

BOOK OF ABSTRACTS
POSTER PRESENTATIONS

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EP1.1

Decoration of plastic substrates with gold nanostructures

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The controlled deposition of metal nanostructures on disposable plastic surfaces is a big challenge in different fields, as the production of optoelectronic devices and the development of solid phases for biomedical or analytical applications [1]. In the last decades, several approaches for the decoration of disposable devices with metal nanostructures were proposed. Apart from physical methods (i.e., sputtering, vapor deposition, etc.) which are suitable for flat surfaces or, in more general, accessible substrates, the use of ligands or polymers for the binding or in-situ formation of metal nanoparticles directly on surfaces with different geometries has been reported [2-3]. For the best of our knowledge, there are no approaches for the decoration of bare plastic using already synthesized metal nanostructures.

Here, we propose the decoration of plastic substrates with metal nanostructures using an easy, maskless and industrial compatible method. Different commercial plastics (polystyrene, PS, polyethylene low density, PE-LD, polyethylene high density, PE-HD and styrene-butadiene block copolymer, SBC) were successfully decorated with citrate-capped Au nanoparticles and polyvinylpyrrolidone-capped Au nanorods. The entire process, in both cases, can be triggered and tuned by the presence of a poor solvent obtaining a controlled deposition of the metal nanostructures on the plastic surfaces. The approach was optimized in terms of incubation time and temperature, and starting concentration for the metal nanostructures dispersion thus obtaining morphologies with different degree of organization and coverage. All the prepared substrates were characterized by scanning electron microscopy and the obtained patterns were correlated with the synthesis' parameters. We believe that the principle behind this approach could be expanded to other metal nanostructures obtaining a fast and simple method for the decoration and valorization of bare plastics.

Keywords: gold nanostructures, plastic decoration, controlled deposition

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EP1.2

Diffusion of Patchy Nanoparticles

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Patchy nanoparticles (PN) are complex structures that are ubiquitous in different synthetic and biologically occurring systems, such as grafted nanoparticles, organelles, and viruses. Due to the morphological features of PN they can be characterized according to their translational (\overline{D}_t) and rotational (\overline{D}_r) diffusivity. Computationally, the rigid multi-blob (RMB) methodology [1] can be exploited to study and characterize various nanoparticle morphologies. Here, we use RMB to model patchy nanoparticles, and construct them by discretizing the structures as a set of rigidly connected spherical beads. The core of the nanoparticles is represented as a spherical shell of multiple blobs, and the effect of different patch morphologies is investigated using various patch shapes such as rods, mushrooms and tetrahedra. Our results reveal that the rotational diffusion of the NP provides a characteristic fingerprint of the patch morphology. Furthermore, we investigate the effect of patch arrangement adopting both uniform and random patch distributions. In general randomness in the patch distribution decreases the hydrodynamic drag of the particles facilitating their transport. However, as the density of patches increases, both the translational and rotational diffusivity stabilize and become independent of the patch distribution. The hydrodynamic radius of the different NP models is also computed and compared available experimental data for synthetic nanoparticles evidencing a satisfactory approximation of the RMB methodology adopted.

Keywords: multi-blob, patchy nanoparticles, rotational diffusivity, translational diffusivity

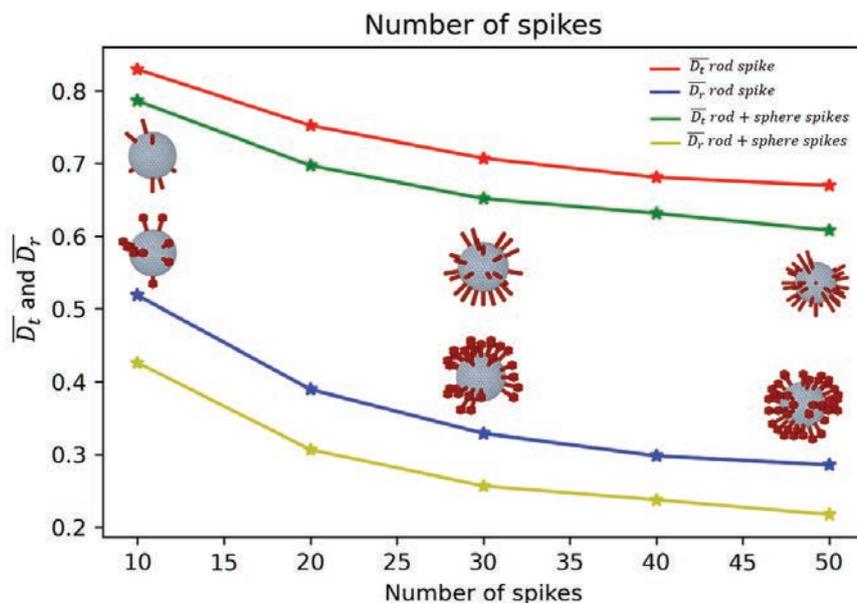


Figure 1. Effect of patch morphology on the overall translation and rotational diffusion of patchy nanoparticles.

