wetting phenomena. Here we present a novel technique, scanning droplet adhesion microscopy [1], able to measure small adhesion forces between water drop and superhydrophobic surface with remarkable sensitivity three orders of magnitude higher compared to state-of-the-art techniques (Figure 1a). The microscope allows detailed wetting characterization even of challenging non-flat surfaces, like the butterfly wing (Figure 1a-1c). The measured droplet adhesion forces are given in the form of wetting maps (Figure 1d-e), that present a new concept for visualizing imperfections and local variations in wetting. The outstanding sensitivity of the microscope allows revealing wetting heterogeneity of micropillar model surfaces previously assumed to be uniform. Furthermore, we will show that the pinning and depinning forces on superhydrophobic micropillars when the drop is advancing or receding from pillar to pillar could be quantified for the first time using scanning droplet adhesion microscopy. Our results show that droplet adhesion correlates with water-repellency and is a sensitive measure for demanding superhydrophobic surface characterization. This technique presents a potential key tool for improving superhydrophobic surfaces, giving the opportunity to study and understand how wetting of model surfaces and especially on irregular surfaces is related to the microscopic surface features.

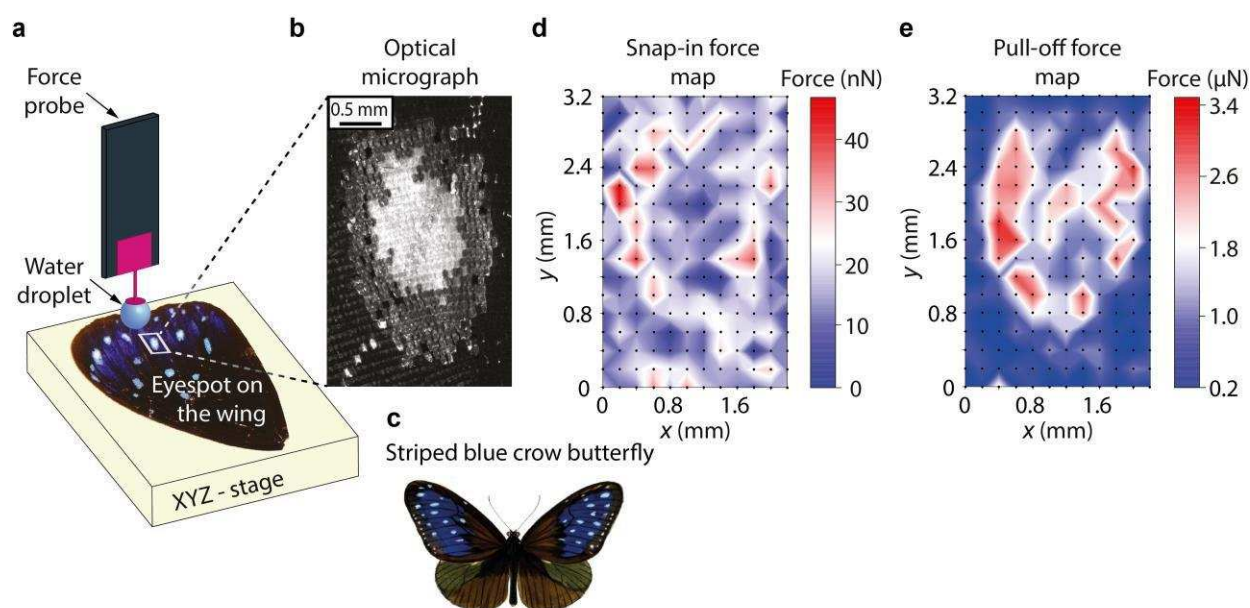


Figure 1. Concept of scanning droplet adhesion microscopy to construct wetting maps showing (a) schematic diagram of the microscope (not to scale), (b) optical micrograph of scanned eyespot area on the wing of (c) striped blue crow butterfly with corresponding (d) snap-in and (e) pull-off force maps.

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Epidermis-Inspired Robust Superhydrophobicity

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Since the advent of biomimetics, superhydrophobic plants [1,2] have received much industrial and research interest [3]. Their natural durability stems partly from the strongly cohesive properties of multi-scale organic tissue. Today, although a myriad of synthetic variants has been achieved [3-5], real-world impact continues to be diminished by the poor chemical-structural stability of nano-microstructures required for retaining superhydrophobic states [6]. Here, we present a bi-layer composite design that biomimics the soft but tough nature of organic tissues in plants, enabling enhanced abrasion resistance. This was achieved by a self-stabilized, sprayable polyurethane-acrylic colloid (Fig. 1) [7].

Upon spray-forming, the colloidal solution self-assembles into a micro-roughened surface that is reminiscent of the epidermal layers of superhydrophobic plants. During the same process, the pre-polymer undergoes complete interpenetration, forming stable; tough and elastic interpenetrated polymer networks (IPNs) [7]. The sequential deposition and integration of a superhydrophobic nanomaterial facilely imparts superhydrophobic functionalities. These hierarchically textured superhydrophobic IPN films demonstrate enhanced thermal-mechanical, abrasion, chemical and photo-stability (Fig. 2).

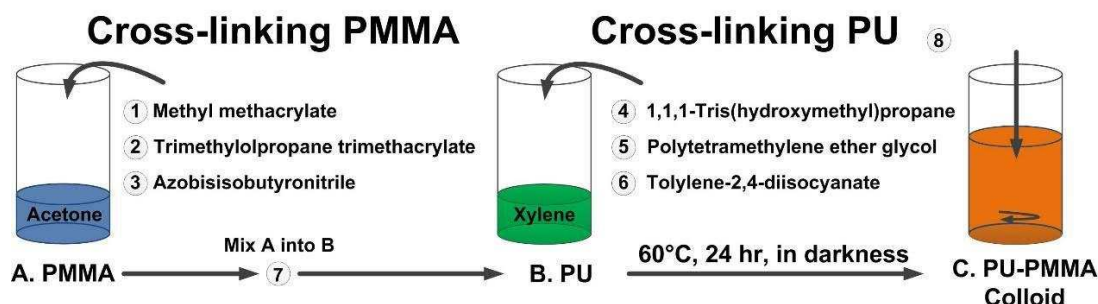


Figure 1. Synthesis of a sprayable stable PU-PMMA pre-IPN colloid.

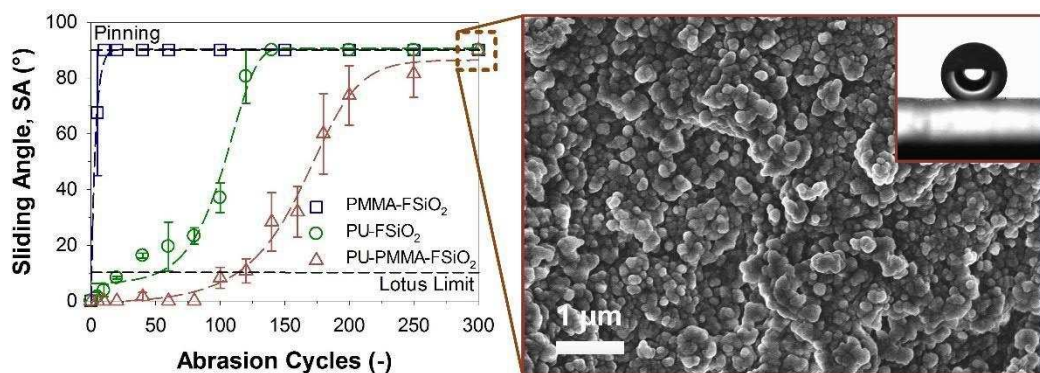


Figure 2. Abrasion resistant superhydrophobic PU-PMMA-based interface vs. controls.

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Combination of Functional Nanoengineering and Nanosecond Laser Texturing for Design of Superhydrophobic Aluminum Alloy with Exceptional Mechanical and Chemical Properties

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Industrial application of metallic materials is hindered by several shortcomings, such as proneness to corrosion, erosion under abrasive loads, damage due to poor cold resistance or weak resistance to thermal shock stresses, etc. Solving the problem of prolonged outdoor performance of metallic materials will have a great impact both in fundamental studies and in industrial application. In recent decades, the great efforts of the scientific community have been devoted to the design of superhydrophobic coatings robust against mechanical loads and electrochemical impacts typical of real harsh exploitation conditions.

In this work, using the aluminum-magnesium alloy as an example of metallic materials, we show that surface nanoengineering based on the laser chemical processing and texturing followed by chemical surface modification by hydrophobic agents, can be used as a versatile and powerful tool for controlling the mechanical and chemical properties of a material with a superhydrophobic coating.

The most important innovative point of the approach for fabrication of superhydrophobic coatings developed here consists in the simultaneous effective use of surface laser texturing, applied to impart multimodal roughness, for task-oriented modification of the physicochemical properties of a thick surface layer of the material itself. Such integration of topographical and physicochemical modification leads to specific surface nanostructures such as nanocavities filled with hydrophobic agent and hard oxynitride nanoinclusions. The combination of superhydrophobic state, nano- and micro features of the hierarchical surface, and the appropriate composition of the surface textured layer allowed us to provide the surface with the outstanding level of resistance of superhydrophobic coatings to external chemical and mechanical impacts [1]. In particular, experimental data presented in this study indicate high resistance of the fabricated coatings to pitting corrosion, superheated water vapor, sand abrasive wear and rapid temperature cycling from liquid nitrogen to room temperatures, without notable degradation of superhydrophobic performance.

The strategy of tuning the laser treatment regimes to obtain the desired chemical composition and structure of surface textured layer, applied here for the aluminum alloy, can be effectively used to design durable superhydrophobic coatings for a wide variety of materials [2,3].

Acknowledgements: The work was supported by the Russian Foundation for Basic Research (grant #17-03-00142) and by the Program for fundamental studies “Nanostructures: Physics, Chemistry, Biology, and Bases for Engineering” of the Presidium of the Russian Academy of Sciences.

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Wettability of magneto-polymer coatings: effect of the composition and external magnetic fields

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Controlling the surface wettability and, in particular, achieving the effect of superhydrophobicity is associated with the formation of a hierarchical relief on the surface in one way or another. In this work, we study the possibility of creating tunable hydrophobic and superhydrophobic coatings based on the so-called magnetoactive elastomers (MAEs) whose structure and properties can be controlled by external magnetic fields. MAEs consist of a soft silicon matrix filled with magnetic microparticles. When a magnetic field is applied to a MAE, magnetic particles within a soft polymer matrix tend to form chain-like aggregates aligned with the field lines and if the magnetic field is perpendicular to the MAE film surface these magnetic chains can grow from the bulk material to its surface producing some mountain-type surface relief [1]. Magnetic-field induced roughness defines rather high values of the water contact angles on a MAE surface [1].

A series of magnetoactive elastomer (MAE) coatings consisting of a silicone matrix and (carbonyl iron particles of 3 – 5 μm in diameter and NdFeB particles with a wide size distribution) have been synthesized and their hydrophobic properties have been investigated in various magnetic fields of disk-shaped permanent NdFeB magnets. Concentration of magnetic filler in MAEs has been varied in the range of 60 – 80 mass%. MAEs elastic modulus has been varied in the range of 4-50 kPa. It has been shown that the contact angle for MAEs based on carbonyl iron grows with external magnetic field. Its values in magnetic field are larger for MAEs containing higher concentrations of magnetic particles. Furthermore, the rate of hydrophobicity enhancement with magnetic field is higher for anisotropic coatings synthesized in magnetic field of 80 mT perpendicular to their surface.

Magnetic field induced hydrophobicity of MAE coatings crucially depends on the elastic modulus of polymer matrix. A soft polymer matrix allows more efficient structuring of magnetic filler which is essential for modulating the surface roughness. The highest value of the contact angle obtained at MAE coating containing 66% of plasticizer was equal to $163^\circ \pm 2^\circ$ in the magnetic field of a stack of 9 disk-like permanent NdFeB magnets of 5mm x 3mm.

Contrary to iron-filled MAEs coatings based on NdFeB particles demonstrate a slight decrease of the contact angle in external magnetic fields which could be explained by either partial surface exposure of particles under magnetic field or much larger sizes of the particles and, hence, the characteristic size of the surface relief.

In summary, this work demonstrates that MAEs are very promising for development of coatings with controllable by magnetic field wettability.

Acknowledgements: Financial support of the Russian Foundation for Basic Research (grant No. 16-29-05276) is gratefully acknowledged.

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Wettability of carbon nanotube fibers

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Carbon nanotubes (CNTs) have received considerable attention owing to their unique 1D structure, and their exceptional mechanical and electrical properties combined with light weight. Assembling them into a fiber is a way to circumvent the difficulties of manipulation and dispersion of individual CNTs and to make them more accessible for applications, e.g. as reinforcement in polymer composites and as electrode casted with polymer electrolyte in energy devices. For these applications, the interfacial adhesion between the CNT fibers and the thermoplastic matrix plays a critical role, in particular for the mechanical performance of the composite materials. Therefore, accurate characterization of the wettability of CNT fibers is one of the most important cornerstones to improve the development of these composite materials.

In this work, the wettability of thin CNT fibers (15 to 20 μm in diameter) was studied by precisely measuring dynamic contact angles of single fibers by using a tensiometer combined with a synchronized optical observation [1,2]. The optical method allowed us to observe the pinning and fluctuation of the contact line, which were triggered by defects on the CNT fiber surface. The contact angle values obtained from both the optical and the Wilhelmy methods are similar, indicating that sorption did not play a significant role during the wetting measurements. Based on a modified Cassie Baxter equation, the equilibrium contact angles on CNTs [3] were derived theoretically by measuring contact angles of CNT fibers at the microscale (Figure 1). The surface energy components of CNTs were obtained from the contact angle measurements, revealing that CNTs have a much smaller polar component than the non-polar component. This result was moreover confirmed by X-ray photoelectron spectroscopy.

The compatibility between the CNTs and various matrices (PP, MAPP, and PET on one side and PVA and PVDF on the other side targeting respectively polymer composite and supercapacitor applications) were estimated by calculating wetting parameters like the work of adhesion, spreading coefficient, and wetting tension. Accordingly, PVA-CNT composites presented the best combination of wetting parameters, showing a high theoretical work of adhesion and wetting tension.

This study offers an in-depth understanding of the wettability of CNT fibers associated with the fiber diameters and surface structures. Further investigations will include experimental studies to validate the predicted adhesion between the CNT fibers and the matrices in order to achieve CNT fiber composites with optimized mechanical properties.

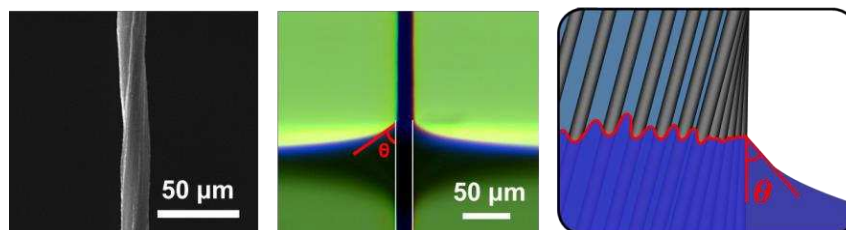


Figure 1. (Left) SEM image of a CNT fiber, (Middle) Liquid meniscus formed around a CNT fiber, (Right) Model of a CNT fiber infiltrated with a liquid.

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Magnetically tunable surface roughness and wettability of soft magnetoactive elastomers

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Dynamically responsive surfaces receive increasing attention in different areas of modern technology, such as touch-based interface systems and devices. Magneto-active elastomers (MAEs) belong to materials with promising properties for this group of applications [1,2]. MAEs are dispersions of micrometer-sized ferromagnetic particles embedded in a soft elastomer matrix. They were found to be suitable also for some non-conventional applications, such as magnetically tunable substrates for biological cell cultures [3].

We investigated surface topographical modifications of a soft magnetoactive elastomer (MAE) in response to variable applied magnetic field. The analysis was performed *in-situ* and was based on optical microscopy, spread optical reflection and optical profilometry measurements. Optical profilometry analysis showed that the responsivity of magnetic field-induced surface roughness with respect to external magnetic field was in the range of $1 \mu\text{m}/\text{T}$. A significant hysteresis of surface modifications took place for increasing and decreasing fields. Investigations of sessile water droplets deposited on the MAE surface revealed that field-induced topographical modifications affected the contact angle of water at the surface. This effect was reversible and its responsivity to magnetic field was in the range of $20^\circ/\text{T}$. Despite the increased surface roughness, the apparent contact angle decreased with increasing field, which we attributed to the field-induced protrusion of hydrophilic microparticles from the surface layer [4].

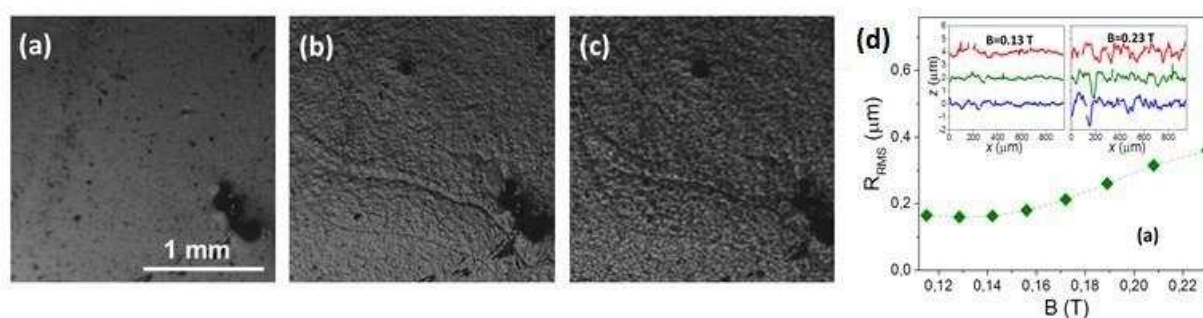


Figure 1. Magnetic field-induced modifications of surface roughness.

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Dewetting dynamics of a thin polymer film embedded in an immiscible matrix

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In this work, we describe a model trilayer dewetting experiment elucidating the effect of solid, no-slip confining boundaries on the bursting of a liquid thin film in a viscous environment.

This experiment was inspired by an industrial polymer processing technique, multilayer coextrusion, in which thousands of alternating layers of two polymers are stacked atop one another. As showed in a systematic study of multilayer coextrusion of polystyrene (PS)/poly(methyl methacrylate) (PMMA), when pushed to the nanoscale limit, the individual layers are found to break up on time scales shorter than the processing time whatever the processing conditions [1-2].

To gain insight on this dynamic problem, we directly observe the growth rate of holes in the middle layer of a PMMA/PS/PMMA trilayer system, wherein the distance between the inner PS film and solid boundary can be orders of magnitude ($\sim 10\text{ }\mu\text{m}$) larger than its thickness ($\sim 100\text{ nm}$). In otherwise identical experimental conditions, thinner films break up faster than thicker ones. This observation is found to agree with a scaling model that balances capillary driving power and viscous dissipation with, crucially, a no-slip boundary condition at the solid substrate/viscous environment boundary. In particular, even for the thinnest middle-layers, no finite-size effect is needed to explain the data.

The dynamics of hole growth is captured by a single master curve over four orders of magnitude in the dimensionless hole radius and time, and is found to agree well with predictions including analytic expressions for the dissipation [3-4].

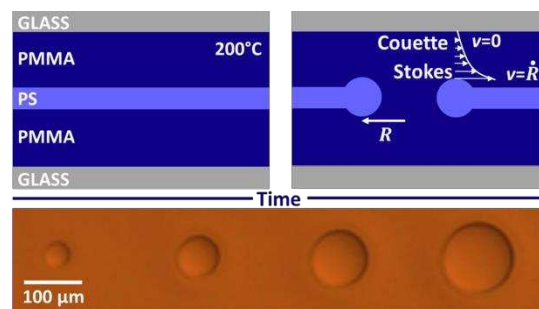


Figure 1. Schematic of the model experiment

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Preparation of highly hydrophobic cellulose based material by deposition of self-assembled octadecyltrichlorosilane layers

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Self-assembled layers obtained with using alkyltrichlorosilanes are the subject of intense study due to their high application potential in material engineering, especially for surface modification. The most frequently used precursor for generating self-assembled monolayers on a variety of substrates (such as SiO_2 , Si, Al_2O_3) is octadecyltrichlorosilane (OTS) [1, 2]. By controlling the surface pretreatment, the water content in the growth solution and the deposition time, the 3D siloxanes networks attached to the surface by chemical bonds can be formed. The 3D self-organized structure of the OTS with hydrophobic tails deposited on the material leads to enhancement self-cleaning properties and reduction adhesion of water droplets to the surface.

The presented research concerns formation of OTS coating layer on the cellulose fibres of tested filter media. The modification renders the filter surface to be a superhydrophobic and can be successfully applied for diesel fuel dewatering as a single stage water separator. In such system the filter material performs a role of barrier for dispersed water droplets and enables the oil to pass through the pores. The water droplets collected on the surface undergo the coalescence process, and after reaching a reasonable size detach and settle down upstream the separation barrier.

The work comprises the surface modification and characterization of cellulose filter material modified with organosilane such as octadecyltrichlorosilane (OTS). The selected compound due to their self-assembling properties enabled to obtain highly hydrophobic surface in a relatively simple procedure. In presented work the cellulose was exposed to the 1%vol. organosilane solutions in n-hexane by the dip-coating method for various times at ambient temperature [3, 4].

To characterize the used separation materials, the measurements of static contact angle (CA) and sliding angle for water droplets were carried out. The sliding angles were measured for water droplet volume 50 μl . These parameters define the ability of the filter material to repel water and thus prevent its accumulation on the surface due to high mobility.

Based on those measurements, the best materials were selected for full-scale modifications and their separation performance was verified in water separation experiment. For this purpose the cellulose based separator in the form of pleated thin wall screens was constructed (total height 80 mm, height of pleats 15 mm, number of pleats 44).