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EP1.3

Delineating the origin of primary and secondary cracks in the deposit of colloidal ellipsoids

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Desiccation cracks are often observed in nature, such as on dried river beds, ancient paintings, and colloidal films. The formation of cracks facilitates the release of stress energy that accumulates in a drying particulate film. The origin of the stress-energy is attributed to the differential shrinkage of the particulate film due to the competition between the capillary forces and the constraint offered by the substrate. [1-2]

Here we investigate the formation of primary and secondary cracks in the coffee ring-shaped dried deposits obtained by evaporating sessile drops containing hematite ellipsoids, as shown schematically in Figure 1. Two distinct types of cracks form in the deposit, one along the circumferential direction (primary cracks) and the other along the radial direction (secondary crack). The primary cracks always nucleate at the top surface of the deposit and then propagate into the interior of the particulate deposit. In contrast, the secondary cracks always nucleate at the bottom surface of the deposit, which is in contact with the solid substrate. We also discuss methods to completely suppress the formation of secondary cracks by varying the aspect ratio of ellipsoids and adding a small fraction of spherical particles to ellipsoids. We also observe the formation of surface wrinkles on the drying particulate deposit. These wrinkles, which are regions of high-stress, showed a one-to-one spatial correspondence with the morphology of secondary cracks.

Keywords: Desiccation cracks, shape anisotropic colloids, drying induced self-assembly, coffee-ring effect, particulate film.

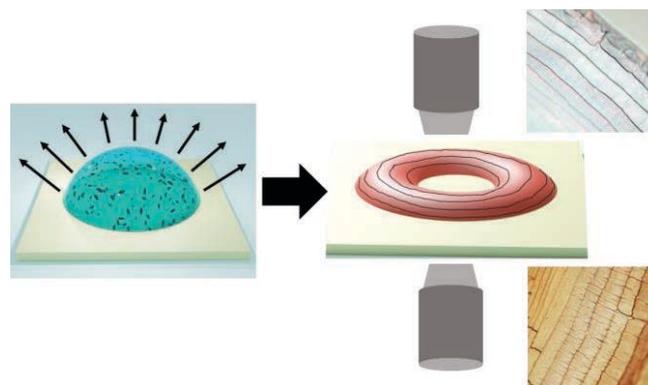


Figure 1. Evaporating sessile drop resulting in a coffee-ring like deposit accompanying cracks. Different imaging modes show only primary crack and secondary cracks in the ring-like deposit.

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EP1.4

Multi-walled carbon nanotubes supported by copper(II) oxide nanoparticles in the construction of ion-selective electrodes

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In recent years, all kinds of nanomaterials and nanoparticles have become very popular among scientists. Due to their unique properties, compared to conventional macro-sized materials, they have many applications in photovoltaics, electronics, optoelectronics, sensing and biosensing [1]. In potentiometry, they are used for the construction of ion-selective electrodes with solid contact as transducers enabling the transfer of charge between an electron-conductive solid electrode and an ion-conductive ion-selective membrane [2]. Nanomaterials can be successfully used for this purpose thanks to their high charge transfer, electrical capacities and also high surface to volume ratio [3].

Ion-selective electrodes are popular sensors used in potentiometry due to the relative simplicity of implementation and use as well as low equipment costs. The elimination of the internal solution allowed the miniaturization and shape change of them, improved the mechanical resistance and facilitated transport and storage [4]. The additional modification with nanomaterials allows for the improvement of analytical parameters of the sensors, including the stability and reversibility of the electrode potential, shortening the response time and often extending their life time.

The research of ion-selective electrodes sensitive to copper(II) ions, in which copper(II) oxide nanoparticles and multi-walled carbon nanotubes were used as an intermediate layer between the membrane and the inner electrode and as a component of the membrane were described. The obtained sensors were characterized by estimating the basic analytical parameters using potentiometric methods (slope, limit of detection, linearity range, potential stability and reversibility) and impedance spectroscopy (membrane resistance and low frequency capacitance). It was found that the simultaneous addition of copper(II) oxide nanoparticles and multi-walled carbon nanotubes to the membrane mixture most effectively lowers the membrane resistance and increases the low-frequency capacitance. As a result, the parameters of the electrode are improved.

Keywords: nanoparticles, copper oxide, carbon nanotubes, potentiometry, ion-selective electrodes, impedance spectroscopy

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EP1.5

USAXS: Resolving μm -sized particles on a lab system

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The Anton Paar SAXSpoint 5.0 small-angle X-ray scattering system offers an optional Bonse-Hart USAXS module. Two pre-aligned precise channel-cut (CC) assemblies (by AXO Dresden) are mounted on a compact module (Figure 1) which is installed in the SAXSpoint 5.0 sample chamber.

The module extends the measuring range of particle sizes upto 2.6 μm . The USAXS module is automatically moved in and out of the X-ray beam enabling the automatic switch between USAXS, SAXS and WAXS measurements.

Hence, without any manual user interaction, fully automatic X-ray scattering experiments can be performed in the q -range from

- 1) ultra-high resolution ($q_{\text{min}} = 0.0012 \text{ nm}^{-1}$) in USAXS mode and
- 2) high resolution ($q_{\text{min}} = 0.01 \text{ nm}^{-1}$) in SAXS mode to a
- 3) high WAXS range ($q_{\text{max}} = 49.3 \text{ nm}^{-1}$)

Keywords: USAXS, X-ray, particle, size, Bonse-Hart

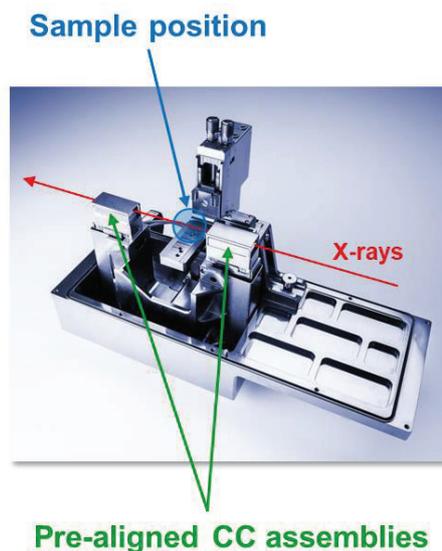


Figure 1. The Bonse-Hart USAXS module uses two pre-aligned 4-bounce channel cut (cc) assemblies

EP1.6

**The properties of calcium phosphate bioceramics
derived from different avian eggshells**

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Calcium phosphates are minerals of great importance e.g. in bioengineering, chemistry, cosmetics, agriculture, medicine, water remediation. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has attracted the greatest attention as a main constituent of human hard tissue: bones and teeth. Hence, the calcium phosphates are still in the interest of many scientists according to its safety, biocompatibility, biodegradability [1,2]. Development of new low-cost production technologies will make biomaterials widely available to those most in need.

The scope of this study was the synthesis of bioceramics composed of calcium phosphates using raw, uncalcined eggshells as a precursors of calcium ions. Eliminating calcination step reduces the energy input. Hen's, quail's, duck's and pigeon's eggshells were used. The hydrothermal synthesis at alkaline pH was carried out in two ways: using eggshells with organic membranes and ones carefully pilled off from organic inner layer. Biphasic/multiphasic bioceramics were obtained depending on the eggshells used. Nevertheless, the most stable hydroxyapatite predominated in each material. The presence of organic membranes apparently influenced the composition of the materials obtained from hen's and pigeon's eggshells, while in the case of quail's and duck's eggs the effect was insignificant.

Keywords: calcium phosphates, eggshells, bioceramics

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EP1.7

Influence of pH on the formation and structure of two-antennary oligoglycines in aqueous solutions

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In the last decades plenty of different strategies for targeted drug delivery were elaborated and tested and the interest in this area continues to grow up to nowadays. It turned out that one of the most important features of the tested systems should be their degree of biocompatibility.

In the present study aqueous solutions of a relatively new class of biocompatible structures called tectomers are investigated [1]. They are synthesized as a result of preliminary molecular design. Each oligoglycine molecule consists of a core from alkyl portion with different number of carbon atoms and two oligoglycine antennae attached to both ends of the core chain. These molecules exhibit amphiphilic properties in aqueous solutions and one can alter their hydrophilic/hydrophobic balance by changing the number of C-atoms in the core and the length of the antennae.

Once dissolved in water the oligoglycines form a variety of self-assembled aggregates of various shapes and structure, depending on the conditions of their preparation and the final pH value of the system [2, 3]. The presence of amino groups at both ends of oligoglycine molecules, and several polar amide bonds in the side chains, which can be involved in formation of hydrogen bonds predetermine the pH sensitivity of the aggregates formed in aqueous solution. In addition, the presence of ethanol traces, as well as temperature changes on these nanostructures also affect the formed tectomers.

The obtained experimental results from several complementary physico-chemical techniques in the pH range 2-7 are presented and discussed. The significant differences in the size, the form and the stability of the tectomer complexes as a function of pH are promising features for controlled encapsulation and transportation of slightly soluble medicines in the human body and other potential applications in the fields of medicine, pharmacy, and environment protection.

Keywords: amino acids; bola-amphiphiles; hydrogen bonding; oligopeptides; tectomers

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EP1.8

Effect of pH-regulation on the capture of lipopolysaccharides from E. coli HB101 by four-antennary oligoglycines in aqueous medium

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Four-antennary oligoglycine molecule is composed of four hydrophilic oligoglycine antennae (Gly₇), linked to a central carbon atom. In aqueous media supramolecular species (tectomers) are built spontaneously based on the network of intra- and intermolecular hydrogen bonds (Polyglycin II). In previous studies it was demonstrated that such nano-sized aggregates could be used as registration and capturing agents for toxic bacterial lipopolysaccharides even in trace concentrations of the latter (0.1-0.5 µg/l) [1,2]. As each antenna of the oligoglycin molecules is terminated by an amino group, they are prone to be affected by changes in the pH-value of the aqueous medium. This allows the onset of variations in the supramolecular self-assembly, which influence their interactions to lipopolysaccharides.

The purpose of the current work is to study the effect of pH on the zeta potential, the dimensions and the surface properties (at watersolution/air boundary) of aqueous systems containing four-antennary oligoglycine, lipopolysaccharide and their mixtures. The research methodology includes Dynamic light scattering (DLS), Transmission electron microscopy (TEM), Profile analysis tensiometry (PAT) and Thin liquid film technique. Essential information is extracted regarding the most favourable pH range in view of most efficient capture of the bacterial endotoxins.

Keywords: Lipopolysaccharides, Oligoglycine, Tectomers, Surface tension, Surface dilational rheology, Microscopic foam films

Acknowledgement: The present investigation is financially supported by Bulgarian National Fund for Scientific Research through Project “Design and Characterization of Soft Nanostructured Materials Based on Antennary Oligoglycines”, № KII-06-H39/5.

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EP1.9

Electrokinetic properties of vitreous mesoporous membranes doped with silver iodide

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The interest in glasses doped with silver compounds in the nanoscale state is due to the possibility of their application in nanobiotechnology, sensorics, and photonics. The aim of this research was to study and compare the structural and electrokinetic parameters of silica porous membranes and membranes doped with silver iodide in 10^{-4} – 10^{-1} M NaNO_3 and KNO_3 solutions.