Experimental results presented in this work show that modification of selected type cellulose with organosilane provides a high efficiency of water separation from commercial grade of low sulphur diesel with addition of biocompounds (concentration of biodiesel ~7% as required by EU legislation), where in recent years major operation problems of filters have been reported.

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Exploiting the stability of wettability of superhydrophobic electropolymerized polyaniline surfaces under high ionic strength scaling medium

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There are two classical models that describe the relation between interfacial tension and contact angle for rough surfaces, the Wenzel [1] and the Cassie-Baxter [2].

Self-cleaning surfaces such as ones found on lotus leaves combine chemical composition and hierarchical structure to minimize interaction between water and the surface [3] leading to a superhydrophobic effect. Aiming to mimic that effect this work presents an electropolymerized polyaniline surface prepared onto metal substrates that showed a highly rough topography with hierarchical structures which was functionalized with perfluorocarbon chains, leading to a superhydrophobic surface, with contact angle tending to 180°. Otherwise, the non-functionalized polyaniline is superhydrophilic, with a contact angle tending to 0°.

Inorganic scaling tests showed that sinking the functionalized electropolymerized polyaniline surface in scaling medium with high ionic strength enabled to observe that during 16 hours of scaling test the non-wetting condition was replaced by a wetted surface.

To investigate the stability of the wettability of the prepared surfaces, quartz crystal microbalance analyzes were conducted with the electropolymerized polyaniline non-functionalized and functionalized. The results showed that the former, which is superhydrophilic, presents the Wenzel state of wettability, and the latter, which is superhydrophobic, presents the Cassie-Baxter state of wettability. Both profiles of wettability along time were compared under deionized water and showed to be stable over 16 hours. With the aim to understand the change in wettability state observed in the scaling test, the functionalized polyaniline surface was assessed under different non-scaling medium with high ionic strength at the quartz crystal microbalance.

The profiles of the wettability determined by the quartz crystal microbalance, as function of time, differs significantly among the systems, which indicates a dependence of the stability of wettability state with both, surface and solution composition. As regarding to this work, the ionic solution composition.

Impregnating the functionalized polyaniline surface with a fluorinated oil leads to a slippery liquid infused porous surface (SLIPS) [4]. Sinking it in the brine, even under magnetic stirring, results in a stable surface. While the air film completely escapes during the scaling test for non-impregnated surfaces, the fluorinated oil remains over it. Water is able to expel the air trapped on the surface and wet it, but is not able to do the same with the fluorinated oil, since it is better stabilized by the fluorocarbon chain present onto the polyaniline surface by the functionalization.

Thereby, is concluded that superhydrophobic surfaces that lies on Cassie-Baxter phenomena are not enough to be employed in circumstances that they have to be in direct brine contact for long periods, such as inorganic scaling or corrosion prevention. In the other hand, an oil impregnated surfaces show to be promise at under brine applications that are needed to last longer.

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Influence of the presence of surfactants on wetting properties of hydrophobic filtration materials modified with MTMS-based aerogels

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Separation processes of water/oil systems meet a lot of obstacles due to surfactants presence. Addition of such amphiphilic molecules changes interfacial properties of water/oil dispersion systems and additionally affects wetting properties of hydrophobic filtration materials by its adsorption on the surface. It was found in literature that reduction of solid/liquid interfacial tension results in the decrease of water contact angle [1, 2]. This phenomenon negatively influences the effectiveness of diesel fuel separation materials and their lifetime, especially due to fact that commercially available diesel fuel is enriched in lubricity enhancers, anti-corrosion additives and anti-depositions detergents which possess a surface activity [3]. Due to this fact, adsorption of single and mixed surfactant systems at hydrophobic surfaces dedicated to diesel fuel dewatering was investigated.

The aim of work was study on wetting properties of cellulose-based material modified with organosilica aerogel prepared from methyltrimethoxysilane (MTMS) precursor. The used aerogel is porous and lightweight material, characterized by high oil sorption capacity and water/oil separation selectivity. Due to the large specific area and strongly hydrophobic properties, it is a promising material as filter surface modifier dedicated to water/oil separation. Aerogel was deposited on material surface by in-house developed method based on spray coating.

In order to characterize the properties of separation materials, measurements of static contact angle (CA) for water droplets and water/solid interfacial tension measurements were carried out. Moreover, the chemical composition of material surface was verified by analysis of spectra obtained by Fourier transformed infrared spectroscopy (FTIR). As a test liquid the calibration oil for diesel fuel injectors was used. The surfactants such as: monoolein and polyisobutylene succinimide (PIBSI) with controlled concentration were added to the diesel fuel to change its composition and properties.

In Figure 1 the sorption of monoolein (initial concentration equal to 0.002 g/g) from diesel fuel by pure MTMS-based aerogel versus time is shown. The results confirm that surfactants sorption on the aerogel surface occurs, which in turn affects the wettability of the material originally modified with aerogel.

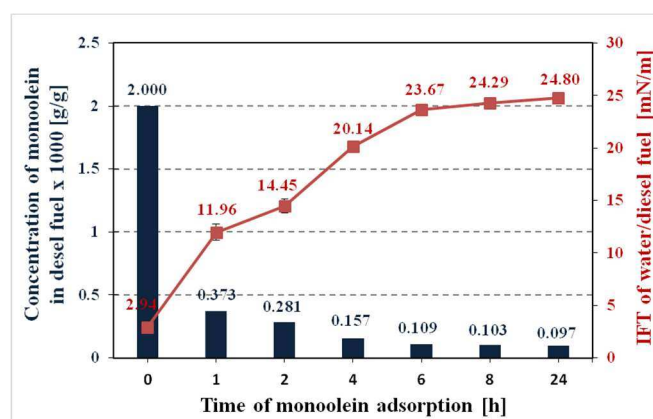


Figure 1. Sorption of surfactant (monoolein) from diesel fuel by MTMS-based aerogel.

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Millisecond fluid pattern formation in the nip of a gravure printing machine

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The motion of a liquid meniscus in the nip between a rotating gravure cylinder and a planar glass substrate is known to develop hydrodynamic instabilities such as the Saffman-Taylor finger instability [1]. We study the millisecond time scale of the developing finger patterns from a straight meniscus, and the fully developed pattern [2-3] from direct observation with high-speed camera techniques. The characteristic length scales, namely finger frequency, finger width and length, are determined as functions of the printing velocity and the raster width of the gravure pattern.

From Saffman and Taylor's experiment, the finger frequency of a retracting liquid-air meniscus is known to scale as $Ca^{1/2}$ with the capillary number, as far as flat surfaces are concerned. This proves to be the case, irrespectively of the kind of the liquid, i.e. of whether Newtonian liquids, polymer solutions or particulate dispersions are used. In the case of a periodic gravure pattern, considered in this experimental study, the flow pattern is more complicated. The problem is essentially unresolved.

In this study the shape of the contact line is observed using a substrate carrier that contains a glass prism enabling the optical access to the nip, which at the same time functions as the glass substrate (Fig. 1 left) [4]. In the initial phase of pattern formation, finger growth is initiated on the scale of the periodic raster of the gravure cells (Fig. 1 right).

This indicates that microscopic fluid flow between the gravure cells and the meniscus on the scale of few tens of μm has substantial impact on the meniscus motion and dynamics. In the later stages, this passes over to a different regime of pattern formation where the length scales of the hydrodynamic flow outside of the cells, i.e. in the nip dominate, and gravure pattern only has a marginal effect. The data for the finger length is obtained for various operation conditions and liquid properties. Finally a scaling for the finger length is found which is able to predict this value for under different conditions.



Figure1. Left: Lab-scale gravure printing unit with substrate carrier with inserted prism for direct observation. Right: Fully developed fluid finger formation in the nip of the gravure printing machine at 1 m/s using ethanol as printing fluid.

Acknowledgements. We kindly acknowledge the financial support by the German Research Foundation (DFG) within the Collaborative Research Centre 1194 “Interaction of Transport and Wetting Processes”, projects A03 and C01.

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Drop groove interaction in turbulent shear flow

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The interaction of drops with grooves plays an important role in many applications, e.g. process engineering, multiphase transport, printing, ice accretion and automotive exterior water management. For all of them a better understanding of the relevant physics is essential. In order to achieve this understanding an extensive basis of experimental data is helpful. Isolating distinct effects requires generic experiments, as are presented in this study. The interaction of shear driven drops with a groove is investigated in a fully developed turbulent Hagen-Poiseuille flow [2], shown in Figure 1. This permits obtaining a constant wall velocity gradient and attack velocity (shown in Figure 2) throughout the entire test section. Deriving models and validating numerical simulations is possible with this data. Dianat *et al.* [1] numerically simulated rivulets in turbulent shear flows at lower Reynolds numbers whereas Gurumurthy *et al.* [3] focused on the capillary effects within grooves and corners. This study aims at providing further insight to fluid groove interaction as well as introducing novel approaches to physical models.



Figure 1. Turbulent Hagen-Poiseuille flow wind tunnel.

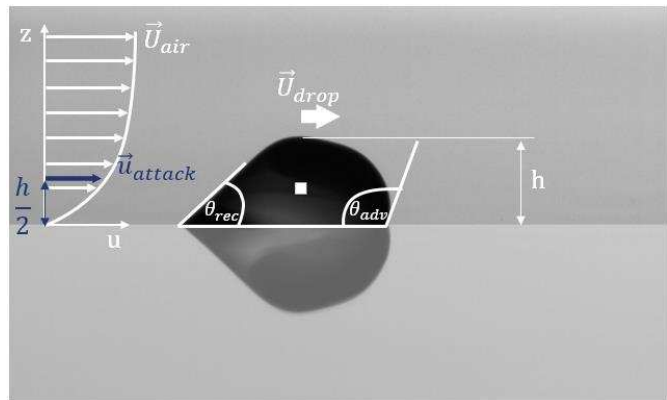


Figure 2. Definition of geometric parameters and attack velocity.

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Drops of pure liquids and mixtures on substrates with nanostructured porous coatings: Impact, imbibition and evaporation

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The heat transfer during impact of cold drops onto hot walls is determined by the outcome of drop impact, including spreading/deposition, rebound or splashing. The outcome and hydrodynamics of the drop impact strongly depend on the wetting properties of the pair substrate/fluid and on the substrate temperature. Experimental investigations have shown that both hydrodynamics and heat transfer resulting from drop impact can be controlled using nanostructured coatings of the wall surface [1]. On impact, droplets can penetrate into pores of the coatings, which can prevent rebound or splashing. The Leidenfrost temperature can be shifted by using the coatings towards higher temperatures compared to smooth surfaces [2]. However, the detailed mechanisms of liquid spreading, imbibition into the porous structure and evaporation are still not understood, and the influence of parameters of the liquid, solid and gas on these processes has not yet been investigated.

In order to understand the mechanisms of coupled momentum and heat transfer processes in the event of drop impact on porous surfaces, drop impact experiments followed by evaporation on substrates with nanostructured porous coatings are carried out in the present work.

Nanofiber mats, which are used as coatings, are produced by an electrospinning process. Polyacrylonitrile (PAN), which is partially wettable by water, is used to spin the nanofiber mats. The main influencing parameter of the coatings is their thickness, which strongly influences the imbibition process. Pure liquids (water and ethanol) and their binary mixtures are used to investigate the influence of mixture effects. All experiments are conducted in a closed test cell in air. The relative humidity and temperature inside the cell are independently adjustable in order to investigate the influence of evaporation and diffusion rates into the gas phase on the imbibition dynamics. The environmental conditions are especially important at the late stages of imbibition [1].

The dynamics of drop impact and wetting are captured by a monochrome high-speed camera in a side view, whereas the imbibition into the pores of the surface is observed by a monochrome camera in a top view (Figure 1). The results have been processed using image analysis, and the dynamics of the drop on the top of the coating as well as the dynamics of imbibition for different fluid compositions and environmental conditions have been studied.

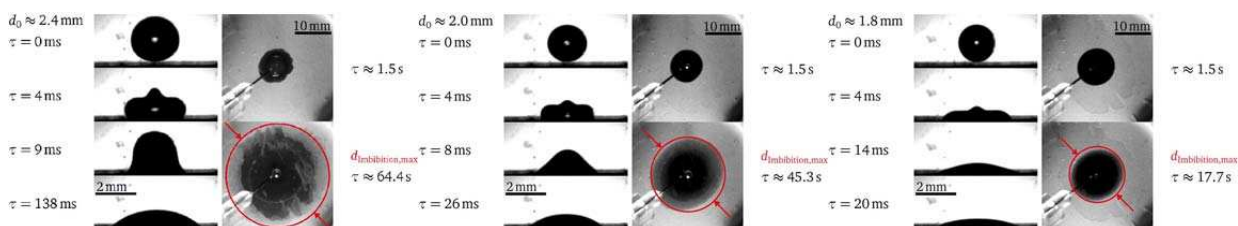


Figure 1. Camera recordings of drop impacts in a sideview (left) and a topview (right) with different fluid compositions of water and ethanol. *Left:* Pure water ($M_{\text{water}}/M_{\text{water+ethanol}} = 1.0$). *Center:* Water-ethanol-mixture ($M_{\text{water}}/M_{\text{water+ethanol}} = 0.5$). *Right:* Pure ethanol ($M_{\text{water}}/M_{\text{water+ethanol}} = 0.0$).

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Organic lenses on water: Spreading followed by contraction. Role of water solubility

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Spreading of one liquid over another is a process that is important for biological systems, as well as for many applications in the fields of pharmaceuticals, coating deposition technology, oil spills, the food industry and many others. In many cases, for the droplet of an organic liquid deposited onto the aqueous phase, initial spreading of a droplet is followed by its contraction into a lens. The equilibrium situation will correspond to the coexistence of a liquid lens with a monomolecular or polymolecular film of organic liquid on the surface of the aqueous medium. Benzene on water [1] represents a typical system showing abovementioned behavior. In this contribution, we present the equation for the calculation of benzene lens angle based on the disjoining pressure isotherms. We show that the evolution of water content in a benzene lens is responsible for spreading/ contraction of the benzene lens on water due to interplay of different types of surface forces in the benzene film. The influence of water content on the thickness of a benzene film atop of water and on the instant lens angle is considered.

Acknowledgements: The work was supported by the Program for fundamental studies “Actual problems of surface physicochemistry and creation of new composite materials” of the Presidium of the Russian Academy of Sciences.

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Experimental investigation on the influence of the substrate softness on drop retention

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The retention of a drop under the influence of external body forces (i.e.: gravity, centrifugal) acting parallel to the substrate has become a topic of great interest in the last decade [1]. The pioneering work led by Fumridge [2] to study the shape of a drop which is on the verge of movement paved the way for further investigation by Extrand and Kumagai [3] on the retention force of a droplet and its shape development. In spite of numerous applications and growing interest in wetting of soft substrates [4], very little is known on retention of drops on such substrates. In this work we investigate the influence of the substrate mechanical properties on the shape, advancing and receding contact angles and the retentive force of a droplet under the action of a centrifugal force. The experimental setup, called Kerberos, consists of a substrate holder, a tilting and rotating head which is capable of individually manipulating the components of gravitational and centrifugal forces [1]. Polydimethylsiloxane (PDMS) has been used to coat glass slides. The ratio between the base and cross-linking agent used for preparation of the polymer substrates has been varied to obtain substrates with different elastic properties. A drop of 30 μl has been placed on the substrate and then the external centrifugal force was applied. Three cameras positioned at right angles to each other captured the shape of the drop as the rotational speed increased until the droplet started to move. A custom made Matlab image processing tool has been used to process the images.

The evolution of the shape of the droplet as it experiences increasing centrifugal force was investigated. It was found that for hard substrates there exists a linear dependency between the ratio of the receding and advancing contact angles and the Bond number which was also reported previously by Jacobi et. al. [5]. On soft substrates we observed a deviation from this dependency at higher Bond numbers. Critical Bond number, at which the droplet starts to slide, significantly increases on soft surfaces ($G = 1 \text{ kPa}$) in comparison to hard surfaces ($G = 703 \text{ kPa}$) (Fig 1).

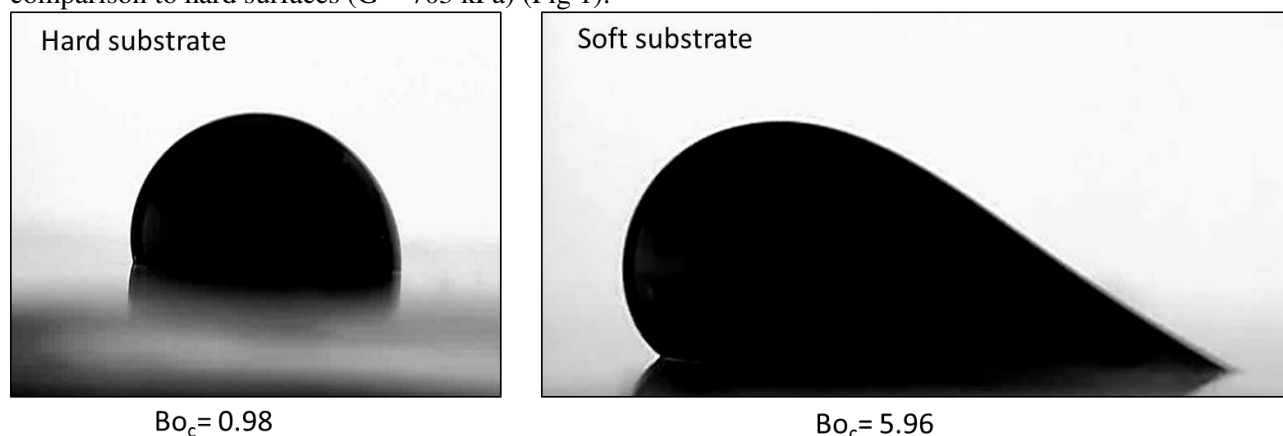


Figure 1. Influence of the substrate softness on the critical shape water.

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Particle detachment from fluid interfaces: Theory vs Experiments

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Microparticle adsorption and self-assembly at fluid interfaces are strongly affected by the particle three-phase contact angle θ . On the single-particle level, θ can be determined by several techniques, including colloidal-probe AFM, the gel-trapping technique (GTT) and the freeze-fracture shadow-casting (FreSCa) method. While GTT and FreSCa provide contact angle distributions measured over many particles, colloidal-probe AFM measures the wettability of an individual (specified) particle attached onto an AFM cantilever. Here, we extract θ for smooth microparticles through the analysis of force-distance curves upon particle approach and retraction from the fluid interface; see Figure 1 and Reference [1]. From each retraction curve, we determine: (i) the maximal force, F_{\max} ; (ii) the detachment distance, D_{\max} ; and (iii) the work for quasistatic detachment, W . To relate F_{\max} , D_{\max} and W to θ , we developed a detailed theoretical model based on the capillary theory of flotation. The model was validated in three different ways. First, the contact angles, evaluated from F_{\max} , D_{\max} and W , are all close in value and were used to calculate the entire force-distance curves upon particle retraction without any adjustable parameters. Second, the model was successfully applied to predict the experimental force-distance curve of a truncated sphere, whose cut is positioned below the point of particle detachment from the interface. Third, our theory was confirmed by the excellent agreement between the particle contact angles obtained from the colloidal-probe AFM data and the ensemble-average contact angles measured by both GTT and FreSCa. Additionally, we devised a very accurate closed-form expression for W (representing the energy barrier for particle detachment), thus extending previous results in the literature.

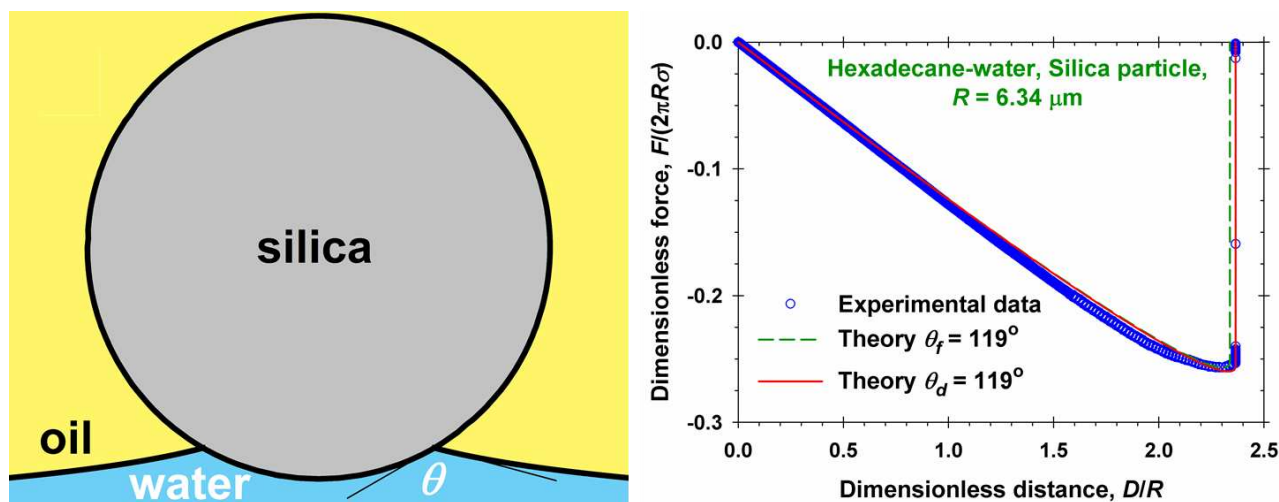


Figure 1. Microparticle sitting at the oil-water interface (left); Comparison of theory vs experiment (right).