To obtain porous glasses doped with silver iodide (8B-NT MIP-Ag and MAP-Ag), we used 8V-NT silica vitreous membranes. Microporous (8V-NT MIP, pore radii 1.5-1.6 nm) and macroporous (8V-NT MAP, pore radii 18.4-25.2 nm) disks were impregnated in an AgNO_3 aqueous solution, and then in a KI solution. X-ray fluorescence analysis has shown that MIP-Ag and MAP-Ag consist of Ag_2O - 0.27 and 0.91 wt. %, respectively. The results of the efficiency coefficients α , equal to the ratio of the specific electrical conductivities of the pore solution and bulk solution, were shown that modification of MAP matrices with silver leads to a decrease in α . The electrokinetic potential (ζ) was found by the streaming potential method. The ζ -potentials were calculated by the Helmholtz-Smoluchowski equation taking into account the surface conductivity and the electric double layers overlap. It was established that $|\zeta|$ -potentials for silver-modified MAP-Ag glasses are lower than for silica MAP glasses. It should be noted that $|\zeta|$ -potentials for MAP and MAP-Ag glasses in NaNO_3 solutions are higher than in KNO_3 .

Keywords: Porous glass, Silver iodide, Electrokinetic potential

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Interactions between dodecyl sulfate and α -tocopherol intercalated simultaneously in Mg-Al hydrotalcite interlayer

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Hydrotalcite-like compounds are often used as hosts for intercalation of anionic species. They consist of positively charged hydroxide layers and interlayers containing anions and water molecules. In suitable organic solvents, the layered structure can be swollen or even delaminated. Thereafter, restacking procedure can be used for intercalation of other species.

In our work, the Mg-Al hydrotalcite intercalated with dodecyl sulfate (HT-DS) was prepared by coprecipitation of Mg and Al nitrates under nitrogen in the presence of sodium dodecyl sulfate in aqueous solution. The product was swollen in chloroform, assisted by ultrasonic agitation. To this colloidal dispersion, α -tocopherol was added and the structure was restacked by solvent evaporation.

Powder X-ray diffraction showed a decrease in $d(003)$ basal spacing, which changed with content of α -tocopherol in the samples. The $d(003)$ basal spacing of 3.40 nm was determined for the HT-DS sample whereas values ranging from 2.90 to 3.01 nm were found for samples intercalated simultaneously with dodecyl sulfate and α -tocopherol in amounts from 0.3 to 0.9 wt.%. Molecular simulations were used to model the arrangement of the molecules in the interlayer; interaction between dodecyl sulfate aliphatic chains and hydrophobic α -tocopherol molecules can be expected.

Analogous samples with higher content of intercalated α -tocopherol were synthesized using a bottom-up approach, when the coprecipitation of Mg and Al nitrates was carried out in the presence of colloidal solution of α -tocopherol, solubilized in aqueous sodium dodecyl sulfate solution. This method led to high incorporation of α -tocopherol (up to 21.5 wt.%) in the hydrotalcite interlayer. The $d(003)$ basal spacing of the obtained products was between 3.43 and 3.63 nm, i.e., considerably larger in comparison with that of the pure HT-DS.

Keywords: hydrotalcite, layered double hydroxide, α -tocopherol intercalation, molecular interactions

Acknowledgements: The Authors thank the Ministry of Education, Youth and Sports of the Czech Republic for financial support (project ChemJets2 CZ.02.2.69/ 0.0/0.0/18_053/0016974).

In-Situ Monitoring of Hard Core-Soft Shell Particle Assembly at air-water interface

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Photonic nanostructures have great potential to further fuelling technological advancements by controlling the flow of light within the desired frequency range. Several methods have been developed to fabricate such materials at various length scales. One of the routes is colloidal assembly, which has advantages over other routes especially in terms of cost and time efficiency due to the parallel nature of its process [1-2]. Hard core-soft shell (HCSS) type hybrid particles are ideal building blocks for such materials via colloidal assembly process, for they can have a variety of properties, fine-tunable interparticle distance [3] as well as possibilities to be assembled into surprisingly complex structures despite their isotropic shape [4].

Previously, our group has investigated on 2D assembly behaviour of silica core-poly(N-isopropylacrylamide) (PNIPAM) shell particle monolayers at different interfaces [5]. Recently we have observed noticeable differences in assembly behaviour of the same type but larger micron-sized particles during the monolayer transfer from air-water interface to the substrate surface, see Figure 1. This gives more prominence to the importance of in-situ observation. With the aim of revealing microstructure formation at interfaces, structural changes during the transfer and their correlations to the particle sizes/structures, we have built an in-situ microscope and small angle light scattering set up combined with a Langmuir trough. Here we demonstrate in-situ observation of 2D colloidal crystal assembly via compression of variously sized/structured HCSS particles at air-water interface.

Keywords: Colloidal photonic crystal, hard core-soft shell particle, monolayer compression isotherm, microstructure at interface, microgel morphology

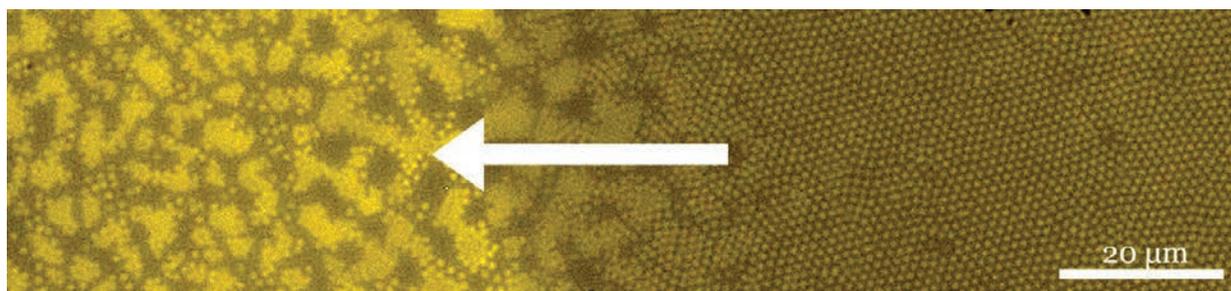


Figure 1. Monolayer at air-water interface (right side) and at water-substrate interface (left side) during drying.

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In situ formation and growth of inorganic nanoparticles in copolymer microgels

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Already for many centuries the optical properties of noble metal nanoparticles fascinate people in many different research fields. While in Middle Ages noble metal nanoparticles decorated stained glass windows in churches, today we can observe growing interest in fields such as sensing, photovoltaics and metamaterials. Coatings consisting of surfactants and polymer ligands or the introduction of nanoparticles into hydrogels further stabilize and enhance the processability of such particles. Especially the latter provides a versatile method to obtain nanoparticles with semi-transparent shells that are variable in their size and properties but also maintain excellent colloidal stability.

In literature, a common strategy to introduce nanoparticles into an microgel-network is the encapsulation by polymerization of monomers and cross-linker-molecules in presence of the nanoparticles. While providing a consistent and well understood method, encapsulation can be challenging and more complex regarding limitations of the utilized systems.

With our experiments, we want to highlight the in situ formation of nanoparticles inside microgels as a supplementary route to the encapsulation that is typically limited with respect to microgel size and monomer composition.

This work presents new findings regarding a possible mechanism (**Fig. 1a**) and influences on the in situ formation and growth of inorganic nanoparticles in pNIPAM-based copolymer microgels. For that purpose, microgels with different amounts of comonomers have been synthesized and characterized (**Fig. 1b**). As we confirm that a clever composition of the microgels is essential for a successful formation of nanoparticles within the microgels, additional experiments revealed that the formation of gold nanoparticles in these microgels happens on an ultra-short timescale and is strongly dependent on the charge present in the microgels [1]. We can control the number of formed nanoparticles in the microgels and also successfully realize a subsequent particle growth.

Keywords: Microgels, Nanoparticles, Transmission electron microscopy, Hybrid materials

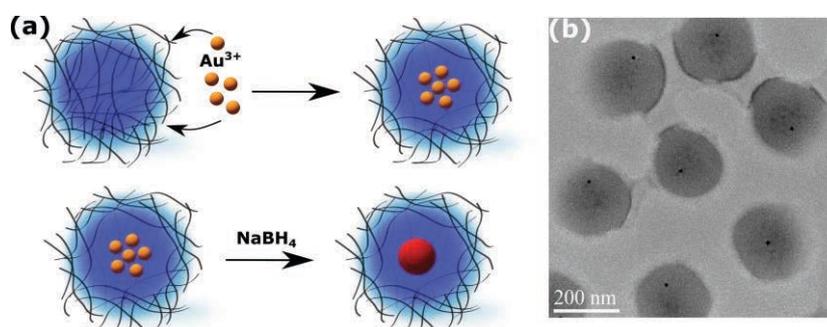


Figure 1. Simplified representation of the mechanism during the in situ formation of gold nanoparticles in copolymer microgels. The colored areas roughly visualize different compositions of the microgels with varying amounts of the comonomers (**a**). HR-TEM image of single gold nanoparticles formed after the in situ synthesis in pNIPAM-based copolymer microgels (**b**).

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EP1.13

The initial pH value impact on the properties of calcium phosphate materials derived from eggshells

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Hydroxyapatite (HA) as a major component of human hard tissue, is one of the most promising and studied materials for medical, environmental and agricultural purposes. Numerous studies proved that the obtained, biphasic calcium phosphate materials (BCP) combines the beneficial properties of both calcium phosphates- HA and β -TCP forms[1,2].

One of the most common procedures is the hydrothermal synthesis of HA using synthetic reagents, but the use of common biowaste- eggshells as a calcium donor as well as the reduction of energy input are an effective solutions due to economical and environmental aspects[1,3].

Therefore, in the presented research, the procedure was analysed with the use of raw eggshells as the calcium ions precursor at initial pH values ranging from 1.1 to 12.4. The products were analyzed by means of the SEM, XRD and FTIR techniques. At smaller pH values the DCPD and OCP phases prevail and the content of HA increases with the more alkaline environment. Applying the procedure at $pH_0 = 10.6$ (Figure 1a) allowed for obtaining the material composed of HA and β -TCP at the most desirable ratio in terms of biomedical application[1]. The analysis of calcium ion release profiles in the artificial human saliva(AHS) proves that the calcium content decreases during soaking. The products obtained at smaller pH values tend toward a higher calcium concentration which is related to the larger DCPD as well as OCP contents. Moreover, after soaking the material presents different morphology and composition characteristics(Figure 1b).

Keywords: calcium phosphates, hydroxyapatite, eggshells, bioceramics, remineralization.