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Controlling Nanodrop Passage Through Capillary Nanovalves by Adjusting Lyophilic Crevice Structure

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The passage or blockage of nanodrops through a nano-valve made of nanocrevice is explored by proof-of-concept simulations, including many-body dissipative particle dynamics and Surface Evolver [1]. Although it is generally believed that the drops wet lyophilic crevices readily, we show that the penetration of the drops into such crevices with specific structures can be prevented. The morphological phase diagram in terms of the contact angle (θ_Y) and wedge angle (α) are constructed and three regimes are identified: non-penetration and partial penetration, in addition to complete penetration. It is interesting to find that as long as α is small enough, the drop always runs away from the crevice even on lyophilic surfaces, leading to the non-penetration state. For intermediate α and small θ_Y , the drop tends to break up and only a portion of liquid wets the crevice, corresponding to the partial penetration state. Our simulation results demonstrate that a lyophilic capillary nanovalve for controlling the droplet passage can be fabricated by simply adjusting the wedge angle of the crevice (Fig. 1).

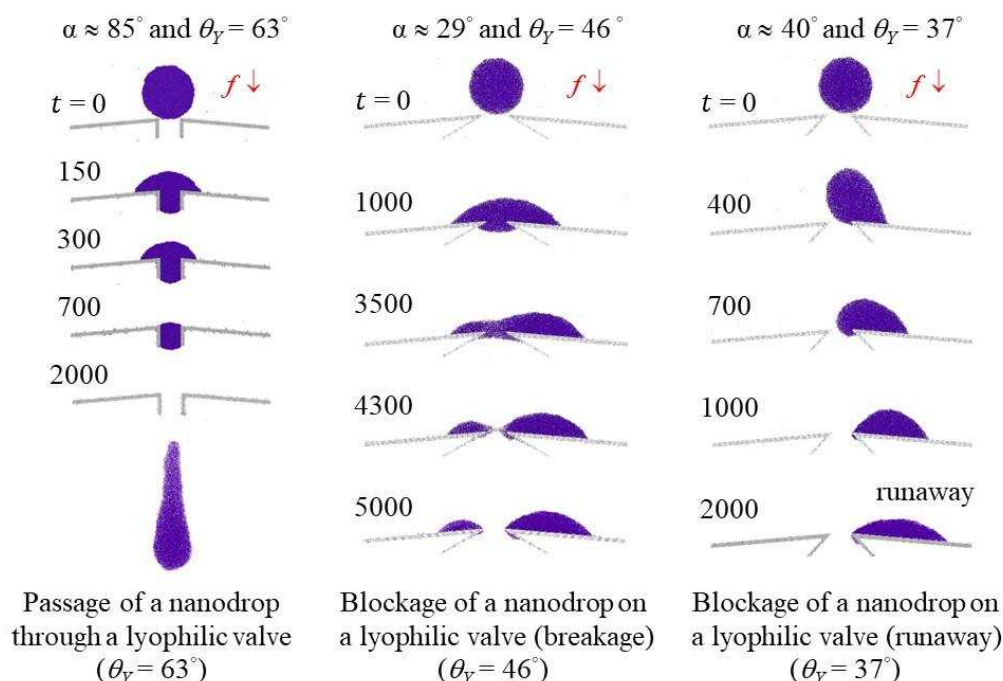


Figure 1. The structure of the lyophilic nanocrevice characterized by the wedge angle (α) is critical for resisting or allowing the penetration of the drops through the opening of the crevice.

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Smart zwitterionic sulfobetaine silane surfaces with switchable wettability for aqueous/nonaqueous drops

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Smart surfaces with switchable wettability for both aqueous and non-aqueous drops based on zwitterionic sulfobetaine silane (SBSi) have been fabricated [1]. The wettability transition occurs from a total wetting (contact angle, CA $\approx 0^\circ$) to partial wetting (as high as CA $\approx 75^\circ$) state. The surfactant solution (aqueous or non-aqueous) rinse (for 5 s) acts as stimuli and the reversal of surface wettability is achieved simply by pure water rinse. The reversible behavior of the switchable wettability of a SBSi surface can be repeated for at least 100 cycles. Various cationic surfactants are used as stimuli for aqueous drops and anionic surfactants are employed for non-aqueous drops. This unique wettability-switching property is attributed to basal surfactant adsorption driven by electrostatic attractions between the charged surfactant head groups and zwitterionic groups of SBSi (Fig.1). Such rapid surfactant adsorption is also responsible for intriguing drop fission and dewetting phenomena, shown by stimuli drops casted on clean SBSi surfaces. Thus, this smart switchable wettability surface can be employed to fabricate intelligent devices for controlling motility and sensing.

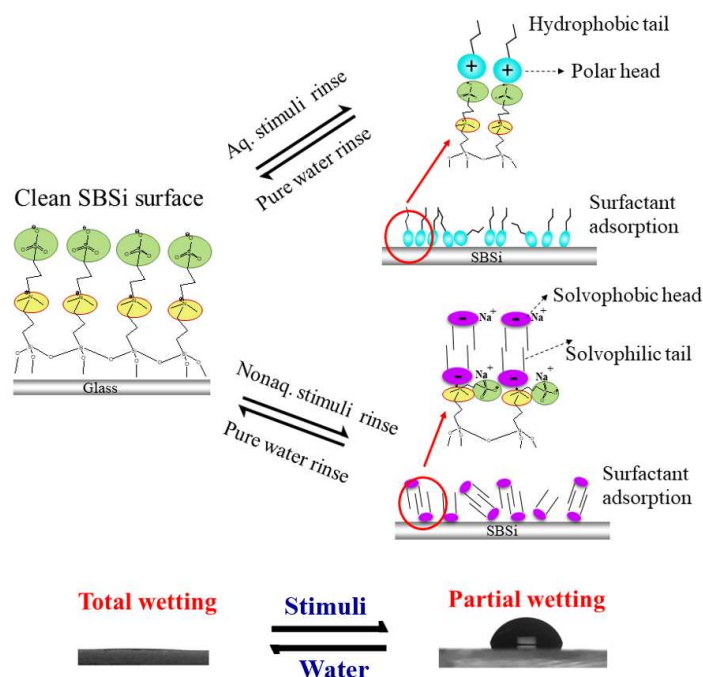


Figure 1. Smart surfaces with switchable wettability for both aqueous and non-aqueous drops based on zwitterionic sulfobetaine silane (SBSi) have been fabricated. The surfactant solution (aqueous or non-aqueous) rinse (for 5 s) acts as stimuli and the reversal of surface wettability is achieved simply by pure water rinse. The reversible behavior of the switchable wettability of a SBSi surface can be repeated for at least 100 cycles.

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Solvent- and Ion-Specific Effects on the Structure of Micelles and Micelle-like Aggregates

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The structure of an ionic micelle is a result of a series of molecular interactions, amongst them hydration of head and tail groups and electrostatic interactions of the ionic groups and counterions. The exact shape of a micelle and the resulting hydration signatures has been a long-lasting problem, and different micelle models have been proposed that predict different hydration patterns. We present atomistic simulations of micellar solutions and discuss the resulting hydration patterns and different ion effects.

We also discuss salt effects in solutions that form non-traditional micelle-like aggregates, so-called surfactant-free microemulsions comprising water, a poorly water-soluble compound, and a hydrotrope like ethanol. We show that - in contrast to the ion-specific adsorption observed at typical interfaces - salt effects arising from the differential adsorption of anions and cations at non-polar aggregates are surprisingly low [1].

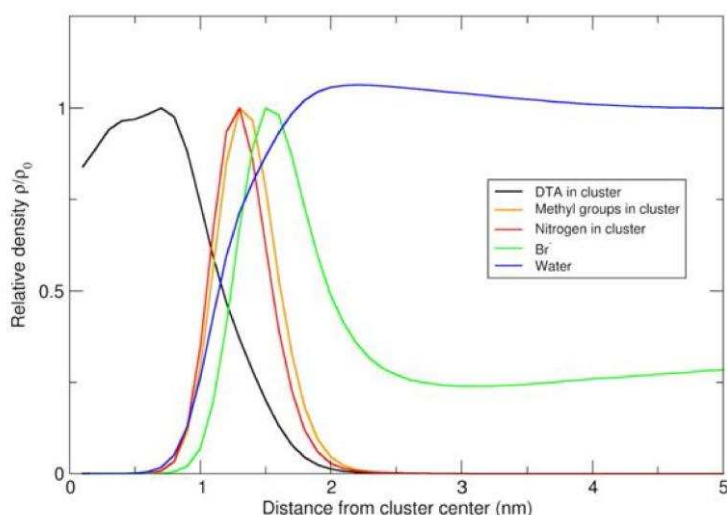


Figure 1. Radial Structure of an ionic micelle.

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Polyoxometalates as a case study of super-chaotropes

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Ionic species, such as polyoxometalates (POMs) or (metal-) boron clusters, are at the frontier between ions and (charged-)colloids due to their nm size [1]. We show here that the large size and low charge density of POMs, compared to classical ions, are responsible for a peculiar behavior called “super-chaotropy” (see fig. 1). This property refers to the strong propensity of nano-ions to adsorb at neutral polar interfaces, via non-specific interactions. The super-chaotropy scales with the charge density and, to a lesser extent, with the polarizability. It has strong effects on phase transitions in soft matter and can, for example, give an explanation on the origin of the famous “POM-etherate” phase formation. A simple way for evaluating and classifying nano-ions, such as POMs, according to their super-chaotropy is proposed here [2]. The super-chaotropic behavior of nano-ions opens opportunities in separation science [3], catalysis, and for the design of nanostructured hybrid materials [4].

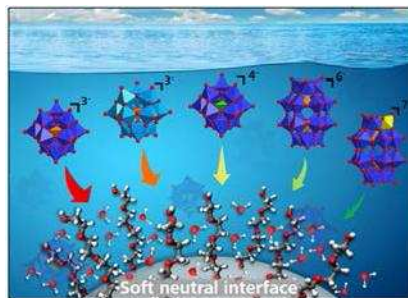


Figure 1. Ranking of Keggin- and Dawson-type polyoxometalates in the Hofmeister series according to their ability to adsorb on polar neutral surfaces.

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Specific Ion Effects in Non-aqueous Solvents: the Curious Case of Glycerol Carbonate

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Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, shortly GC) is a dense, viscous, water soluble solvent (see left panel in Fig. 1). The high dielectric constant and dipole moment make it a suitable non-aqueous green solvent for several salts in different applications, e.g. in the technology of lithium-ion batteries, cement, sugar cane treatment, cosmetics and detergents [1-3]. Like other cyclic carbonates (ethylene and propylene carbonate), GC dissolves significant amounts of inorganic salts [4,5].

In this work we carried out solubility, conductivity, rheology, DSC, NMR and FTIR experiments on solutions of different potassium salts in glycerol carbonate.

The results suggest that in the case of KF, the solvent becomes oversaturated and leads to the formation of a glassy liquid where GC molecules and KF ion pairs are intercalated in a rather ordered tridimensional structure, stabilized by cation-dipole interactions while the basic anion participates in hydrogen bonding [6], as depicted in the right panel of Fig. 1.

A similar behavior was observed in the presence of other basic (HB-acceptor) anions, such as carbonate, cyanate and phosphate. On the other hand, if the anion is not an HB-acceptor (as in the case of Cl^- , Br^- and NO_3^-), then its interaction with the solvent molecule is minimal. However, in the case of iodide, we recorded another peculiar behavior that is probably related to strong non-electrostatic interactions between I^- and the GC ring as shown particularly by NMR, DSC (glass transition temperature), and FTIR results.

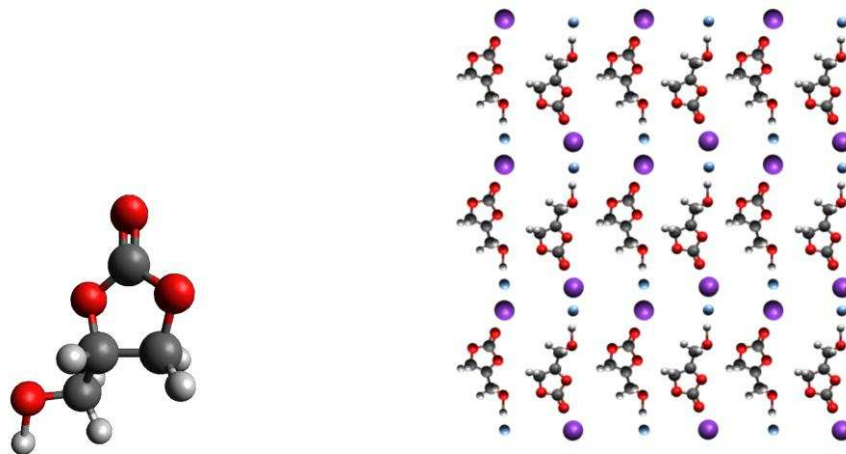


Figure 1. Left: chemical structure of glycerol carbonate. Black, red and white sphere represent carbon, oxygen and hydrogen atoms, respectively. Right: schematic structure of a KF oversaturated solution in glycerol carbonate. Purple and light blue spheres represent K^+ and F^- ions, respectively.

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Inducing protein reentrant condensation with polyvalent anions

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Reentrant condensation (RC) describes the ability some polyvalent ions have to precipitate proteins at low concentrations and then resolubilise them at higher concentrations. Whether RC will be induced is dependent on protein net charge, ion net charge, ion concentration and ion species. Trivalent cations such as yttrium (Y^{3+}) and lanthanum (La^{3+}) induce RC of acidic proteins and their mechanisms have been studied extensively [1]. We use protein solubility, static light scattering, dynamic light scattering, and zeta potential measurements to understand the molecular mechanism for RC by polyvalent anions such as pyrophosphate (SPP) and tripolyphosphate (STPP), which have been studied to a smaller degree than the cations [2].

Figure 1 shows the phase diagram for lysozyme solutions with the polyanions SPP and STPP along with a plot of the protein-protein interactions (PPI), as quantified in terms of the reduced osmotic second virial coefficient, B_{22}^* measured along the solubility boundary.

Basic proteins have a net positive charge and repel each other through long-range electrostatics when no counter anions are present. The initial lysozyme concentration (precipitation) occurs when the polyvalent anions STPP/SPP interact with solvent-exposed basic residues via electrostatics, which neutralize the long-range repulsive interactions between lysozyme molecules and allows protein cross-linking (precipitation) to take place. Further increasing SPP/STPP concentration after this causes resolubilization because lysozyme net charge has been reversed from positive to negative. While this mechanism follows what has been proposed for the behavior of acidic proteins with trivalent cations, there are also fundamental differences. Lysozyme precipitation occurs almost immediately when in the two-phase region, so that the boundaries shown in figure 1 correspond to the thermodynamic solubility of the precipitated phase. The solubility boundary occurs at much lower values of B_{22}^* than observed with acidic proteins, possibly indicating a fundamental difference in the nature of the protein-protein interactions. Interestingly, citrate does not induce reentrant condensation of lysozyme at similar strengths of protein-protein attractions despite having a similar charge, size and shape to SPP; highlighting the importance of ion-specific effects.

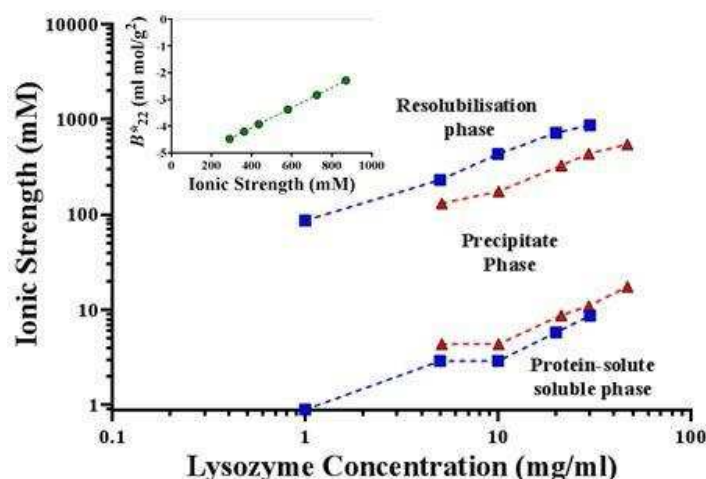


Figure 1. Phase transition data for lysozyme RC induced by SPP (red) and STPP (blue). Inset shows PPI quantified in terms of the reduced osmotic second virial coefficient (B_{22}^*) along the solubility boundary

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The interfacial layer in nanoconfinement: an experimental and modelling approach

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The experimental characterization of the interfacial layer at the surface of inorganic nanoconfinement filled with water and ions is a scientific challenge but is of great interest to understand the specific chemical processes occurring into the nanoporosity. Indeed, the strong interactions between water molecules and pore surfaces modify the water structure [1] and slow down its dynamics from nanoscale to macro-scale [2]. Also, the presence of solvated ions and the ions adsorbed on the nanopores surface modify the electrostatic interactions in the system and thus the ions energy landscape [3].

To determine the ions energy landscape modification into the interfacial layer, we propose an original approach (Figure 1) coupling experimental model systems and molecular dynamics simulations. The model systems consist in parallel and planar silica surfaces spaced of 3 and 5 nm (nanochannels) filled with electrolytes containing cations having more or less kosmotrope properties. These filled nanochannels were characterized using hard X-Ray reflectivity (27 keV at ESRF) during their filling with XCl_2 solutions at 1 M ($X = Mg^{2+}$, Ca^{2+} and Ba^{2+}). From X-ray reflectivity curves, the electron density profiles were extracted directly by inverse Fourier transform, assuming the symmetry of the profile [5]. In parallel, ions and water distribution in these nanochannels were simulated varying the spacing size and the charge of the silica surface to fit the X-ray reflectivity data. The results highlight that the distance between two silica planar surface and the nature of the cations (size and hydration) impact the filling kinetics of nanochannels ($Mg^{2+} > Ca^{2+} > Ba^{2+}$) and the ions distribution at the silica surface.

This innovative approach coupling the experiments and the simulation is expected to bring a better understanding of water and ions distribution inside nanoconfined media to *in-fine* relate it to the physico-chemical processes occurring in nanoconfinement.

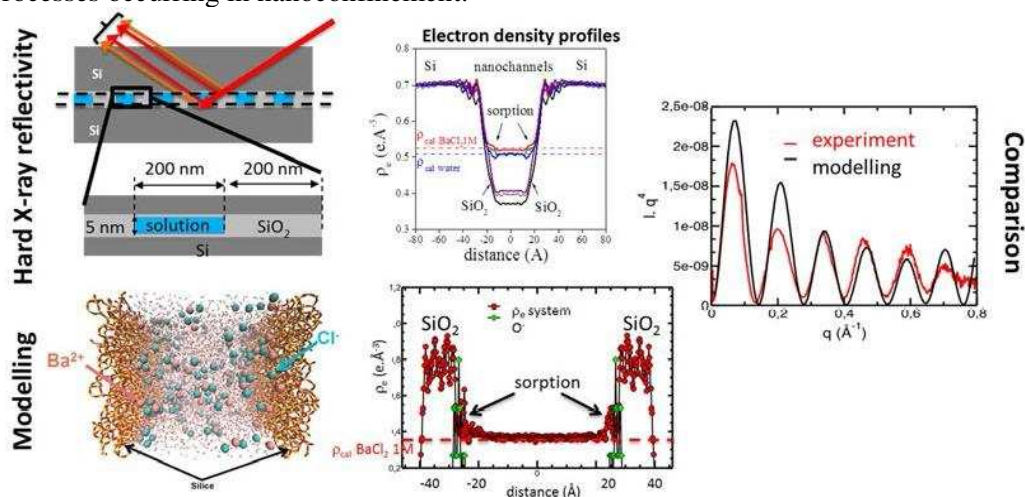


Figure 1. Methodology used in the study.

Acknowledgements: The authors would like to thank Thomas Zemb for the fruitful discussion.

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Effect of cationic structure on the micellization of surface active ionic liquids: A thermodynamic study

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In this work the influence of cation structure on the micellization process at surface active ionic liquids (SAILs) in water is investigated by isothermal titration calorimetry (ITC) at temperatures between 298.15 and 318.15 K. First, 1-dodecylimidazolium bromide ($[C_{12}im]Br$) was studied and then the length of alkyl chain on the N3 position is varied from methyl- (1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$)), ethyl- (1-dodecyl-3-ethylimidazolium bromide, $[C_{12}eim]Br$), to butyl- (1-dodecyl-3-butylimidazolium bromide, $[C_{12}bim]Br$). In next step, the N3 was replaced by S atom in 3-dodecylthiazolium bromide ($[C_{12}thiaz]Br$) as analogue of $[C_{12}im]Br$. Structures of all investigated systems are presented in Figure 1.

ITC experimental data were analyzed by help of an improved model, yielding the values of critical micelle concentration, cmc, enthalpy, $\Delta_M H^\theta$, degree of counter ion binding, β , aggregation number, n , standard heat capacity, $\Delta_{MC_p}^\theta$ and Gibbs free energy, $\Delta_M G^\theta$ of micellization. It was found that the investigated systems behave mainly like common ionic surfactants and already investigated SAILs [1]: the micellization process of investigated systems was detected as endothermic at low temperatures and exothermic at high temperatures; the values of cmc are decreasing with the increasing length of alkyl chain on N3 position. Between $[C_{12}thiaz]^+$ and Br^- weaker interactions were found in comparison to those between $[C_{12}im]^+$ and Br^- what can be ascribed to more expressed aromaticity of thiazolium ring [2]. Moreover, it has been reported that the H-bond interaction energy between water (or ligands) and S atom is much smaller than between water and N3 in imidazolium ring [3]. Thus, the micellization properties of $[C_{12}thiaz]Br$ are more in line with $[C_{12}eim]Br$ due to the hydrophobic character of ethyl- group.

$\Delta_{MC_p}^\theta$ values were further discussed, regarding the removal of water molecules from contact with nonpolar surface area upon micelle formation. It can be concluded, that the ethyl- and butyl- chain on N3 position are folded during the micellization process and thus they are (at least) partially removed from contact with water.