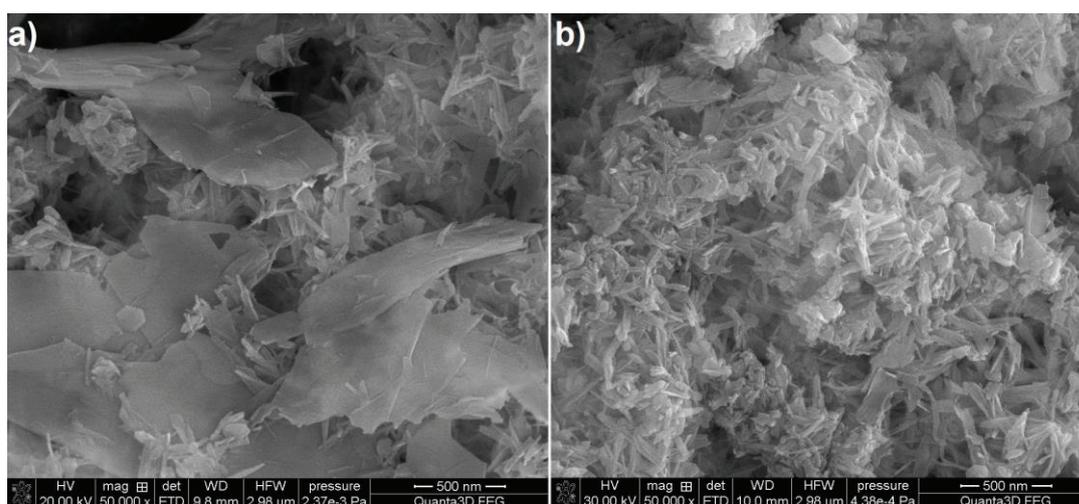


Figure 1. SEM pictures of the product obtained at $pH_0=10.6$ before (a) and after (b) soaking in AHS solution.

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**Nanostructured emulsions in water – stabilized with laponite nanoplatelets.
Study of Laponite concentration with conductance measurements**

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We show the possibility of creating a dense cover around lipid-based liquid crystalline droplets using laponite nanoplatelets as stabilizer [1]. This is an interesting route for the design of new Colloid-ISAsome assemblies in which dense protective armours could be advantageous such as controlled delivery. We used Phytantriol (PT, 3,7,11,15-tetramethylhexadecane-1,2,3-triol) as the lipid to create the nanostructured drops, and laponite colloids (radius of 12.5nm, thickness 1nm).

The investigation of the structural by means of CRYO-TEM microscopy, DLS, and SANS with contrast variation conditions have been determined [2-4].

Herein, we use ionic conductivity measurements methods (conductivity meter Five Easy™ F30 by Metler Toledo, constant cell electrode of 1.06 cm) as trigger to deduce the ratio between the free Na⁺ and the adsorbed laponite on the droplets – as Na⁺ ions are the only detectable compound with conductimetry in these systems.

Evaluating the concentration of Na⁺ ions freed by laponite, we show that the quantity of laponites adsorbed onto cubosomes are similarly at low and high concentrations (Fig.1). Work is in progress in order to gather more data and help in understanding the conditions in forming such complex and interesting smart assemblies.

Keywords: smart assemblies, nanoplatelets stabilizer, conductivity

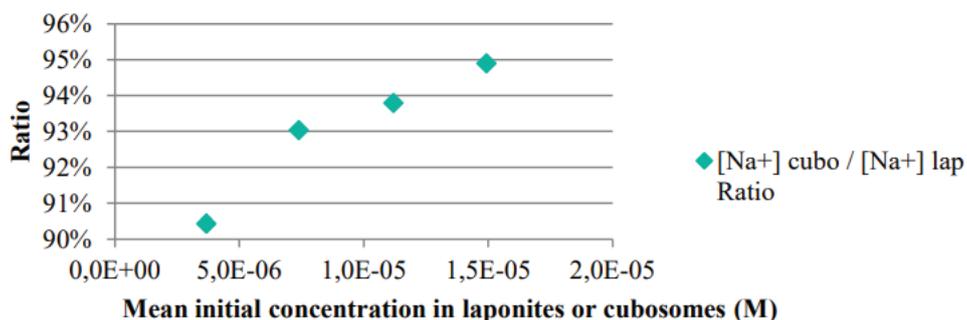


Figure 1 : Study of Ratio of [Na+] concentration versus concentration in laponites

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EP1.15

Nanoencapsulation of metal salt catalysts for polyurethane formulation

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Nowadays polyurethanes are widely used in the coating and adhesive industry. Many different technologies exist to apply coatings and adhesives on substrates and technologies in which crosslinking or adhesion could be controlled are of greatest interest. Indeed, this would offer new possibilities for complex coating/adhesive systems. For this purpose, Covestro has already developed reagents called blocked polyisocyanates; they are derivatives of isocyanates which can only be activated via thermal trigger. In a similar approach, the encapsulation and controlled release of reactive polyisocyanate or catalyst would offer new perspectives toward enhanced technologies.

Therefore, the work presented here is focusing on the nanoencapsulation of metal salt catalysts into polycaprolactone (PCL). This polymer is particularly relevant as its low melting point (60°C) offers a very easy trigger release. The encapsulation is performed via two techniques (Fig. 1) leading to different outcomes: nanoprecipitation (also referred as interfacial deposition in the literature) [1] and emulsion-solvent diffusion (ESD) [2].

This encapsulation reveals itself to be very challenging due the catalysts being ionic and water soluble to a very low extend, however, not negligible. Indeed, direct encapsulation of pure catalysts is only partially successful, as metal traces are detected in solution outside of the nanoparticles. Thus, the presence of special additives in combination with a pertinent selection of surfactants, are necessities for the successful encapsulation of such compounds.