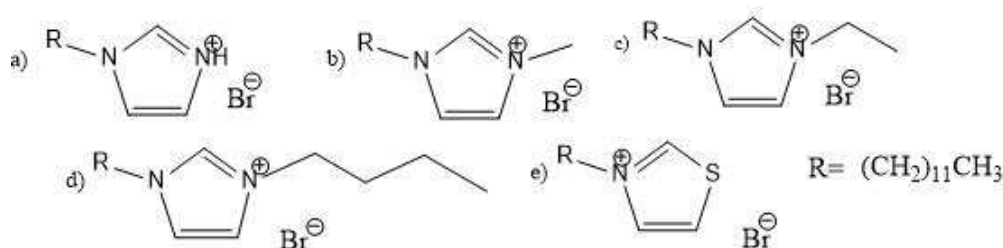


Figure 1. Structures of investigated systems: a) $[C_{12}im]Br$, b) $[C_{12}mim]Br$, c) $[C_{12}eim]Br$, d) $[C_{12}bim]Br$, e) $[C_{12}thiaz]Br$.

Acknowledgements: This work was financially supported by the Slovenian Research Agency through grant No. P1-0201 and Ministry of Education, Science and Technological Development of Serbia under project contract ON172012.

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Influence of hydroxybenzoates on micellization of surface active imidazolium based ionic liquids

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Due to the vast combinations of surface active imidazolium based ionic liquids (SAILs) with different counter-ions, SAILs offer a great opportunity to study ion-specific effects during a micellization of such systems [1]. In many ways, their behaviour is identical to those observed by “usual” ionic surfactants: for example, the micellization process is endothermic at low temperatures and exothermic at high temperatures, where counter-ions have an important role on magnitude and change of sign of the observed heat effects. It was already confirmed that the hydrophobicity of counter-ions evidently contribute to the heat capacity change and the water accessible surface area removal upon burial of non-polar group from the contact with water at micellization process. Even more, it can be assumed that all hydrophobic anions are partially incorporated in the micelles [2,3].

In this contribution we will investigate the influence of hydrophobic character of hydroxybenzoates (namely sodium 2-, 3-, and 4-hydroxybenzoate) on micellization of 1-dodecyl-3-methylimidazolium cation. The thermodynamic study of the micellization process will be carried out by isothermal titration calorimetry in a broad temperature range. Experimental data will be analysed by help of corresponding model [4] and the obtained results will be discussed and compared to a previously published results in order to gain more information about ion-specific effects.

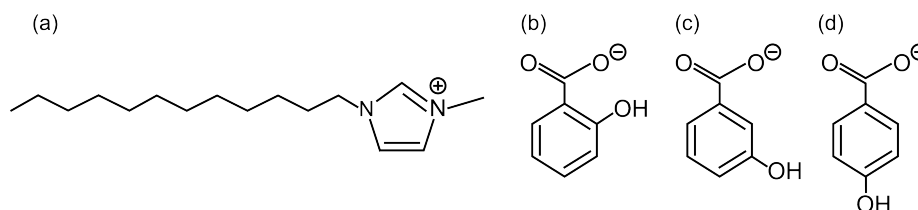


Figure 1. Structures of a) 1-dodecyl-3-methylimidazolium cation, b) 2-hydroxybenzoate, c) 3-hydroxybenzoate, d) 4-hydroxybenzoate.

Acknowledgements: This work was financially supported by the Slovenian Research Agency through grant No. P1-0201 and Ministry of Education, Science and Technological Development of Serbia under project contract ON172012.

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The law of matching water affinities – misinterpretation of specific ion effects

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The inability of electrostatic theories to take into account other effects than Coulomb interactions when describing aqueous systems is widely acknowledged in scientific community. Therefore, other approaches invoking empirical laws for upgrading or even replacing electrostatic theories are often used for improving prediction power of quantitative theories. The concept of kosmotropic and chaotropic ions, being the base of Hofmeister series, forms also the fundament of the law of matching water affinities – a law being highly cited in past two decades in the realms of theoretical physical chemistry and biochemistry [1]. This law [2], relying on standard heats of solution of crystalline alkali halides and their solubility in water, was proposed as one of rules of thumb for explaining ion-specific effects in (biological) aqueous systems. The essence of this law is statement that pairs of either small or large ions of opposite charge form contact ion pairs while no ion pairs are formed between small (strongly hydrated) and large (weakly hydrated) ions. Due to formation of contact ion pairs release of hydrated water is expected.

The extensive formation of contact ion pairs between small cation and small anion as well as between large cation and large anion, postulated by the law of matching water affinities, however, seems not to be experimentally supported. Namely, the experimental thermodynamic [3] and transport [4] data obtained for aqueous solutions of alkali-metal halides show very poor evidence for formation of ion pairs and this holds true also for LiF, a salt containing the smallest alkali metal and the smallest halide ion.

In our work, the direct test of formation of contact ion pairs upon mixing two aqueous solutions containing different ions was applied. By the use of isothermal titration calorimetry, enthalpies of mixing were measured at 25 °C for mixing pairs of aqueous solutions of two alkali metal halide salts of the same concentration. The preliminary results show that the thermal effects are small upon mixing 0.02 molar salts solutions. This is valid also for the case of mixing CsF and LiI solution, i.e. the experiment that according to the law of matching water affinities should be accompanied by large thermal effects. Thermal effects became larger for all combinations of salts studied when concentration of salts were increased. The experiments made for e.g. mixing 0.10 molar LiI_(aq) with solutions of caesium halide salts of the same concentration showed that the thermal effects increase with the diminishing size of halide ion. This trend, however, cannot be explained by the formation of contact ion pairs since the measured enthalpies of mixing are far too small to be provoked by the dehydration in the first solvent layer surrounding the ions. Instead, the different strength of hydrogen bonds in the hydration layers [5, 6] of halide ions and consequential changes in the hydrogen-bonded network around ions may be the most probable explanation of the observed effects.

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Neurotransmitter acetylcholine in water: the futures of hydration

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Acetylcholine (ACh) is the main neurotransmitter involved in the transmission of nervous excitation in the central and peripheral nervous systems [1]. The action of neurotransmitters arises from specific interactions with cholinergic receptors. However, to reach those these signaling molecules neurotransmitters have to diffuse across the synaptic cleft where they interact with water and other dissolved molecules and ions. Thus, neurotransmitters are hydrated in the synaptic cleft. Hydration can impact on their biological activity and change the rapid metabolism of neurotransmitters in the synaptic cleft [2].

We present the results of a study of the hydration structure of ACh cation in aqueous AChCl solution at infinite dilution and ambient conditions. Because of the destructive effect of the enzyme acetylcholinesterase, acetylcholine chloride (AChCl) is used in the study of the stimulating cation of ACh on cholinergic receptors. To this end, we used the integral equation theory (IET) in the 1D- (one-Dimensional Reference Interaction Site Model) and 3D-RISM (three-Dimensional Reference Interaction Site Model) approaches. The calculations were performed for two stable conformations of AChCl in water, i.e. for the trans, gauche (TG) and the trans, trans (TT) conformers [3]. Furthermore, it has been shown that the TT conformer is recognized by acetylcholinesterase and muscarinic receptors, whereas the folded TG form is recognized by nicotinic receptors [4, 5].

The structural features of ACh hydration are analyzed on the base of radial and spatial distribution functions. As a result, for both conformers we have defined the appropriate interparticle distances between functional groups of ACh and water molecules, partial and total hydration numbers, the numbers of H-bonds formed by ACh with water. It was found that the TT conformer of ACh is better hydrated in comparison with TG form of ACh.

Acknowledgements: This work was partly supported by the Russian Foundation for Basic Research (grant No. 18-43-370003-r_centre_a).

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Investigations on the co-ion effect of the surface charge and aggregation behavior of silica nanoparticles

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Using gel time experiments and potentiometric titrations we have studied the effect of anions on the charging behavior of commercial amorphous silica nanoparticles, Ludox[®] TM. While counterions have been reported to exhibit clear ion specific effects on a wide variety of charged surfaces, whether co-ions/anions could affect the surface charge and gel times of colloidal silica has not been established to any great extent. Gel times were determined with the presence of a large variety of anions (Cl^- , NO_3^- , ClO_3^- , ClO_4^- , SO_4^{2-}) and with the K^+ and Na^+ cations. Surface charge densities (SCDs) as a function of pH was derived from titrations using the corresponding acid (i.e. HCl , HNO_3 , H_2SO_4) to the anions investigated (Cl^- , NO_3^- , SO_4^{2-}) and the titrations were run from pH 10 to pH 3. The concentrations with respect to cations were in the range 0.10–0.50 M for our experiments.

Our results could be explained by looking at the mean ionic activity coefficients (γ_{\pm}) of the salts studied, which are connected to the degree of ion pairing between the cations and the anions in water; a low γ_{\pm} corresponds to more extensive ion pairing. Especially the determined gel times showed great differences, e.g. 0.50 M NaCl vs. 0.50 M NaSO_4 : 13 minutes vs. 154 minutes, but also the SCDs revealed a distinct co-ion effect.

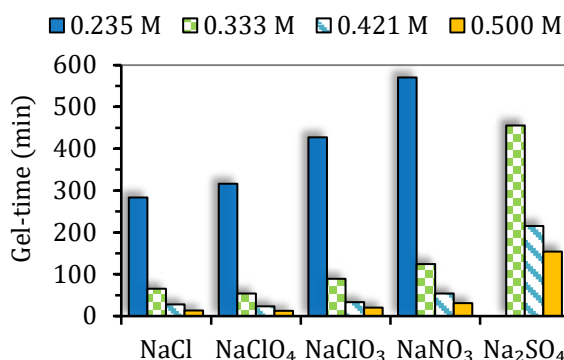


Figure 1. Gel-time measurements of TM silica nanoparticles in the presence of a variety of salts and cation concentrations.

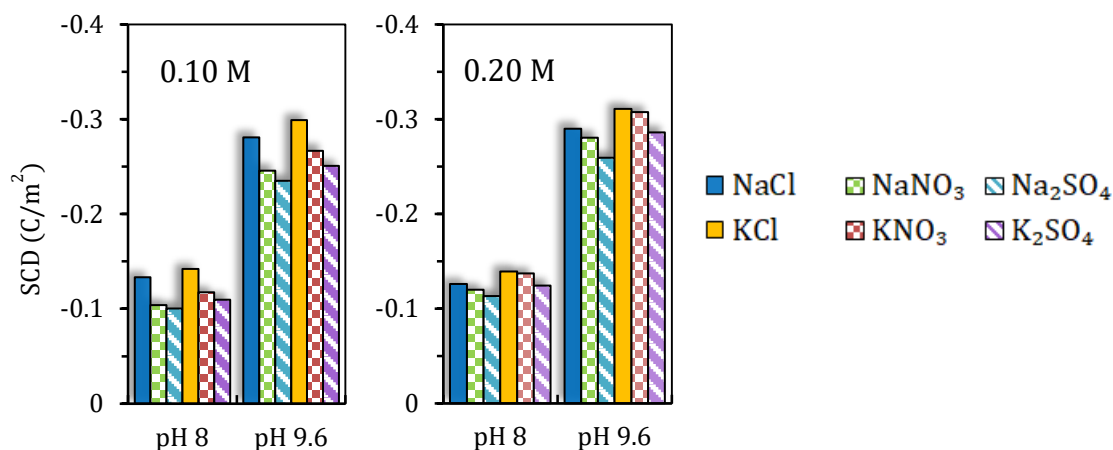


Figure 2. SCDs obtained by potentiometric titrations of TM silica nanoparticles in the presence of a variety of salts and with cation concentrations of 0.10 and 0.20 M.

Static magnetic field influence on water

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Water is the fundamental substance necessary for the all life on our planet. It is nutrient source and the place where chemical reactions happen, therefore living organisms, as well as agriculture and industry, cannot function without water. Thus, it is necessary to know its structure and geometry to understand its properties. The phenomenon of magnetic field (MF) influence on water has been studied for many years, especially in the aspect of preventing scale deposition at higher temperature. It was found that water exposition to a magnetic field may allow elimination of harmful chemicals used for water softening [1].

However, it is also interesting if MF affects the structure of the water which may be important in various applications. Although changes in some physicochemical properties of water have been reported, the mechanism dealing with how magnetic treatment influences solutes or substances in water is still controversial [2-3].

The aim of this study is to investigate the influence of static magnetic field acting at static and kinetic condition on the changes in the macroscopic properties of water, i.e.: conductivity, viscosity, density, enthalpy of evaporation and surface tension. Water was exposure to static magnetic field at room temperature. These changes in the physical–chemical properties of water are correlated with the changes the molecular interactions. Based on the experimental results possible mechanism of MF influence on water will be presented.

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A mean field theory of solvent ordering around ions and surfaces

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Electrostatic interactions have long been recognized as playing a significant role in determining the behavior of charged colloidal solutions [1]. These interactions are typically mediated and screened through the presence of mobile ions. The solvent is typically treated as a uniform background dielectric continuum and considered to play a minor role; however, alignment and structuring of the solvent around charged surfaces and mobile ions can significantly influence the manner in which they mediate the interaction between charged colloids [2,3].

We incorporate solvent structure and its interaction with surfaces and mobile ions and solutes into the Poisson-Boltzmann formalism. Our model aims at understanding the interplay between the diffuse double layer and the polarization of water due to a surface-induced dipolar ordering. We derive conditions for the optimal polarization at the surface and for the sign inversion of the electrostatic potential. In addition, we examine the influence of solvent ordering around surfaces and ions on the interaction between charged surfaces.

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Partial least squares regression for determining the dissociation constants from the UV-Vis spectra without calibration

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Overlapping of the spectral bands, variations caused by the aggregation of the colloidal system and inaccessibility of the pure species spectra, all present common problems in the determination of experimental dissociation constants (K_a) of weak acid or base species on surfaces of colloidal particles. Chemometric methods for reduction of spectral information measured via UV-Vis spectrophotometry, such as the principal component analysis (PCA), were proposed as solution of this problem, and enable capturing the relevant protonation model parameters [1–3]. In the present poster, an improved method for K_a determination from the UV-Vis spectra, based on partial least squares regression (PLS), is proposed and compared with PCA.

By means of PLS, an optimal protonation model is determined from the dependence of the experimental spectra (X) and the protonation species concentration (Y) matrices, both defined for a set of varied pH values. This is achieved through maximization of the covariance between the X- and Y-scores [4], performed within the PLS-regression routine for testing the dependency of X on trial Y_i . The latter are calculated from the Henderson-Hasselbalch equation (model) for varied discrete values of $K_{a,i}$. The expected $\langle Y_i \rangle$ is given by the model which results with the least predictive error, which is in the present work defined as the mean squared error (MSE) of the leave-one-out cross validation. The number of the PLS components is also determined from the global minimum of MSE, while the property of MSE that it follows a χ^2 distribution, enables calculating the 95 % confidence interval (CI) of K_a .

The accuracy and precision of the PLS-based method was compared with the results obtained by means of a PCA-based method [3]. For this, the analyzed X data were computed as superpositions of model spectra of the pure components in the pK_a and pH ranges of 2-9 and 4-7, respectively, to which random noise in spectral intensity and a random constant baseline were added. The results of the test presented in Fig. 1 clearly indicate that the PLS-based method outperforms the PCA-based method both in accuracy as well as precision of the determined pK_a value. This is particularly true if the expected pK_a lies outside of the probed pH range.

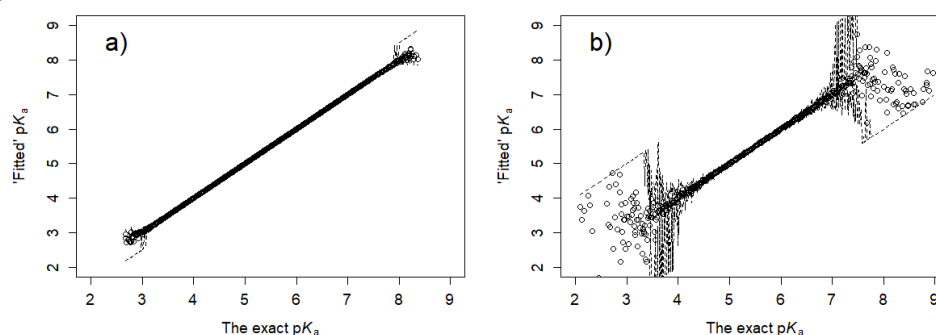


Figure 1. "Fitted" vs. the exact pK_a for the PLS-based method (a) and the PCA-based method (b). The dashed lines represent the 95% CI.

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Hydration behavior of alcohols in aqueous solution as studied by dielectric relaxation measurements

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Alcoholic substances are widely used in the formulation of skin care and hair care products for the purpose of moisturization or preservation [1-2] in cosmetic and pharmaceutical industries. Although alcoholic substances are essential ingredients, these often cause serious damages to the hydrogel formation processes used in skin moisturizing creams and hair conditioners [3]. In order to use these alcoholic substances effectively in the process of commercial product manufacture, we should understand the hydration behavior and mechanisms of the alcohols in aqueous system because most of cosmetic and pharmaceutical products are water based mixtures. Hence, we investigated the hydration behavior of alcohols such as 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, glycerol, erythritol, xylitol, and sorbitol in aqueous solution by using extremely high-frequency dielectric relaxation measurements up to 50 GHz at a temperature of 25 °C.

The obtained dielectric spectra were decomposed into some dielectric relaxation modes described by Debye-type relaxation modes. The hydration number per molecule for the alcohols were determined from the reduction ratio of the dielectric relaxation strength of free water in aqueous solution using a method described in the previous study [4].

The hydration number per hydroxy group of liner mono-alcohols such as 1-propanol, 1-butanol and 1-pentanol was determined to be ca. 4, and that of branched mono-alcohols, 2-propanol, 2-butanol and 2-pentanol, ca. 5 showing the characteristic hydration behavior of isolated hydroxy groups without intramolecular hydrogen bond formation [4]. On the other hand, the hydration number per hydroxy groups of polyalcohols such as glycerol, erythritol, xylitol and sorbitol was determined to be 1 to 2. The number substantially less than that for the mono-alcohols manifests that adjacent hydroxy groups in the polyalcoholic molecules effectively form intramolecular hydrogen bonds. The relationship between the hydration number per hydroxy group and the positions of hydroxy groups (and also distances between hydroxy groups) in the polyalcohols is discussed.

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Counterion binding in the adsorbed film and micelle of dodecyltrimethylammonium bromide and bisdodecyltrimethylammonium sulfate mixture.

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Competitive binding of binary mixed counterions to the headgroups has been investigated in the surface adsorbed films and micelles of dodecyltrimethylammonium bromide ($C_{12}TABr$)–bisdodecyltrimethylammonium sulfate ($C_{12}TA_2SO_4$) aqueous solutions.

Counterion binding of Br in the adsorbed films and micelles was evaluated by total reflection and transmission X-ray absorption fine structure (XAFS) techniques [1] at beamline BL-7C of the Photon Factory of KEK, Japan. It was conducted at 25°C and atmospheric pressure. Mole fraction of counterions in the adsorbed films and micelles was obtained from phase diagram constructed by our thermodynamic analysis [2] of surface tension data. In transmission XAFS for micelles, the signal owing to the bulk solution was subtracted through calculation of the concentration of monomer surfactants using phase diagram.

The obtained extended XAFS χ spectra were linear combinations of the spectra of fully hydrated bromide ions (free Br) and partially dehydrated bromide ions bound to the headgroups of the surfactant ions (bound Br) of the adsorbed films. The fraction of bound Br α for the $C_{12}TABr$ – $C_{12}TA_2SO_4$ mixture was almost same as that for pure $C_{12}TABr$ in micelles as shown in Figure 1(a). This was in accord with the fact of ideal mixing of counterions deduced from Excess Gibbs energy of mixing two kinds of surfactants in micelle [2] that was almost 0 as shown in Figure 1(b). In contrast, the α value for the $C_{12}TABr$ – $C_{12}TA_2SO_4$ was larger than that for $C_{12}TABr$ at adsorbed film, meaning that Br^- binds in preference to SO_4^{2-} in the mixed system. Such binding led to negative excess Gibbs energy. We discuss the relation between the binding and miscibility of counterions from the viewpoint of the difference in shape for planar adsorbed films and spherical micelles.

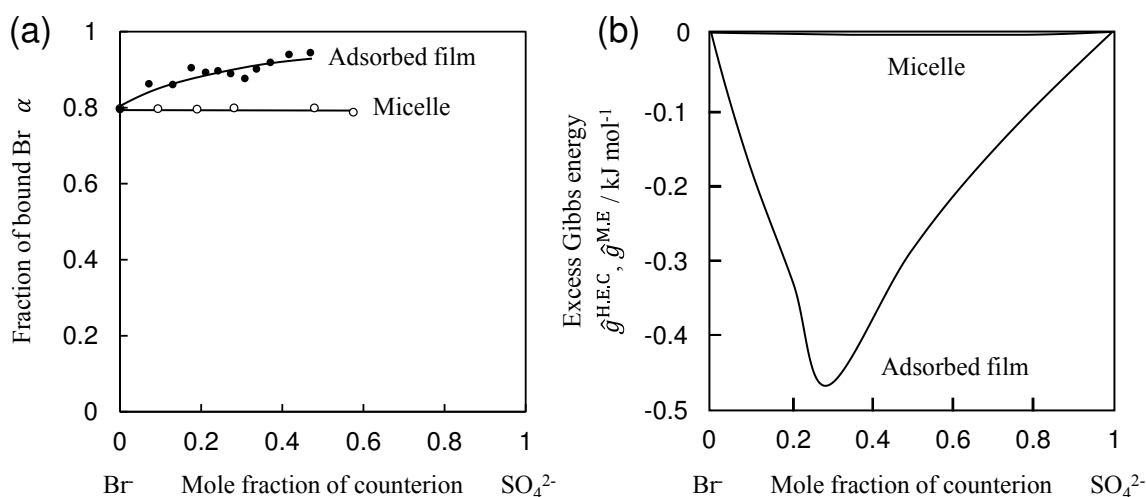


Figure 1. (a) Counterion binding of Br and (b) Excess Gibbs energy of mixing two kinds of surfactants in adsorbed films (at 45.5 mN m^{-1}) and micelles.