Keywords: Nanoencapsulation; Metal salts; Polyurethane

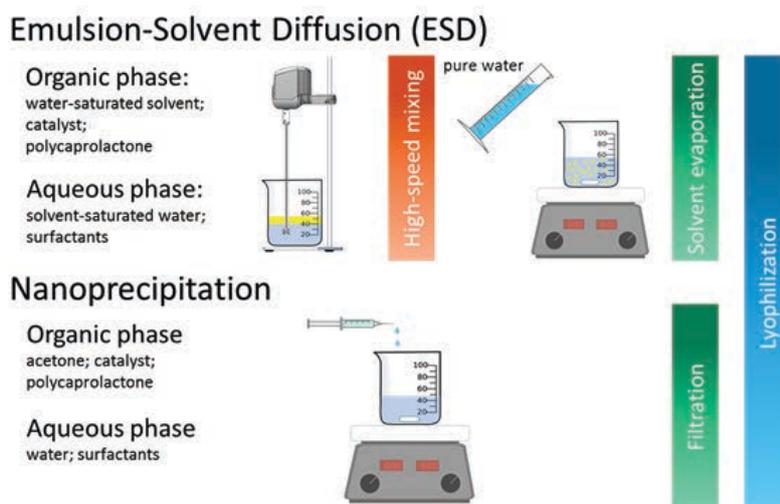


Figure 1. Nanoencapsulation techniques.

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Temperature dependent behaviour of Soft-Colloidal Crystals

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Microgels made from poly-N-isopropylacrylamide (PNIPAM) have attracted much interest in the past 20 years due to their thermoresponsive behavior and their soft nature. For higher concentrated particle dispersions, it is known that microgels tend to assemble in crystalline structures which makes them a promising model-system to investigate soft particle interactions. [1, 2] Additionally, due to their soft nature, microgels in a dense packing offer the opportunity to exceed the hard sphere limit of 0.74 in volume fraction. For ordered structures and interparticle distances slightly below the visible range of light, these 3D crystals can exhibit a sharp diffraction peak. The optical activity in the range of visible light promotes UV-Vis absorbance spectroscopy as a fast and precise method to investigate such soft colloidal crystals.

In this work we study the influence of the particles volume fraction in the dispersion and induce crystal melting or recrystallisation, by changing the temperature. The quality of the colloidal crystals can be improved by a precisely controlled annealing process with defined heating and cooling rates (Figure 1). When slow cooling rates are applied, the particles swell slowly and have time to rearrange and well-ordered crystal structures are formed. Temperature dependent UV-Vis absorbance spectroscopy is suitable to perform in-situ studies on the melting and recrystallisation of such thermoresponsive colloidal crystals which possess a diffraction peak and can be considered as photonic crystals.

Keywords: colloidal crystals, microgels, poly-N-isopropylacrylamide

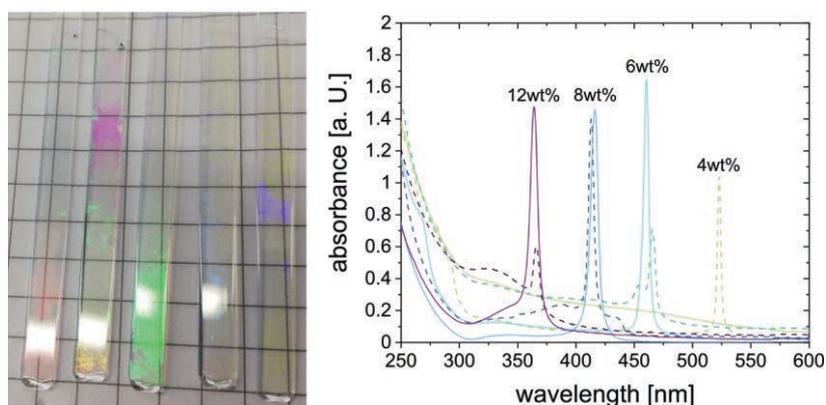


Figure 1. Photograph of colloidal crystals in thin-wall capillaries (left). Comparison of UV-Vis absorbance spectra of prepared (dashed lines) and annealed samples (lines) (right). After the annealing process, the Bragg-peaks are more intense and secondary peaks disappear.

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Controlling structural and physico-chemical properties of CeO₂ nanoparticle superlattices through the encapsulation into an amphiphilic double layer.

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Nanoparticles are used in various fields for their specific properties, which can be further implemented if induced to form superlattices [1-2]. In this respect, we recently synthesized cerium oxide nanoparticles (CeO₂-NPs) by thermal decomposition of Ce(NO₃)₃·6H₂O, using as capping agents either octylamine or oleylamine, to evaluate the effect of alkyl chain length and temperature on NP properties [3]. The NPs thus obtained were extensively characterized by means of several techniques, such as Wide-angle X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), UV-vis, Fluorescence, Raman, and FTIR spectroscopy allowing us to define the role of the synthesis conditions in affecting the shape and size of NPs as well as their optical properties. In fact, octylamine increases the concentration of Ce³⁺ resulting in a wide absorption throughout the whole UV-vis region. On the other hand, oleylamine increases the relative quantum yields of CeO₂-NPs.