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Ion-specific effects on the Human Insulin fibrillation process.

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Insulin is largely used as regulator of the sugar blood level of people affected by diabetes and therefore it is one of the therapeutic proteins with the largest production volume. In physiological conditions its predominant form is a zinc-coordinated hexamer in equilibrium with the dimeric form, while at low pH it is mostly present as monomer.¹ Spontaneously, insulin forms biologically inactive aggregates (fibrils) and the process is promoted by low pH, high temperature, strong agitation, type and concentration of dissolved ions.² The fibrils are characterized by large beta-sheet content and the kinetics of their formation can be monitored via the thioflavin T (ThT) fluorescent assay. Indeed, due to the intercalation in the beta-sheet structures of the fibrils, ThT gives rise to a new excitation maximum at 450 nm and enhanced emission at 482 nm, whereas free ThT is essentially non-fluorescent at these wavelengths.

This investigation aims at elucidating the role of the anions, in relation to their specific properties, on the insulin aggregation mechanism by means of ThT fluorescent assay. We found that the aggregation kinetics proceeds differently below and above the physiological concentration of salt (150 mM). At 50 mM the formation of insulin aggregates follows the sequence $\text{SCN}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{ClO}_4^- > \text{Cl}^-$, suggesting that chaotropic ions are more effective in screening the monomers charge thus promoting the aggregation process. At higher ionic strength (500 mM) the trend of aggregation appears to be reverse: $\text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{ClO}_4^- > \text{SCN}^- > \text{SO}_4^{2-}$. The reversal of the series is a common behaviour in aggregation studies and might be related to the stronger adsorption of chaotropic ions compared to kosmotropic ions.³ Indeed, the strong ion-binding of chaotropic ions may lead to a charge inversion and to the onset of electrostatic repulsion between the monomers with a significant delay in the aggregation process.

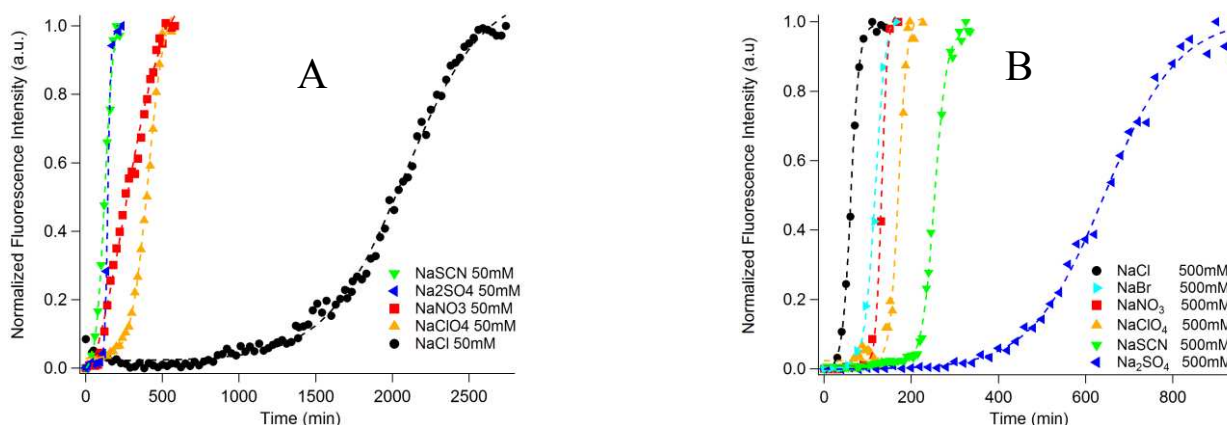


Figure 1. Aggregation kinetic of Insulin acidic solutions (HCl 25mM) in presence of different salts at the concentration of: (A) 50 mM and (B) 500 mM.

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Adhesive and repulsive forces between calcite surfaces

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Calcite is a common mineral resource and its consumption reaches over 4 billion tonnes each year. It is a major ingredient in paper, paints and plastics, however, its role is generally limited to an inert filling phase or pigment. On the contrary, calcite in biomaterials has usually a very specific and advanced function. The properties of calcite in many colloidal systems are governed by strong repulsive forces related to surface hydration of this highly hydrophilic mineral[1,2]. Modification of calcite properties by affecting surface hydration layer offers remarkable potentials in materials science.

In this study, we investigated interactions between calcite surfaces in water, electrolyte solutions and in dicarboxylic acids solutions using Surface Forces Apparatus (SFA) and Atomic Force Microscope (AFM). In the SFA, we investigated both the forces and recrystallization of nm-scale rough calcite substrates prepared by atomic layer deposition. In AFM we studied forces between cleaved single calcite crystals. With both techniques we probed μm -scale nominal contacts. Our goal was to recognize at which conditions repulsive hydration forces between calcite surfaces can be suppressed.

Our findings indicate that strong hydration repulsion between calcite surfaces in water is additionally enhanced by repulsive effects related to recrystallization of this moderately soluble mineral. Recrystallization produces mechanical repulsive effects due to force of crystallization upon mineral growth and due to significant increase in roughness of contact regions. We show that nm-scale rough surfaces gave rise to repulsive effects due to asperity deformations that were up to 2 orders of magnitude stronger than hydration effects at a given separation. Also, recrystallized calcite layers with multiple asperities were more prone to pressure-driven deformation.

We measured adhesive forces between calcite surfaces in concentrated salt solutions. Presence of adhesive forces was related either to EDL screening and VdW dominance at high electrolyte ionic strength ($>500\text{ mM}$) and/or due to disruption of hydration layer on calcite surfaces, now populated by a high number of partially dehydrated cations. We also show that recrystallization and roughening of calcite layer was enhanced at high electrolyte concentrations due to an increase in both solubility and dissolution rate of calcite [3]. As recrystallization produces strong mechanical repulsion, this effect can counteract the adhesive forces expected in concentrated electrolytes. Recrystallization effects were investigated in NaCl, CaCl₂ and MgCl₂ salts, were cation-specific and depended on ionic strength.

Adhesive forces between calcite surfaces were additionally measured in presence of soluble dicarboxylic acids. We studied these interactions as a function of hydrophobic chain length and found adhesive forces only for long-chained dicarboxylic acids (50 mM adipic and pimelic acids). Dicarboxylic acids have high affinity towards calcite surface and we observed that their adsorption passivated calcite surface, preventing it from major recrystallization. Adhesive effects between calcite surfaces in dicarboxylic acids could be related to disruption of hydration layer by hydrophobic chains of adsorbed organic molecules or other electrostatic effects.

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Binding of lanthanide salts to phospholipid monolayers: Dramatic effects of the anionic ligands

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Lanthanides are used in many important technologies. Given the difficulty to extract them from ores, their separation from complex mixtures and their recycling is a pressing technological problem [1]. We have recently found that the strong interaction of phospholipids with lanthanides can be used to create useful separation guidelines for lanthanides. The careful study of lanthanide interactions with lipid model systems is also of great interest in biology (e.g. MRI, or studies of membrane proteins in bicelles) [2].

In this work we have examined the interaction of several lanthanide ions with Langmuir monolayers of phospholipids (DPPC but also DHPC and DMPE). We have found that this interaction, which is stronger for heavier lanthanides, depends on the anion of the salt used, which often acts as a ligand [3]. Surprisingly, strong ligands tend to enhance the lanthanide-lipid interaction, the opposite being true for weakly coordinating anions. This finding explains results in older biophysical literature [4], but also the effect of the acid used on the separation of lanthanides from nuclear waste by extraction [5].

Using GIXD (grazing incidence X-ray diffraction) we found that lanthanide salts have a complex effect on the structure of the LC phase of lipid monolayers. For example, the usual NN-tilted phase of DPPC is replaced by NNN-tilted phases in the presence of cerium nitrate and sulfate, but not of cerium chloride, while the unusual (for DPPC) untilted phase appears at high pressures for strongly interacting salts (erbium and ytterbium nitrate). Ln-DMPE interactions are much weaker than Ln-DPPC ones, due to the tighter structure of the DMPE monolayers. Thus the salt type appears to play a role analogous to the temperature in modifying the phase diagram of phospholipid monolayers. PM-IRRAS measurements show that the lanthanide binding takes place mostly at the phosphate groups, and is accompanied by significant dehydration of the headgroups, as observed before for calcium binding to phospholipid mono- and bilayers [6].

The conclusion is that both metal and anion contribute to lanthanide salt-lipid interactions, rendering this chemistry highly specific. This work lays down some basic rules for separations based on lanthanide interactions with surface organic groups.

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Influence of salts on rheological properties of colloidal systems and its possible relation with Hofmeister series

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Interplay of various interactions may enable very fine-tuning of physical properties of colloidal systems. Successful exploiting of such tuning is of enormous importance for practical applications (e.g. in pharmaceutical and paint industry, wastewater treatment plants, ...) but obtaining full understanding of mechanisms taking part in such systems is possible only through basic research.

While it seems that Coulombic effects in solutions of charged colloidal solutes with added simple salts can be rather well forecasted[1] far more questions are left unanswered in case of hydration phenomena. This holds true both for polar and non-polar surfaces of (colloidal) solutes as well as for simple inorganic ions. Leaving aside interactions between two partially hydrophobic surfaces where consideration of hydrophobic hydration at quantitative level will probably not be solved in near future, in recent two decades a lot of effort was dedicated to solving mystery of ion-specific effects in aqueous systems, i.e. to discover the secret of Hofmeister series. Although being noted already at the end of 19th century during study of solubility of proteins in salt solutions, accumulation of experimental proofs of rather universal validity of Hofmeister series is still in progress[2]. Due to its relevancy for understanding physico-chemical properties of the given system a large interest of scientific community to understand mechanism of this phenomenon exists. No firm explanation of these effects, however, has been obtained yet[3].

A correlation of Jones-Dole B coefficients derived from measured viscosities of aqueous salt solutions with Hofmeister series is widely acknowledged. Nevertheless, the exact origin of differences between salts is not identified yet although it is attributed to the volume occupied by the hydrated ions[4]. In view of some theoretical studies (e.g. [5]), such origin may be traced to the varying strength of hydrogen bond in hydration layers of ions. Following this idea, rheological properties of chosen colloidal systems (polyethylene glycol, gelatine, agar, and carboxymethyl cellulose salt) where hydrogen bonding is expected to play a significant role were examined in aqueous media with simple salts added.

The results clearly show a significant influence of added salts, sometimes already at low concentrations. This effect is far greater than the effect of salts itself dissolved in pure water and sometimes also of different direction as the one described by Jones-Dole B coefficient. Opposing effects obtained for addition of MgCl_2 and K_2SO_4 , both having almost the same hydration number, undoubtedly show that water withdrawing effect of the salts is not the one responsible for occurrence of Hofmeister series. In light of characteristics of chosen systems, ion-induced disruption of networks of hydrogen bonds may be blamed for observed changes of rheological properties.

One may agree with the claim that Hofmeister series is a complex phenomenon[6], however, according to measured rheological properties of chosen colloidal systems, influence of ions on the strength of hydrogen bonds in aqueous solutions[7] may be of one of the most important if not even the most important source of ranking of ions into Hofmeister series[5].

Acknowledgements: This study was supported by the Slovenian Research Agency (ARRS) through the Program 0103–0201.

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A combined electrophoretic and light scattering approach to elucidate the molecular origin of reverse Hofmeister series effects

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We have carried out a systematic study of specific ion effects on lysozyme solutions using static light scattering to characterize protein-protein interactions (in terms of the osmotic second virial coefficient, B_{22}) and electrophoretic light scattering to approximate the diffuse layer potential of lysozyme. Lysozyme has long been used as a model system for specific ion effects in part because its solubility behavior follows the reverse Hofmeister series, where chaotropes rather than kosmotropes are more effective salting-out agents [1]. A key question we address is how chaotropic anion binding alters protein-protein interactions (and protein solubility) as computational work indicates ion binding mainly alter electrical double layer forces between proteins [2,3]. To check this hypothesis, B_{22} and electrophoretic mobilities for lysozyme have been measured as a function of pH and salt concentration with different anions spanning the range of the Hofmeister series. We found that under low ionic strength conditions, the measured zeta-potential does not always correlate with the trends in protein-protein interaction measurements. In particular, with increasing ionic strength, chaotropic anions such as thiocyanate are more effective at inducing protein-protein attraction than is the kosmotropic anion sulfate, although the zeta potential remains less positive in sulfate solutions over all ionic strength. The results demonstrate that chaotropic anion binding to proteins induces short-ranged attractive forces between proteins of non-electrostatic origin, rather than changing electrical double layer forces.

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Charge Regulation and the Properties of the Stern Layer at the Solid-Liquid Interface: Ion Specific Effects

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Direct force measurements based on atomic force microscopy (AFM) were carried out to study the charge regulation and Stern layer properties at the solid-liquid interface. The forces between silica and sulfate latex particles were measured in LiCl, NaCl, KCl, and CsCl solutions. The measured force profiles were interpreted with Poisson-Boltzmann theory, which enables to extract the diffuse layer potential and regulation parameter for the surface. These two parameters enable to calculate the properties of the inner layer, such as Stern layer capacitance. Stern layer capacitance is increasing with increasing salt concentration and strongly depends on the type of ion. The largest capacitances are observed in CsCl and are decreasing in the KCl, NaCl, LiCl order, which is consistent with the direct Hofmeister series. These trends can be understood when the Stern layer thickness is calculated from the Stern layer capacitances. The Stern layer thickness correlates with the hydrated cation radius, see Fig. 1b. Therefore, the hydrated cation radius determines the inner layer capacitance and affects the charge regulation properties of the solid-liquid interface. The Stern layer properties extracted from force measurements are in agreement with recent experiments based X-ray photoelectron spectroscopy in a liquid microjet [1,2].

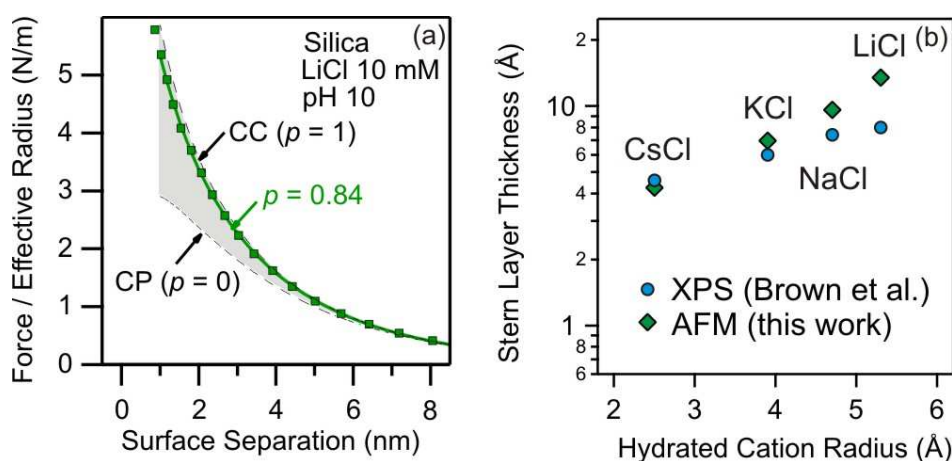


Figure 1. (a) Force between two silica particles immersed in 10 mM LiCl. The shaded area is bound by constant potential (CP) and constant charge (CC) boundary conditions. The experimental forces are typically between these two bounds. The regulation parameter can be extracted from such force curve. (b) Stern layer thickness at the silica interface in CsCl, KCl, NaCl, and LiCl solutions. Results from XPS and AFM methods are compared.

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Interactions of lyotropic anions with micelles of dodecyl phosphocholine.

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The term “specific ion effects” refers to phenomena, in which ions of the same charge have considerably different effects in physicochemical, environmental and biological systems. To understand specific ion effects we have used lipid micelles of dodecylphosphocholine (DPC) as useful membrane-mimetic systems [1-3]. These micelles are widely used in biochemistry to solubilize membrane proteins in water [4]. The effects of electrolytes on micelle structure can be quantified through the critical micelle concentration (CMC), the aggregation number (Nag), the inner order (relaxation times) and the shape.

In the present work we have used sodium salts with anions that span the chaotropic side of the Hofmeister or lyotropic series. Electrolyte effects on the internal structure of the DPC micelles were studied using electron paramagnetic resonance (EPR) spectroscopy, with 5-doxyl stearic acid as a spin probe. By examining the rotational correlation time (t_{rot}) of the spin probe as a function of salt concentration, it was found that the weakest hydrotropes (NO_3^- and Cl^-) of the Hofmeister series do not affect t_{rot} . Anions with weaker hydration (ClO_4^- and SCN^-) were found to slightly reduce the internal order of micelles. Strongly “hydrophobic” anions like B(Ph)_4^- (tetraphenylborate) and PF_6^- (hexafluorophosphate) significantly increase t_{rot} , to a degree that indicates a significant change in structure. The CMC of DPC was studied through fluorescence spectroscopy, more specifically through static fluorescence quenching of pyrene by excimers. Up to ClO_4^- in the chaotropic series the electrolytes studied did not strongly affect the CMC. The interaction enthalpy of electrolytes with micelles was measured using isothermal titration calorimetry (ITC). It was found that salts with weakly chaotropic anions interact weakly with the micelles in an endothermic way, while the hydrophobic anions interact much more strongly, and the overall interaction is exothermic. The ITC results were fitted to partitioning models [2, 3] to obtain a more direct measure of the ion interaction with the micellar interface.

The combination of the techniques used here and some older NMR results [3] provides clear qualitative and quantitative information about ion-lipid interactions and the ensuing structural modification of the micelles as a function of the type and concentration of the electrolyte used. In agreement with the Hofmeister series, sodium salt-DPC interactions decrease in the order $\text{B(Ph)}_4^- > \text{PF}_6^- > \text{SCN}^- > \text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^-$.

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Hydration and Counterion Binding of [C₁₂MIM] Micelles

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Surface-active ionic liquids based on imidazolium cations are promising targets for micellar catalysis in aqueous solution, yielding enhanced rate constants compared to surfactants based on *n*-alkyltrimethylammonium cations [1]. Moreover, the reaction rate highly depends on the counterion, which implies the interplay between headgroup hydration and counter binding to be central to its catalytic action.

In this context, we present a dielectric relaxation spectroscopy (DRS) study, in combination with viscosity and small-and-wide-angle X-ray scattering measurements, on aqueous solutions of 1-dodecyl-3-methylimidazolium ([C₁₂MIM]) bromide (Br⁻), iodide (I⁻) and triflate (TfO⁻) at 45 °C. DRS is a convenient tool to investigate the structure and the hydration of the micelles as well as the dynamics of counterion binding.

It was found that [C₁₂MIM] micelles were less hydrated than the corresponding *n*-alkyltrimethylammonium micelles, suggesting the loose hydration pattern to be the reason for their higher catalytic effect. The mobility of the adsorbed counterions decreased in the order of decreasing catalytic activity, namely Br⁻ > I⁻ > TfO⁻. Whereas [C₁₂MIM]Br aggregates stayed (practically) spherical over the entire concentration range, rod-like micelles were formed at higher surfactant concentrations in [C₁₂MIM]I(aq) and, in particular, [C₁₂MIM]TfO(aq) systems [2].

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Lanthanide salt adsorption on phospholipid micelles: Probing the role of the anion

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Lanthanide-phospholipid interactions are of great interest in biophysical chemistry since lanthanides have been used as optical or magnetic probes in many biological applications, such as in *in cellulo* or *in vivo* imaging [1]. Lanthanide-lipid interactions have been used to control the orientation of bicelles, used to solubilize and study membrane proteins [2]. Recently lanthanide ion-chelating phospholipid bicelles were used as sensors for temperature-sensitive soft materials [3]. The binding of lanthanides to lipids is strong, and it can often lead to gelation or precipitation of the lipids in the form of lamellar phases or crystals [4]. As lanthanide salts do not dissociate fully in aqueous solutions, we expect that their speciation will affect their interactions with lipids.

We have examined lanthanide ion complexation with the micelles of the zwitterionic phospholipid DPC (Dodecyl Phosphocholine), which are membrane-mimetic systems used in membrane protein studies [5]. Our main goal is to determine which lanthanide species is actually binding to the phospholipid headgroups; to do this we have applied various methods including fluorescence spectroscopy (static and time-dependent), isothermal titration calorimetry (ITC) and rheology combined with theoretical modelling. We have used different salts of Ce^{3+} , Eu^{3+} and Er^{3+} to examine (a) the effect of the metal, and (b) the effect of lanthanide speciation in solution across the lanthanide series. Perchlorate salts were used as reference compounds, since ClO_4^- is considered to be a very weak ligand for the lanthanides. On the other hand ClO_4^- has been shown to interact quite strongly with phospholipid monolayers, bilayers and micelles [6]. Fluorescence experiments focus on Eu^{3+} due to its excellent emissive properties. Theoretical modelling of time-dependent fluorescence data suggest the stoichiometry of the lanthanide-DPC interaction and the related binding constant. ITC experiments showed that lanthanide-DPC interaction enthalpies depend on the nature of the Ln^{3+} ion but also on the counterion of the lanthanide salt. ITC data are currently being simulated with a theoretical model to provide the lanthanide-DPC complexation constant and binding enthalpy and to confirm the stoichiometry of the reaction emerging from fluorescence experiments. Rheology experiments confirmed that even at very low DPC concentrations in the presence of nitrate or sulfate ions (but not in the presence of chloride!) lanthanide-DPC interactions eventually lead to gelation. The critical lanthanide concentration for gel formation was detected by investigating the viscoelastic properties of the gel phase.

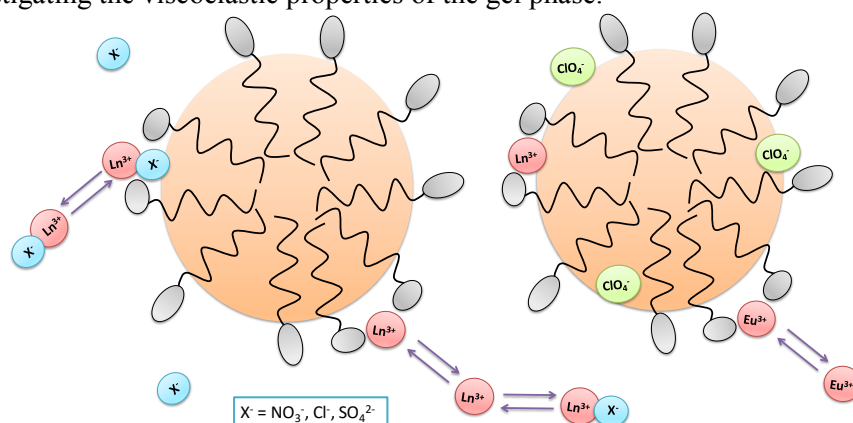


Figure 1. Effect of lanthanide speciation on lanthanide interactions with DPC micelles.

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Colloidal surface assemblies for light harvesting and beyond

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Colloidal nanoparticles offer a range of interesting optical and electronic effects. A prominent example is the localized surface plasmon resonance (LSPR) of metal nanoparticles due to resonant excitations of vibrations of the particles' free-electron cloud by light. Due to the LSPR, plasmonic nanoparticles provide excellent means for controlling electromagnetic near-fields at optical frequencies, which has led to a broad range of applications in various field such as surface enhanced spectroscopy, light harvesting or photonics.

While much research is dedicated to understanding nanoparticle synthesis and tailor their LSPR on the single particle level [1], ordering particles on different length scales opens another powerful avenue towards optical and electronic functionality. Plasmonic particles can couple locally, altering their LSPR, but as well collective long range phenomena can give rise to novel effects. In this context, integrating plasmonic nanoparticles into polymeric shells and / or scaffolds opens novel perspectives for solving this technological challenge. In particular we focus on core-shell particles and controlled wrinkling as a versatile means for surface patterning [2]. We discuss the underlying physico-chemical effects and perspectives for applications in Surface Enhanced Raman Spectroscopy and Photonics, as well as approaches towards tuning of plasmonic coupling effects by mechanical strains.

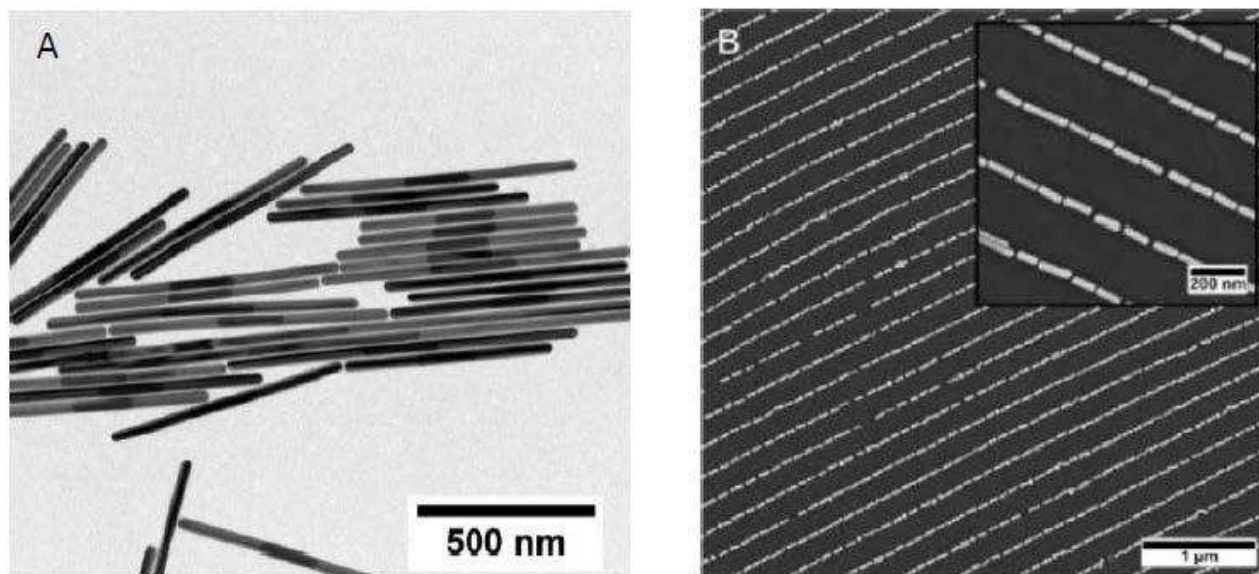


Figure 1. A: Well-defined Ag/Au nanorods with tuneable shape and spectroscopic response [1] B: Ordered assemblies of nanorods up to macroscopic areas [2]

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Dispersions of nanoparticles in ionic liquids for thermoelectric applications: evidencing the key parameters

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Ionic liquids (ILs) are a wide class of solvents, purely constituted of ions, which can be liquid at room temperature and strongly differ from classical molecular solvents. They are used in many applications, mainly as green solvents to replace dangerous organic ones, for example in thermoelectric applications [1]. However, the colloidal stability in ionic liquids is neither well understood nor properly controlled yet.

In previous studies, we addressed the case of iron oxide nanoparticles (NPs; maghemite $\gamma\text{-Fe}_2\text{O}_3$ with a diameter around 10 nm) in ethylammonium nitrate (EAN). We showed that the solid/liquid interface is a crucial point in the dispersion, in particular the nature of the counterion of the charged NPs [2,3].

Our current work is aimed at developing new thermoelectric materials based on ionic ferrofluids that are versatile, cost-effective and non-toxic to assist the economically and environmentally sustainable energy transition. Therefore, we focused on a set of ionic liquids based on imidazolium, pyrrolidinium and ammonium cations, with TFSI anions in all cases, using the same maghemite NPs. We evidence also the importance of the solid/liquid interface, however not only through the nature of the counterion but also through the detail of the NPs surface. Another key parameter is the path used for the transfer of the NPs from the initial solvent water towards the ionic liquid. Playing with these parameters, the NPs can be dispersed in all ionic liquids tested. The quality of the obtained dispersions is analyzed with Dynamic Light Scattering (DLS) and Small Angle X-ray/neutron Scattering (SAXS/SANS).

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Nanoscale structure of planar electrochemical interfaces for lithium power sources by neutron reflectometry

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The performance characteristics of electrochemical energy storage devices are largely determined by the processes occurring at charge separation interfaces and causing modifications of the interface structure. Thus, lithium ion batteries with liquid electrolytes are characterized by the appearance of a specific formation on the electrode surface known as solid-electrolyte interphase (SEI). In addition to the efficiency, the structural properties of this layer (thickness ~10 nm) are important in respect with possible lithium “moss” growth at the electrode-electrolyte interfaces upon battery cycling, the phenomenon which is a problem from the viewpoint of safety. The corresponding operando studies of the planar interfaces are a complicated task which requires elaborate designs of experiment and applications of various methods to monitor a hidden electrode surface being in contact with Li-containing liquid electrolytes [1].

Here, neutron reflectometry (NR) in the specular mode (Fig. 1) was applied to study the SEI formation and Li plating on a thin (thickness ~55 nm) Cu/Ti electrode on Si substrate following the ideas of the previous work [2] and extending the range of the amount of the deposited Li. The nanoscale structure of the Li enriched layer formed on the working electrode (WE) was analyzed in terms of the depth profile of the scattering length density (SLD) obtained from the modelling of the reflectivity modulations as a function of momentum transfer. A principal change in the profile evolution was observed for the nominal Li deposition thickness of above 20 nm, which is an indicator of the start of non-homogeneous lithium plating on the electrode surface.

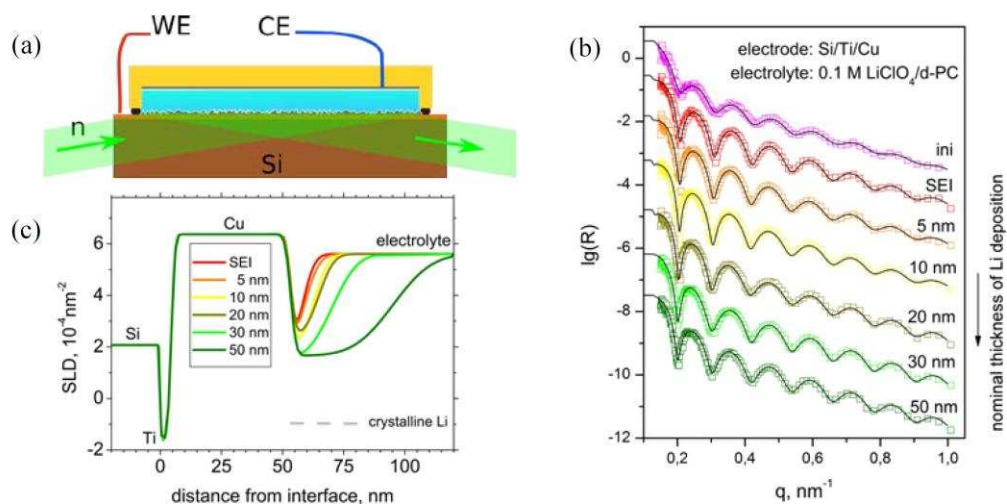


Figure 1. (a) Scheme of NR experiment with electrochemical cell for operando studies; (b) Experimental specular reflectivity curves and theoretical models; (c) SLD depth profiles obtained from NR curves.

Acknowledgements: The financial support of the Russian Scientific Foundation (project N 17-12-01540) is acknowledged.

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Porphyrin Adsorption by Stabilized TiO₂ Nanoparticles

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Dye sensitized solar cells (DSSCs) based on TiO₂ have been studied as an easy to produce, low-cost alternative to classical semiconductor solar cells for a long time [1]. The use of porphyrin molecules as dye in the last years led to DSSCs with efficiencies of up to 13% [2]. We synthesized tunable titania nanoparticles with a diameter of ~2-3 nm using a hot injection method [3]. The produced nanoparticles are stabilized by oleic acid. Special emphasis of our work is focused on the exchange process of the oleic acid with porphyrins designed for a particular application.

This process is studied using a variation of different scattering techniques. One method is the combination of small angle x-ray and neutron scattering (SAXS and SANS) experiments. These are well suited to study core/shell systems. X-rays interact mainly with electrons and therefore SAXS yields information about the inorganic core of the nanoparticles. Neutrons on the other hand are very sensitive to hydrogen and therefore SANS is well suited to get information about the organic stabilizer shell (cf. Figure 1a). This information can be further improved by additional contrast variation measurements.

The UV/Vis spectrum of porphyrins is very sensitive to changes in conformation and can be used to give additional information on the exchange process (cf. Figure 1b) [4]. Lastly X-ray reflectivity measurements can be used to study layered systems on flat substrates. This offers the possibility to study the exchange of oleic acid with porphyrins on TiO₂ Wafers as a test system (cf. Figure 1c).

In the talk an overview over the different techniques will be given. Furthermore their usage in the characterization of the morphology of the produced particles and the ligand exchange from oleic acid to porphyrins will be presented.

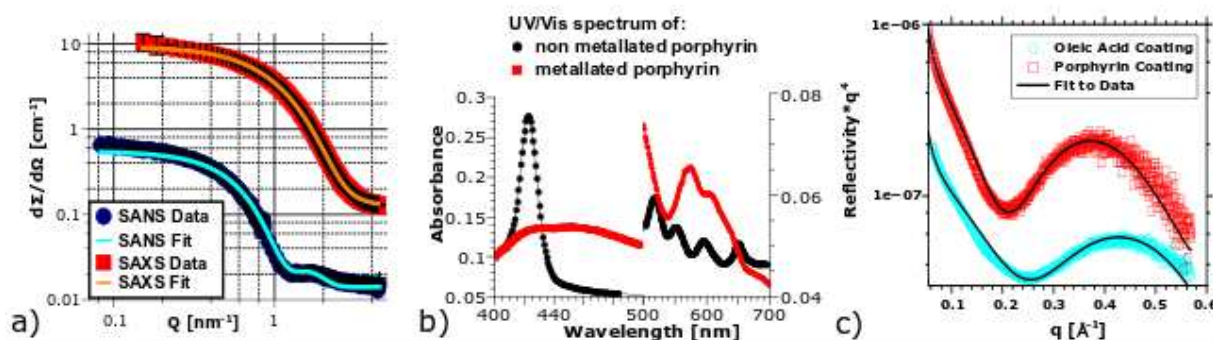


Figure 1: Overview of different techniques used for the characterization of the exchange process of oleic acid with porphyrins on anatase nanoparticles: a) Simultaneous fit to SAXS and SANS data of TiO₂ nanoparticles; b) UV/Vis spectra of metallated and non metallated porphyrin; c) XRR measurements of Rutile Wafers coated with oleic acid and porphyrin

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Spreading of oil droplets on gas bubbles studied with microfluidics

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We report a microfluidic method for studying the fundamental aspects of gas flotation in the wastewater treatment. The developed approach allows to systematically investigate the interactions between gas bubbles and oil droplets in various conditions (oil, water and gas composition, oil concentration, droplet sizes).

Gas flotation is a technique often utilized in solid-liquid and liquid-liquid separation. It relies on the generation of gas bubbles that become attached to the dispersed droplets or particles, and together rise to the surface. Frequently it is used for wastewater treatment, where it aims at removal of the dispersed oil drops from the continuous water phase. For example, in the petroleum production, the oily formation water must be treated before discharge or re-injection, which is commonly performed with gas flotation units.

After attachment, the bubble-droplet aggregate must withstand the turbulence inside the flotation unit in order to rise to the surface. The most stable configuration between a bubble and a drop is an oil film, spread over a gas bubble [1]. Oil spreading, however, is a process that relies on many different aspects, among other things, the physicochemical and interfacial properties of the phases, and the interactions between them [2].

We present a novel microfluidic method for studying the oil spreading over gas bubbles in various conditions (Figure 1). It is based on simultaneous and continuous generation of gas bubbles and oil droplets in a water phase, inside a glass microfluidic chip. Droplets and bubbles then get in contact and start interacting in a wider channel, where the possible spreading occurs. High-speed imaging allows us to record the number of droplets coming in and out of the channel, which is later compared to obtain the percentage of droplets removed through spreading.

We have focused on studying the fundamental aspects of gas flotation treatment of oilfield wastewater. Our method allows to investigate the desired phenomena in dynamic conditions and in relevant size range. With the systematic variation of different parameters, we obtained reproducible trends that agree with the available literature, and extend the knowledge in this research field, for instance through analyzing the gas phase effect on the spreading efficiency. It is our belief that this microfluidic tool can aid in gaining more insight into the fundamentals of gas flotation, which can lead to overall improved performance of this process.

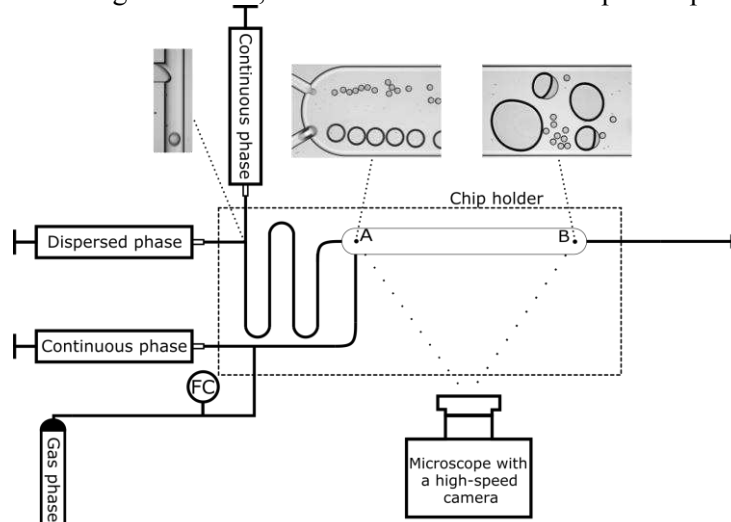


Figure 1. Overview of the microfluidic setup for studying oil spreading on gas bubbles

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Hans Lyklema: a life devoted to Science and Society*

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Hans Lyklema will largely be remembered because of three qualities: (1) his general knowledge of physical chemistry as laid down in the *Fundamentals of Interface and Colloid Science* [1], or FICS (Fig. 1 middle) as he called it himself, (2) his creation of an enormous network including many people, also from Eastern Europe (Fig. 1 left), with which he effectively put Wageningen on the map as an important Colloid and Interface Science institute and (3) his concern for the environment (Fig. 1 right), the latter in particular in later life where he became active member of the Dutch Footprint Club [2].

On Hans 60th birthday, a Festschrift in the form of a special issue of *Colloids and Surfaces* [3] was arranged to which many students and friends contributed. This certainly gives a good impression of the broadness of his interests. It also contains an article [4] by his promotor Theo Overbeek that carefully explains the dominant role of entropy in the electrical double layer. Since that time, the scientific contributions of Hans tend to focus more on the role of entropy in colloid and interface science. In his farewell lecture 5 years later [5], he argues that the Laws of Thermodynamics pose limits to daily life. He carefully explains the role of entropy and entropy production in such processes and Nature's tendency to prefer processes with lowest entropy production. Indeed, it is Interfacial Engineering [5] that is most expedient in achieving the goals that Hans was after.

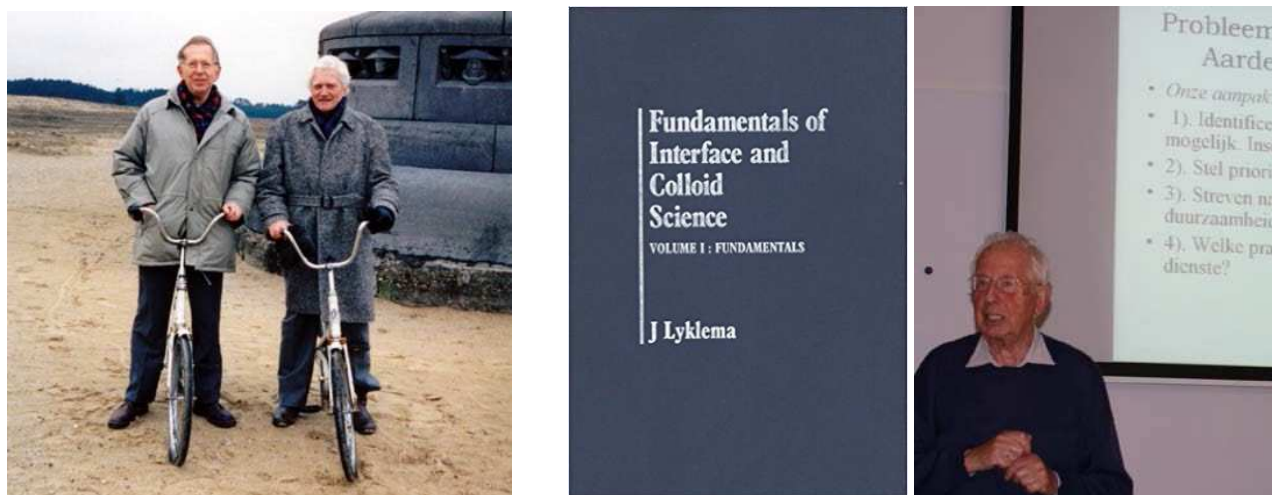


Figure 1. Lyklema with Churaev, his FICS and lecturing at a Dutch Footprint Club meeting.

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*Dedicated to the memory of Prof. Johannes Lyklema, who passed away on 31st October 2017.

In memory of Dotchi Exerowa and Dima Platanov

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In October 2017 the international colloid and interface community had lost two scientists of high professional authority and prominent representatives of European Colloid and Interface Science: Dotchi Exerowa and Dima Platanov. They both had actively developed and promoted the microscopic thin liquid films as an advanced methodology to investigate surface forces and related phenomena in the physics and chemistry of interfaces. Throughout the years they had put much effort in elucidating the impact of thin liquid films as key ingredients of disperse systems, including such that are used in medicine, food, cosmetic and chemical industries, oil processing, etc.

Dotchi and Dima graduated Chemistry at Sofia University “St. Kliment Ohridski” in 1958. The start of their scientific careers coincided with a brilliant period that begun in the late fifties of the 20th century when the basis of surface-forces studies in the vicinity of fluid interfaces was being put down worldwide. Their names are closely related to one of the most successful research instrumentation in the field of surface forces is the microinterferometric thin-liquid-film setup. This unique apparatus is based on a simple and very useful model system – microscopic horizontal liquid film (radius $\sim 100\ \mu\text{m}$). Its key element is the originally designed experimental cells [1]. Using this setup, first experimental verifications of the theory of Derjaguin, Landau, Verwey and Overbeek (DLVO) were accomplished [2] and seminal experimental data about the onset and evolution of ‘dimples’ in the initial stages of formation of wetting films were obtained [3].

Throughout the years the research activities of Dotchi and Dima were running mostly in parallel, with each of them having specific scientific contributions. This was one of the seldom cases when a couple in life had managed to make their own personal independent careers in science with well-distinguished individual achievements. The scientific interests of Dotchi Exerowa focused mostly on the investigation of microscopic foam films and foams. Using the microscopic-foam-film model she and her group have investigated fundamental aspects of the formation and stability of foam films [1,2,4-5]. Starting from the experience on microscopic foam films, Exerowa and her collaborators have correlated the film characteristics to the stability of foam systems [6-8]. Dima Platanov had comprehensively explored three-phase-contact and wetting phenomena [2,3,9-10]. The shape of three-phase contact gas/liquid film/meniscus/solid surface had been studied in detail and the equilibrium profile of the transition zone between a wetting film and the bulk liquid were experimentally obtained, data for ‘contact thickness’ had been determined; the values of film tension and line tension of Newton black films were achieved; the gas permeability through foam films was considered.

Dotchi Exerowa and Dima Platanov had also jointly made valuable experimental and theoretical accomplishments enhancing the knowledge about the properties and interactions in foams, emulsions and related applications. In the recent two decades they had authored together a number of essential review publications and chapters in encyclopedic books edited by eminent colloid scientists [11-16]. Besides, Dotchi was a member of the Editorial Boards of leading colloid chemistry journals (Advances in Colloid and Interface Science, Colloids and Surfaces A, Colloid and Polymer Science, Colloid Journal (in Russian)). In the last decade they had been Section co-Editors for the topic “Thin Liquid Films and Foams” in the Elsevier journal Current Opinion in Colloid and Interface Science.

Through their research activities Dotchi Exerowa and Dima Platanov had developed numerous collaborations with leading scientists and research laboratories in the field of physical chemistry of interfaces and colloids. They were also closely engaged in the development and the organizational advance of the international colloid and interface scientific community. Each of them had been elected twice as Member of IACIS Council; Platanov was President of IACIS (2000 – 2003) and later was elected as Lifelong Member

of the Standing Committee of IACIS Council. He had been Member of the Standing Committee of European Chemistry at Interfaces Conferences (ECIC). Since 2004 he had been Member of the Physical and Biophysical Chemistry Division Committee of IUPAC. In 1997 they co-chaired the 9th IACIS Conference in Sofia; in 2013 they were members of the Scientific Committee of the 27th ECIS Conference in Sofia.

The long scientific careers of Dotchi Exerowa and Dimo Platikanov resulted in mutual inspiration and research collaboration that produced important scientific results in the field of surface forces, thin liquid films, foams and emulsions. Throughout the years they had succeeded in attracting many gifted young people and established two strong research teams: Exerowa in the Department of Interfaces and Colloids (Institute of Physical Chemistry, BAS) and Platikanov in the Department of Physical Chemistry (Sofia University). They both will be remembered by their colleagues, friends, collaborators and former students with their deep passion for science, the wide horizon of the research interests and the keen intuition to address challenging problems. The legacy of their scientific results, teaching and applied activities constitutes a notable contribution to the productive development of the European Colloid and Interface Science.

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Surface forces through microinterferometric thin-liquid-film apparatus: model studies and fields of applications*

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One of the most successful research instrumentation in the field of surface forces is the microinterferometric thin-liquid-film setup. This unique apparatus is based on a simple and very useful model system – microscopic horizontal liquid film (radius $\sim 100\ \mu\text{m}$). The methodology and the equipment target specific cases of close interaction of fluid/fluid and fluid/solid interfaces and the formation of thin liquid films (foam, emulsion and wetting films). The key element of the microinterferometric method is the originally designed experimental cells. They are of three major types: the Scheludko-Exerowa glass tube cell for films at constant capillary pressure, the porous plate cell to monitor the disjoining pressure isotherm of thin liquid films, and the improved Platikanov cell for microscopic wetting liquid films on solid surfaces with different degree of hydrophobicity. Using earlier modification of this setup the first experimental verification of the classical theory of Derjaguin, Landau, Verwey and Overbeek (DLVO) was demonstrated. Particularly useful is the modification “Thin-Liquid-Film Pressure-Balance-Technique”. It allows direct measurement of interaction forces in the microscopic liquid films, gaining the disjoining pressure/film thickness isotherms ($\Pi(h)$) for a wide range of thickness values and pressures, including the transition region of common black/Newton black films, and gives various opportunities for studies on fundamental aspects of the formation, drainage and stability of thin liquid films and related phenomena and systems.

The accumulated knowledge on thin liquid films is successfully applied to solving substantial problems in biology, medicine and pharmacology. One indicative example is the advancement of the original method for early diagnostics of the lung maturity of neonates. As it is well-known, the deficiency of the alveolar surfactant causes lung immaturity and leads to the Respiratory Distress Syndrome (RDS) in newborns. Through the investigation of bilayer films formed from amniotic fluid and components of the alveolar surfactant it is demonstrated that these films may be used for probing the lung surfactant insufficiency. Microscopic foam and wetting films are used as *in vitro* model for the *in vivo* situation at the alveoli interfaces. The approach exhibits a number of advantages providing unique information about the formation and stability of films from pulmonary surfactant and its ingredients. It gives a deeper insight about the physical causes and the range of action of molecular interaction forces at the alveolar surface. Thus the thin liquid films proved to be a particularly useful tool for the assessment of pathological states related to RDS. Furthermore this methodology creates a number of valuable opportunities for the optimization and the development of new generations of therapeutic surfactant preparations.

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*Dedicated to the memory of Dotchi Exerowa and Dimo Platikanov, who passed away in October 2017.

Kåre Larsson – a lifelong curiosity for science and innovation*

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Professor Kåre Larsson
27/2 1937 -25/3 2018

Kåre Larsson was an incredibly gifted and innovative scientist who was also a devoted friend and an inspiring mentor and teacher. He came from a humble background and grew up in a small village in the northern part of Sweden. Already 14 years old, he received national attention for preparing a skin lotion, demonstrating his lifelong curiosity for science and innovation. His academic career was started with a licentiate degree in inorganic crystallography at Uppsala University under the supervision of Prof. Gunnar Hägg. Kåre then moved to work with Prof. Einar Stenhagen at Gothenburg University where he did his pioneering work to determine crystal structures of fats [1]. These findings are still being used today to control and optimize fat crystallization in the food industry. They also made Kåre an internationally recognized scientist. As a crystallographer in Gothenburg he became one of the pioneers in computer science and made important contributions to build up a central computer facility at Gothenburg

University. The initial structural work deepened his interest in the complex structures and phase transformations of lipid molecules in technology as well as biological systems. He used his methodological and mathematical skills, eye for complex structures and interest in turning science into practice to characterize and better understand a range of complex systems, including lipid liquid crystals, surfactant self-assembly, proteins and starch and other biopolymers [2]. In 1975 he was appointed professor in Food Technology at Lund University, where he successfully applied his scientific expertise and innovation to multiple problems in the areas of foods, pharmaceuticals, and chemicals. Kåre was always ahead of his time and his conceptual thinking on food structure was decades before molecular gastronomy made an impact on the world scene. He established strong collaborations with the industry, both nationally and internationally. Bridging the gap between fundamental research and practical applications was natural for Kåre, thanks to his scientific expertise, pedagogic skills and open-minded personality. His respectful approach paired an ability to find simple solutions to complex technical and scientific challenges earned him many successes both in science and industry. His discovery of bicontinuous phases and non-euclidean geometries in lipid systems started a revolution in biology and a conceptual leap of profound importance [3]. Later he realized that these structures could be dispersed into functional lipid nanoparticles, “Cubosomes”, which also became the origin of a pharmaceutical company Camurus (CAMX: Nasdaq STO) that he co- founded. The research on lipid-based cubic phases and their nanoparticles is today booming, thanks to Kåre’s significant contributions [4], and this was also the basis for Kåre Larsson being awarded the first Rhodia Prize of the European Colloid and Interface Society in 2001. Kåre’s outstanding entrepreneurial track-record also includes companies like Larodan (lipids), Probi (probiotic foods) and Bioglan (pharmaceuticals). We remember Kåre as a great and creative scientist who with his gentle and steady presence was always helpful and inspiring to students, collaborators and colleagues – immeasurably valued by all.

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*Dedicated to the memory of Professor Kåre Larsson, who passed away 25 March 2018.

Biomolecular interactions that controls the curvature of the lipid-aqueous interface*

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Lipids in living organisms do not always confined in bilayer structures, but they can also assembly into intriguing 3D structures. Well-defined model system will help us understand the biological implication as well as develop new applications, for e.g. biomedical devices and targeted delivery. Such structures are also generated or evolved with the help of specific lipolytic enzymes.

We will discuss how the lipid self-assembly structure can be change in desired way by adding a particular type of lipolytic enzymes. Here the (oil) triglyceride aqueous interface is important also for other processes like emulsification. Our results show that uptake of water in the triolein phase can occur and this can be affected by the presence of lipolytic enzymes [1].

The lipolysis-induced evolution of a particular structure formed by mixtures of lipids, which invoke different curvatures, is also controlled by the type of lipolytic enzyme. We demonstrated this by using highly structured cubic micellar (Fd3m) nanoparticles of 50/50 (wt%/wt%) soy phosphatidyl choline (SPC)/glycerol dioleate (GDO) [2]. The two types of lipolytic enzymes used were phospholipase A2 (PLA2) that catalyses degradation of the phospholipid component, SPC, and porcine pancreatic triacylglycerol lipase (TGL) that facilitate the hydrolysis of the diglyceride, GDO. Phospholipase A2, which promotes the hydrolysis of the lamellar forming component, SPC, induces a reversed micellar phase (Figure 1). However triacylglycerol lipase, which hydrolysis the reverse phase forming compound, GDO, induces a lamellar phase. The lipid particles were found to retain their integrity throughout the whole time of reaction studied

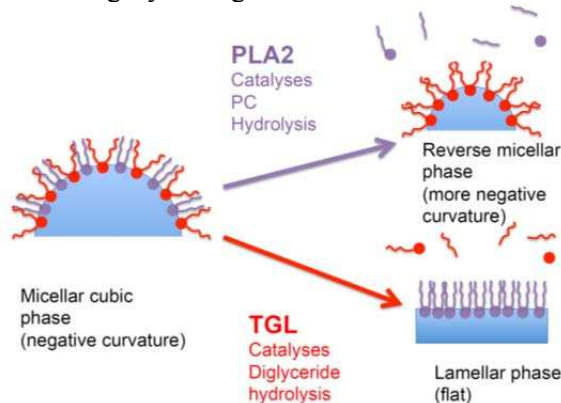


Figure 1. Schematic illustration of the effect of two lipolytic enzymes, triacylglycerol lipase (TGL) and phospholipase A2 (PLA2) on a mixed lipid system consisting of soy phosphatidyl choline (SPC)/glycerol dioleate (GDO).

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In memory of Helmuth Möhwald: Unconventional ideas leading to efficient applications of surface layers*

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Helmuth Möhwald studied Physics at University of Göttingen, where he met Erich Sackmann, his mentor and coach. During his PhD thesis (1974, University Göttingen), postdoc time (IBM San Jose) and habilitation in Physics (University Ulm) Helmuth Möhwald managed to grow sufficiently pure organic charge-transfer crystals to prove one dimensional charge-transfer. From 1978 he went for almost 4 years to industry. This was at Dornier at Ludwigshafen, and he was in charge of lubrication in space, and so he got interested in thin films and their application. In 1981, he got his first professorship at TU Munich in the Biophysics department. There he started to work with monolayers of amphiphiles at the air/water interface which has been the basis of his early career using fluorescence microscopy. Later, setting up his chair in physical chemistry in Mainz from 1987, Helmuth started to develop alternatives to the well-known Langmuir-Blodgett technique to prepare ultrathin organized organic films. The most visible and used achievement was the one of his habilitants, G. Decher, preparing films by alternating adsorption of oppositely charged polyelectrolytes, now known as the LbL technique. After the German

reunification Helmuth Möhwald started together with his two younger colleagues (M. Antonietti, R. Lipowsky) to build-up the first Max Planck Institute in former East Germany. This enabled formation of capsules with defined walls in nm dimensions and much work concerned controlling permeability, mechanics and chemistry in confined space. The success is not only reflected in several hundreds of publications of his co-workers or him but also in a start-up (Capsulation).

As far ECIS is concerned, Helmuth was organizer in Mainz of a memorable of five hundred, without a company making all, but all managed by students, the presence of two Nobel prizes. Without his successful move to merge ECIS and ECIC societies and meetings, we probably would not exist. He was not only a yearly active participant, giving contributed talks, being elected President in 2003 and also Overbeek medalist 2007.

At the end of 2017, Helmuth Möhwald was still in full steam scientific activity as editor of ACS-nano, also working intensely on recycling of windmill magnets using advanced colloidal techniques within the ERC “REE-CYCLE” project: science that will come out in one of the posthumous papers discussed last November in Marcoule will be detailed in contribution of Mario Spadina.

*Dedicated to the memory of Helmuth Möhwald, who passed away in March 2018.

A model for the prediction of rare-earth elements extraction/desextraction by a mixed charged and uncharged extractant microemulsion*

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Liquid-liquid extraction is the most commonly used method to recycle and separate metal ions from highly concentrated aqueous solutions. In most cases, known two extractants dissolved in a solvent are used in the synergistic ratio. Yet, even though the procedure works, the understanding of the phenomena behind it is still unclear to full extent. Currently, mainly the first neighbor supramolecular complexation term is considered, but this does not provide an explanation in the micellization threshold and synergy observed. The industrial scale modeling is, on the other hand, focused on establishing all the possible equilibria and then on the fitting of the apparent constants.

In order to take into account both supramolecular and colloidal terms, we turn to the development of the theoretical models focused on the evaluation of the standard chemical potential of a spherical reverse micelle [1]. Once the standard chemical potential of reverse micelle is known, all the thermodynamic quantities of the system can be evaluated (*e.g.* the apparent constants are now calculated, not fitted parameters). Moreover, the prediction of the extraction efficiency on an industrial scale is straightforward (scale-up potential). To calculate the standard chemical potential of reverse micelle and the specific properties of extraction systems (aqueous phase is an acidic brine in industrial processes and a solvent phase is w/o microemulsion in a Winsor II regime) we consider different contributions the overall free energy, namely organometallic complexation energy as a leading term, a highly bent extractant film formation for the case of the mixture of extractants, entropic as well enthalpic effects associated with mixing of a charged and uncharged extractant (HDHEP and DMDOHEMA) in a film, differences of ion concentrations and water activities between the aqueous and solvent phases, and a weak self-assembly of extractant molecules in common solvents

We will show the strengths as well as the weaknesses of this approach, which requires four parameters per solute-extractant extraction pair (instead of 20-30 fitted apparent constants). All the parameters represent molecular quantities and can be measured to some extent. With this kind of modelling, we were able to quantitatively predict the increase of micellization upon the addition of metal ions in the system (a decrease critical aggregate concentration), the determination of optimal bulk pH, which is crucial for the usage of acids upon leaching and later boosting the extraction efficiency. In addition, we wish to emphasize that the stoichiometry is in fact not constant and is dependent on the initial composition of the system in terms of extractant, ion, and acid concentrations. The model also allows us to gain insights into forces that drive the extraction, particularly the opposing complexation and self-assembly at the one end and the extractant head- groups repulsions and transfer of ion between phases on the other hand [2].

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*Dedicated to the memory of Helmuth Möhwald, who passed away in March 2018.

Ivan B. Ivanov: Remarkable figure in colloid and interface science*

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Ivan B. Ivanov was a remarkable scientist working in the field of colloid and interface science with basic contributions to physicochemical hydrodynamics and thermodynamics of thin liquid films and fluid disperse systems – foams, emulsions and suspensions [1-3]. His most important contributions are related to the theoretical description and experimental investigation of the mass transport processes that govern the thinning of liquid films and interactions of bubbles in foams and drops in emulsions in the presence of surfactants. He developed the quantitative theory of the critical thickness of film rupture by fluctuation capillary waves, which grow spontaneously driven by the van der Waals attraction; see Ref. [1]. Other important problem investigated by I.B. Ivanov, was the effect of surfactants on the rate of drainage of liquid films. The hydrodynamic flow drives the adsorbed surfactant molecules away from the film center, whereas the gradient of adsorption (the Marangoni effect) and the surface diffusion tend to restore the equilibrium and thus oppose the film drainage. Quantitative agreement with the experimental results on film drainage was achieved. The calculations predicted that the planar film between two emulsion drops should drain much faster when the surfactant is dissolved in the drop phase, in comparison with the case when the surfactant is in the outer (continuous) phase, Figure 1. Thus, a hydrodynamic explanation was given to the empirical Bancroft rule, which states that “the phase in which an emulsifier is more soluble constitutes the continuous phase”. Together with the group of Darsh Wasan, Ivanov investigated the phenomenon “stratification”, i.e. stepwise thinning of liquid films formed from surfactant solution. It was revealed that this phenomenon is due to the structuring of spherical surfactant micelles or other colloidal spheres (oscillatory structural forces), rather than to the formation of liquid crystals inside the film [4]. Other of his important contributions are in the fields of capillary forces between particles in liquid films; charge of emulsion drops; properties of protein stabilized emulsions and Pickering emulsions [5], and on the origin of dilatational surface viscosity [6].

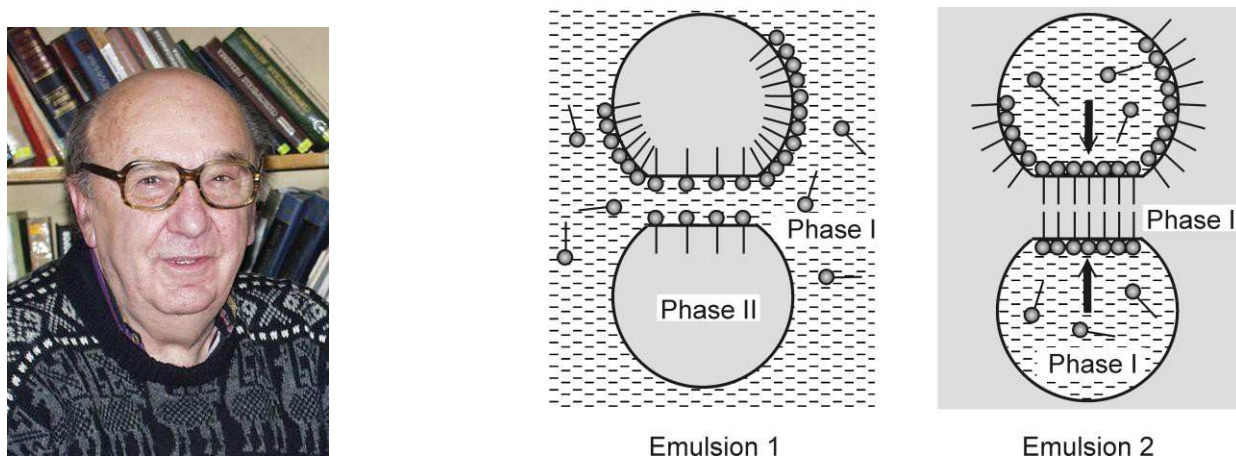


Figure 1. Ivan B. Ivanov and a sketch of his hydrodynamic explanation of Bancroft rule.

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Templated Synthesis of Complex Colloids using Liquid Crystallinity

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Liquid crystals (LC), when confined on the micrometer-scale, exhibit a rich range of internal configurations that reflect energetic contributions arising from surface interactions, elastic strain and topological defects. We are exploring these diverse LC configurations as templates to provide the basis of general and facile methodologies for the templated synthesis of spherical and non-spherical polymeric microparticles with complex internal structure and porosity. This presentation will address two advances related to these microparticles.

First, we have prepared nematic microdroplets of reactive/non-reactive mesogens with distinct internal configurations using a range of approaches, photo-polymerized the reactive mesogen 4-(3-acryloyoxypropyloxy) benzoic acid 2-methyl-1,4-phenylene ester (RM257) within the LC droplets, and then extracted the non-reactive mesogens to yield polymeric particles. We found that LC droplets exhibiting bipolar, radial, axial or preradial configurations template the formation of spindle-shaped, spherical, spherocylindrical or tear-shaped polymeric microparticles, respectively. Each type of microparticle exhibited distinct optical signatures indicating the presence of an internal LC-templated, polymer network.

Second, we have shown that it is possible to program van der Waals interactions with complex symmetries into these colloids that, in turn, direct their heterocoagulation. For example, van der Waal interactions encoded by polymeric microparticles (diameters of 20-80 μm) prepared from LC droplets with bipolar symmetries are observed to undergo coagulation preferentially with small probe colloids (diameter of 1 μm) in the equatorial region relative to the two polar regions. In contrast, uniform probe colloid distributions are measured on the surfaces of polymeric LC particles prepared with an internal configuration that is radially symmetric. These experimental observations and others (e.g., obtained using polymeric particles prepared from preradial LC droplet configurations), when interpreted in the context of kinetic theories of colloidal aggregation, are consistent with the presence of uniform electrical double layer repulsions and non-uniform van der Waals attractions encoded by the anisotropic optical properties of the LC particles. Overall, these results suggest that LC-templated colloids provide fresh opportunities to direct colloidal assembly processes by encoding van der Waals interactions with complex symmetries.

High-resolution simulations in the design of complex fluid interfaces and graphene nanohydrodynamics

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The ability to design multiphase dispersed material systems requires an understanding of hydrodynamic processes that occur at the scale of a single colloidal particle, but that are also influenced by multibody effects involving millions of particles and fluid dynamics scales that are orders of magnitude larger than the particle size. The study of these processes require high-resolution simulation tools that are fast, accurate, and address a range of time and length scale not currently within reach of all-atom simulation methods such as molecular dynamics.

In this talk I will illustrate research in my group by presenting two topics that attempt to address the above challenges. The first topic deals with the development of FIPI, a fast simulation method that we have recently developed. The method allows one to simulate the dynamics of adsorption/desorption of a large number of colloidal particles from fluid interfaces, and the change in interface morphology following adsorption for general interparticle force models. Simulations with up to $\sim 10^5$ particles are feasible with a common desktop computer, providing a tool to explore interesting physics at very moderate computational cost. We have used FIPI to simulate the effect of solid particles on the shape of a pendant drop [1], the transition from buckling to desorption when a particle-covered drop is compressed [2], and working towards applications to clean air technologies.

The second topic deals with the dynamics of sheared dispersions of flexible graphene nanoplatelets suspended in liquids. We are developing a comprehensive investigation of the deformation and exfoliation dynamics of these emerging colloidal systems, combining high-resolution continuum simulations with molecular dynamics. The implications of the work are in the optimisation of liquid-phase exfoliation processes to produce 2D nanomaterials on industrial scale, and the understanding of the flow microphysics in suspensions of graphene materials for applications to printing, coating and fiber drawing.

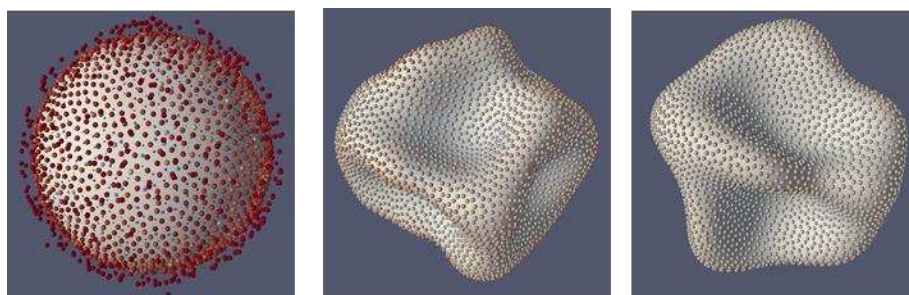


Figure 1. FIPI simulation of a particle-covered drop: change in particle distribution and interface morphology from desorption to buckling as the particle-interface adhesion strength increases (from left to right) for a fixed surface pressure.

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Extraction of Water from Detergent Stabilized Oil-Water Emulsion

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Separation of oil and water from an emulsion is an area of increasing interest because of the ever-increasing emphasis on reducing discharge of oily wastewater streams and for managing accidental oil spills. While several methods to separate oil from water are available, extraction of organic free water at a level or less than the EPA recommendation (<15 ppm) from strongly detergent stabilized emulsions remains challenging. We have been developing methods to extract organic free water from aqueous emulsion by integrating the following two different steps. First method is the conventional eletro-sweeping, but in which a modified electrolysis system is developed to remove oil droplets from an emulsion via charge complexation. The second method uses surface modified metal particles that also complexes with the emulsion droplets. A combination of the above two methods in in conjunction with a polyelectrolyte produces highly pure water as evidenced by UV-Vis spectroscopy, Surface tension measurement and total carbon analysis. The final organic contamination in water was significantly less than 15 ppm.

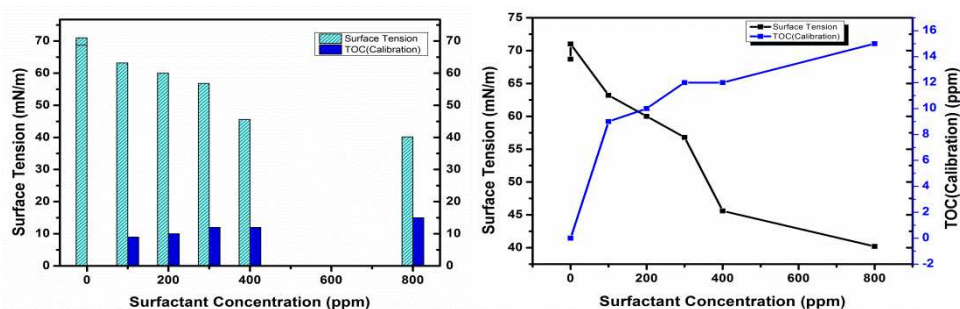


Figure 1. Properties of pure water evidenced by spectroscopic and surface tension analysis

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Recent Advances in Understanding the Molecular Basis of Selectivity in Multimodal Protein Separation Systems

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This presentation will discuss recent advances in understand the molecular bases of selectivity in multimodal protein separation systems. Targeted experiments with different domains of mAbs with varying properties, biophysics, thermodynamics and molecular simulations will be used to shed light on the importance of protein surface cluster properties and multimodal ligand hydration and flexibility on creating selective separations. Hierarchical clustering will be employed to examine preferred ligand conformations and the impact of water and dewetting phenomena for ligands in solution, adsorbed to proteins and immobilized on SAM surfaces. NMR will be used to examine the molecular basis for multimodal ligand binding to the FC region of mAbs both in solution and immobilized on SAM surfaces and the results will be compared to molecular dynamic simulations. Finally, pH and ligand chemistry will be employed to shift domain dominance in mAb multimodal chromatography from (Fab)₂ interactions to Fc binding. The implications of this selectivity for creating integrated downstream purification of biological products will also be discussed.

High-Resolution Temporal and Spatial Organization of Soft Nanostructured Materials by Cryo-Electron Microscopy and Cryo-Electron Tomography

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Self-assembly is a ubiquitous process of soft matter, relating to spontaneous and controlled formation of a wide variety of complex nanostructures by non-covalent interactions. Understanding the precise 3D structure of particles and phases, combined with temporal studies of structure formation and the conditions influencing the final state are key in modern science to revealing biological functions (e.g. of proteins) and utilizing natural and synthetic structures in colloid science, nanotechnology, nanomedicine and more.

We will present two methods: The first, cryo-transmission electron microscopy (cryo-TEM), is an established method for analysing the nanostructure of self-assembled materials at their hydrated state [1-3]. The second, cryo-electron tomography (cryo-ET) is an innovative extension of cryo-TEM, which allows the creation of the three-dimensional (3D) structure from a series of 2D projections. The combination of the two methods is very powerful and enables to reveal for the first time the precise spatial organization of many soft colloids systems such as of wormlike micelles and their networks in solution, and, to directly analyze at bulk conditions nano-scale interactions for example of nanoparticles with lipid membranes. Several examples will be demonstrated.

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Novel nano domains as multi purpose delivery vehicles for bioactives

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In recent years a very significant effort is made to discover and prepare novel nano delivery vehicles for insoluble drugs, large molecular bioactive and chemically sensitive pharmaceuticals.

The novel nanostructures have to be versatile, based on FDA permitted ingredients, fully dilutable in aqueous medium and easy to prepare.

The number of generic bioactive with very limited bioavailability and poor performance is very large.

Many novel formulations are proposed by R&D centers of pharma companies and by scientists, yet only few are crossing the Phase iii FDA requirements on safety and performance.

We will report in this presentation novel modified liquid nano domains that have most of the required requirements and demonstrate enhanced bioavailability for few selected drugs used in four different applications.

The results of these studies was the establishment of successful startup showing promise to variety of generic and innovative pharmaceuticals.

One such example will be the CBD extracted from cannabis.

Pickering emulsions for catalysis

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The hydroformylation of long chain like dodecene is a demanded type of reaction for catalytically activated reactions. The challenge is that the catalyst (Rhodium, Rh) is expensive and has to be recovered after the reaction. For this purpose a two-phase system is proposed with the educt (dodecene) and the product (tridecanal) presenting the oil phase and the catalyst in the aqueous phase.

Surfactant stabilized emulsions are one example for two phases systems. They show a quite impressing high reaction yield. Often there are problems in the following separation step in membranes. The emulsion droplets might become unstable and/or the surfactant can adsorb at the membrane material which leads to a rupture of the emulsion. In addition, surfactant stabilized emulsions are much more sensitive to external parameters like temperature and composition of the system which might change during the reaction. Emulsions which are stabilized with particles, so-called Pickering emulsions, have the advantage that the droplets are mechanically much more stable and robust against changes of external parameters, since the detachment energy of the particles is much higher (up to several 10000 kT) than in case of surfactants (several kT). In this context Pickering emulsions are more suitable for separation processes than surfactant stabilized emulsions.

In terms of reaction yield Pickering emulsions give often a low performance, which is assumed to be caused by low accessibility of the catalyst. The challenge is to increase the yield. Here, physico-chemical fundamental research comes into play. The presentation addresses the relation between the structure, the catalytic performance and the ability for cat-separation of the Pickering emulsion afterwards. Especially, the effect of particle concentration, particle size and shape as well as particle charge are addressed. Examples are Silica particles, halloysite nanotubes (HNT) and polymer particles. HNTs are multiwall, inorganic tubes with negative charges at the outer surface and positive charges at the inner surface. The length of the HNTs in this study is 800 ± 200 nm and the outer diameter is 50 nm. HNTs adsorb laterally at the water/oil interface. Due to the anisotropy of the HNT, the behavior of the nanotubes at the interface is different from spherical particles and the stability of the respective PE is higher which is studied in detail. The HNT surface is modified by a positively charged coating which shows a strong increase in reaction yield.

As an outlook we will speculate about stimuli sensitive particles as stabilizers, in order to trigger the catalytic activity.

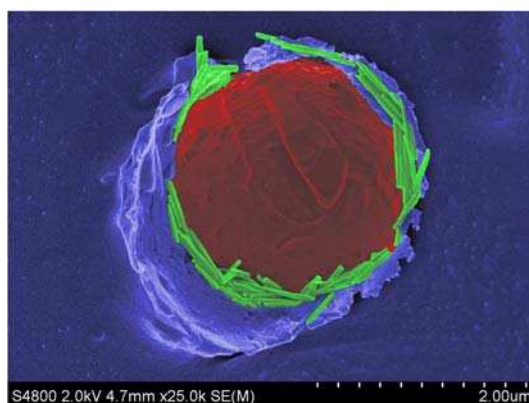


Figure 1. Dodecene in water droplet stabilized by HNTs, Cryo-SEM image [1].

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Aqueous Dispersion of Hydrophobic Pigments at High Solids Concentrations

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We demonstrate the synthesis of hydrophobic pigments that are dispersable in water at high solids concentrations, and that retain their hydrophobicity after drying. We begin by describing the hydrophobic modification of 280 nm Ti-Pure R706 paint pigment, using trimethylsilylchloride as well as other alkyldimethylsilanes, and the aqueous dispersion of these hydrophobically modified paint pigments with conventional polyanion dispersants. Despite the presence of the organosilane capping groups, we observe the same adsorption of the polyanion as in the hydrophilic, native-oxide pigments, leading to the same zeta potentials for polyanion-containing pigments, whether or not they have been hydrophobically modified. When dried, capillary rise and water-uptake measurements of both the hydrophobically modified pigment particles as well as the composite particles with polyanion dispersant demonstrate hydrophobic materials.¹

Next, building on the demonstration above of aqueous-dispersible hydrophobic pigments that retain their surface hydrophobicity after drying, we demonstrate the synthesis of surface modified R706 pigments, consisting of a thin (1 – 3 monolayers) grafted poly-methylhydrosiloxane (PMHS) coating, which (i) are hydrophobic in the dry state according to capillary rise and dynamic vapor sorption measurements and (ii) form stable aqueous dispersions at solid contents exceeding 75 wt. % (43 vol. %), without added dispersant, displaying similar rheology as R706 native-oxide pigments at 70 wt. % (37 vol. %) consisting of an optimal amount of conventional polyanionic dispersant (0.3 wt% on pigment basis).² These surface-modified pigments have been characterized via ²⁹Si and ¹³C CP/MAS solid-state NMR spectroscopy, infrared spectroscopy, thermogravimetric and elemental analysis, and zeta-potential measurements. Based on these data, the stability of the surface modified PMHS-R706 aqueous dispersions is attributed to steric effects, as a result of grafted PMHS strands on the R-706 surface, and depends on the chaotropic nature of the base used during PMHS condensation to the pigment/polysiloxane interface. The lack of water wettability of the surface-modified oxide particles in their dry state translates to significantly improved water-barrier properties in coatings produced with these surface-modified pigment particles.

Acknowledgements: This work was funded by The Dow Chemical Company.

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- [2] Y. Guo, M.K. Mishra, F. Wang, J. Jankolovits, A. Kusoglu, A.Z. Weber, A. Van Dyk, K. Beshah, J.C. Bohling, J.A. Roper III, C.J. Radke, *Langmuir*, 2018, DOI: 10.1021/acs.langmuir.8b01898.

Nature-Inspired Elastic Capsules, Tubes and Hairy Surfaces

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Natural structures such as eggs, embryos, plant seeds, vegetables like the onion, and body parts like the spinal disc, all have multiple concentric layers surrounding a central core. Each layer typically has a unique composition and thereby a distinct function. The synthesis (morphogenesis) of these structures in nature typically proceeds in an “inside-out” fashion, where a core is formed initially, followed by a first shell and then additional shells.

Taking inspiration from the above, we have developed an inside-out technique to synthesize a range of soft materials. First, we have created “onion-like” polymeric capsules with multiple concentric shells surrounding a gelled core [1]. Each polymer shell is formed by free-radical polymerization. A given shell grows outward from the surface of the previous shell; thus, the shell thickness steadily increases with time and can be controlled. Using this technique, we can juxtapose widely different polymers next to each other in a capsule, as shown, for example, in Figure 1. The resulting capsules exhibit a range of unusual properties. One specific property to highlight is the ability of capsules to rapidly swell due to gas evolved from a reaction in the core; such swelling can be violent enough to eject the core.

Multilayered structures in nature also exist in other geometries. Our blood vessels are examples of multilayered tubes, while many tissues in our body have outer layers of hairs called villi and microvilli. We have extended our inside-out technique to cylindrical and planar geometries to create polymeric multilayered tubes and hairy surfaces. The multilayered tubes exhibit spontaneous changes in tube diameter in response to the properties of the flowing liquid, which is reminiscent of blood vessels. The hairy surfaces absorb solutes much more efficiently than a bare surface, akin to the villi-covered surfaces of the gastrointestinal tract.

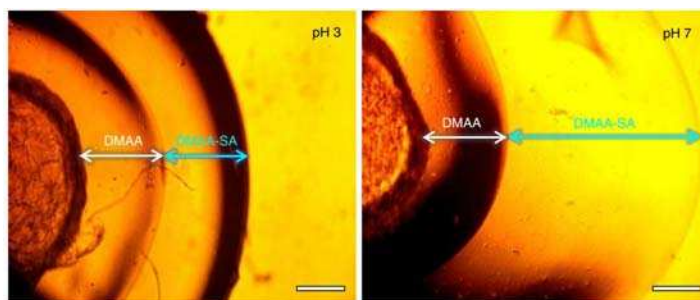


Figure 1. Multilayer capsule with one layer responsive to pH

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STRIPS BIJELs for Modern Engineering in Colloidal Science

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BIJELs, *bicontinuous jammed emulsion gel* structures, are potentially transformative vehicles for modern engineering in colloidal science. BIJELs are made by quenching a miscible oil-water solution through its critical point to drive spinodal phase separation, and stabilizing the bicontinuous channels by a jammed layer of interfacially trapped nanoparticles to form water-continuous and oil-continuous channels in contact across the nanoparticle laden interface. These structures, first discovered more than a decade ago,^{1,2} have tremendous potential in application in fields of practical importance ranging from nanoparticle decorated separation membranes to systems for continuous reactive separations. These fields, associated with the chemical processing industries, require continuous means of fabrication of structures, and fabrication of structures that are sufficiently robust to withstand processing conditions.

We have been developing methods to address these needs. We have developed the Solvent Transfer Induced Phase Separation (STRIPS) process for continuous formation of BIJELs from a ternary system of oil-water-co-solvent. STRIPS BIJELs can be made continuously in a number of configurations, including particles, fibers, planar membranes³ and core-shell configurations.⁴ By using monomer as the oil phase, and subsequently cross linking, polymeric membranes with surfaces densely decorated with nanoparticles can be formed for exploitation in separations. By keeping both phases in fluid form, STRIPS BIJELs can be used for reactive separations. The concept here is that reactions occurring in one of the bulk phases or at the nanoparticle-laden interface form a product soluble in the other bulk phase. Interface transport allows the product to be removed, allowing the system to remain far from equilibrium and promoting further reaction via Le Chatelier's principle. However, as formed, BIJELs can be too fragile and sensitive to changes in solution conditions for use in practical settings. We have developed strategies to strengthen them while retaining their important attributes, including interphase transport, by chemically fusing the nanoparticles. Application of these STRIPS BIJEL materials in ultrafiltration as well as reactive separations will be presented.

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Novel colloidal materials made by interfacial templating and “capillary engineering” of multiphasic liquid systems

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We will discuss the principles and applications of a rich variety of colloidal structures and materials made from multiphasic liquid-liquid-polymer systems. The capillary forces originating at the liquid/liquid interfaces can serve for reconfigurable binding in numerous soft matter systems, including Pickering emulsions, novel responsive capillary gels, and compositions for 3D printing. Alternatively, the liquid/liquid interfaces can also template the formation of a variety of polymer nanomaterials, including nanoparticles, nanofibers, nanoribbons, microrods and microsheets. Both approaches present numerous opportunities for engineering of novel colloidal structures.

We will first present responsive structures made of filaments from magnetic nanoparticles suspended in water-oil systems [1]. The condensed, surface-anchored, lipid shells around the nanoparticles form nanocapillary liquid bridges on contact. The nanocapillary binding results in ultra-high filament flexibility. Similar principles can be used in the assembly of Janus and patchy particles [2] and in the making of self-repairing magnetic gels made of water, polydimethylsiloxane (PDMS) beads, and magnetic nanoparticles. As an example of the application of such structures, we will discuss the development of new 3D printing inks consisting of water, crosslinked PDMS microbeads and liquid PDMS phase. Owing to the capillary binding of the microbeads, suspensions containing certain fractions of liquid silicone precursor behave like pastes, which are flowable at high shear stress but possess the yield stress needed for direct ink writing. The Homocomposite Thixotropic Pastes (HTPs) can be directly extruded and shaped on a 3D printer [3]. The thermal curing of the PDMS bridges yields remarkably elastic and flexible structures. The HTP-3DP inks are biocompatible and can be 3D printed directly as bio-scaffolds under water. They enable new opportunities for making of “active” and reconfigurable structures.

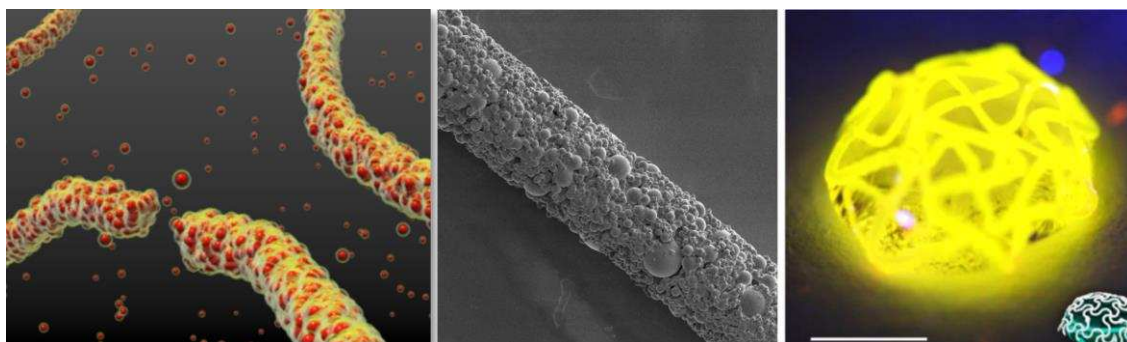


Figure 1. Examples of ultraflexible nanoparticle-liquid filaments, homocomposite 3D printing paste and 3D printed microcapsule around a “liquid marble”.

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Designer emulsions using transient double emulsions

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Generating droplets with controlled interfacial composition and coverage is an important for a wide variety of disciplines, from generating protocells with a possibly complex interfacial composition, over particle based capsules, and for generating droplets designed for fundamental studies of transport and the role of interfacial rheological properties. In the case of soluble surface active components thermodynamics lays down the rules of adsorption, but these rules bring along limitations which can sometimes be enhanced by kinetic aspects. For poorly soluble systems strong interfacial layers are made, but it is not always possible to create these layers in large scale emulsification methods. When those constraints are too stringent classical emulsification methods will not give full and independent control over interfacial composition and coverage, for example when trying to engineer the interfacial viscoelasticity using particles. Microfluidics seems an obvious alternate route, but often fails. Reasons for this can be as mundane as clogging due to problems with solubility or dispersibility and wetting.

In the present work we develop a strategy for producing liquid-liquid interfaces with controlled interfacial composition and concentration by exploiting phase equilibria and slow mixing of the suspending liquids. We will demonstrate the effectiveness of this strategy by generating individual droplets with well-controlled surface coverages and compositions for the case of particle laden droplets and studying their direct effect on droplet deformation and coalescence. The proposed method is widely applicable whenever the need for controlled surface coverage and composition for liquid-liquid interfaces are required.

We demonstrate the control over coverage and composition by creating droplets with surface coverages in a range of 0.20 to 0.90, creating droplets just below maximum coverage and making them undergo arrested coalescence and certain composite droplets or droplets with designer viscoelastic properties, which enable us to perform fundamental studies on the role of interfacial rheology on morphological processes. A general method based on local force balances will be discussed.

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Using water-poor microemulsions and pre-ouzo droplets as selective carriers for solutes

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Hydrometallurgy, the technology used for refining and separating metals from leaching ores to recycling electrical wastes, is based on driving back and forth salts from a water phase to a solvent-phase. This solvent phase contains surface active extractant amphiphile, a “diluent” that is usually a mixture of solvents as well as some water.

In biotechnologies, when it comes to selective extraction of lipids to be separated from proteins, ternary solutions are used. Hydroptropes are used for efficient extraction of all kinds of organic molecules with a high efficiency, in solvent assisted alcoholic extraction [1].

We will illustrate the analogies in micro-structures helping for extraction and give a tentative list of combined mechanisms responsible for solute extraction/stripping equilibria, as shown for the case of rare earths in the graph below.

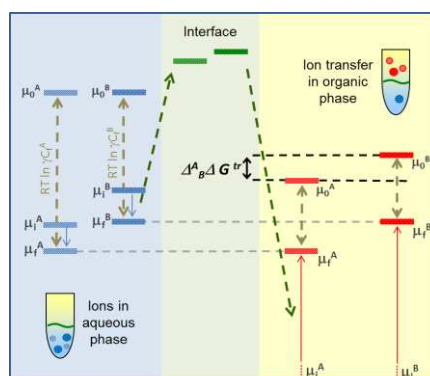


Figure 1. Analysis in terms of chemical potentials of electrolytes in an aqueous phase (in blue), in a water-poor microemulsion called the “solvent phase”. A and B refer to the two electrolytes to be separated, for example are earth and iron nitrates. The reference state has index 0. i and f refer to initial and final state. $\Delta\Delta G^{\text{tr}}$ is the selectivity to be optimized for efficient purification in a real process. The green region corresponds to the interface or interphase at the origin of kinetic retardation in practice.

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