Furthermore, among the synthesized CeO₂-NPs those with the smallest size and the best separation in solution were functionalized by means of interaction between the alkyl chains of capping agents (oleylamine) and those of another amphiphilic molecule (either sodium oleate or oleic acid). The formation of ordered aggregate (due to the oleylamine-oleic acid interaction; such as Frank-Kasper phases) or disordered aggregate (due to the oleylamine-sodium oleate interaction) modifies the physico-chemical properties of CeO₂-NPs, above all the optical properties, which are different from those of single CeO₂-NPs. Finally, MTT assays on eukaryotic cells were carried out with the aim to assess the biocompatibility and the antioxidant activity of selected samples.

Keywords: cerium oxide nanoparticles; encapsulation method; optical properties; superlattices.

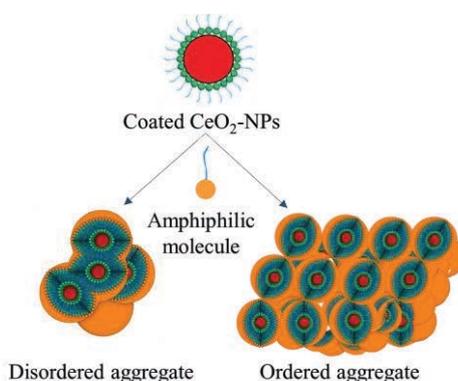


Figure 1. Schematic representation of the functionalization process.

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Microrobots from Toposelective Nanoparticle Deposition

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Microrobots are artificial micron and nano-scale objects that can convert energy sources such as light or chemicals into directed motion, much like motile microorganisms. This autonomous motion can transport matter at the microscale and even induce the mixing and pumping of fluids without external agitation. As a result, microrobots offer tantalizing opportunities for performing autonomous tasks at small scales in applications ranging from targeted drug delivery to environmental remediation and energy conversion. However, fabricating them in a scalable fashion for specific purposes remains challenging.

Janus microswimmers are arguably the simplest class of microrobots, relying on surface patches with different physiochemical properties to self-propel in the presence of an external gradient. Here, we propose a novel method combining the scalable Pickering-wax emulsion technique [1] with nanoparticle deposition to produce Janus microswimmers. Functional nanoparticles are asymmetrically attached to wax embedded SiO₂ microparticles via a post-modified poly(pentafluorophenylacetate) (pPFPAc) polymer with silane and nitrodopamine functionalities [2]. From this toposelective thin film deposition, we decorate the functionalized portion of the SiO₂ microparticles with commercial photocatalytic nanoparticles to obtain large (~100 mg) batches of light-responsive microrobots. Supporting the nano-catalysts on microparticles also significantly enhances their processability, overcoming a key limitation to the application of nanoparticles.

By utilizing silane and metal oxide-catechol chelation chemistry, the described approach lends itself to that attachment of a range of inorganic nanoparticles, demonstrated by the attachment of commercial TiO₂, SrTiO₃, and Fe₂O₃. Furthermore, the use of a post-modified pPFPAc backbone presents the opportunity to exploit other coordination chemistries through the introduction of various functional groups. Therefore, we expect our toposelective nanoparticle deposition to provide a modular, “off-the-shelf” approach for designing microrobots with composite thin films of functional nanoparticles dependent on the desired application.

Keywords: Janus microswimmers, photocatalytic, active matter, scalable, active Brownian motion

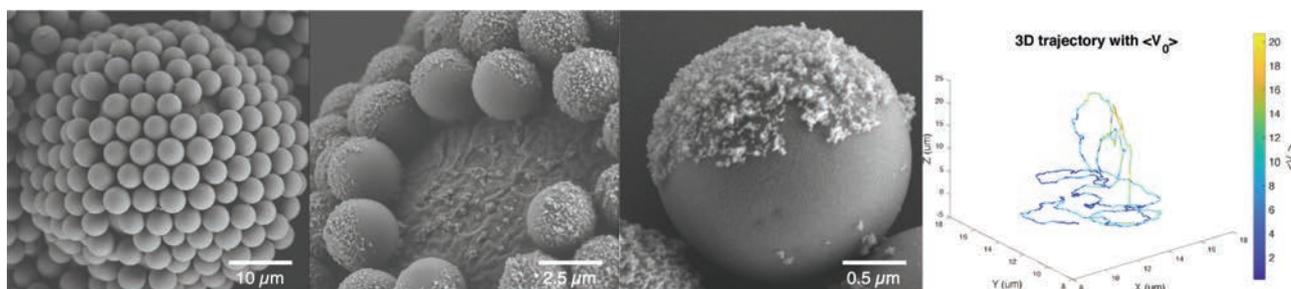


Figure 1. (Left to Right): SiO₂ – Wax colloidosome; Colloidosome after functionalization with TiO₂ P25 and pPFPAc; Janus microswimmer; 3D self-propelling particle trajectory with orientation-dependent velocity

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Shaping the surface of silica particles by the competition between two silanes

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The synthesis of silica nanoparticles in a controlled and uniform way is easily achieved through the Stöber process [1]. However, such synthesis provides only smooth particles. In the last years, new synthesis protocols have been developed to engineer the roughness of silica particles, for example, by heterocoagulation [2]. Another promising route is the association of two different silanes, which, under special conditions, will create golf ball-like particles [3] with controlled morphology in a single reaction. Through this study, we perform an extensive screening of the ratio between the two silanes, TEOS and VTMS, and the concentration of ammonia in the suspension, to demonstrate the synthesis of different particles, whose surface is characterized by AFM. This approach enables the creation of large quantities of well-defined rough particles, e.g. as model systems in dense suspension rheology.

Keywords: Rough silica colloids, morphogenesis, buckling

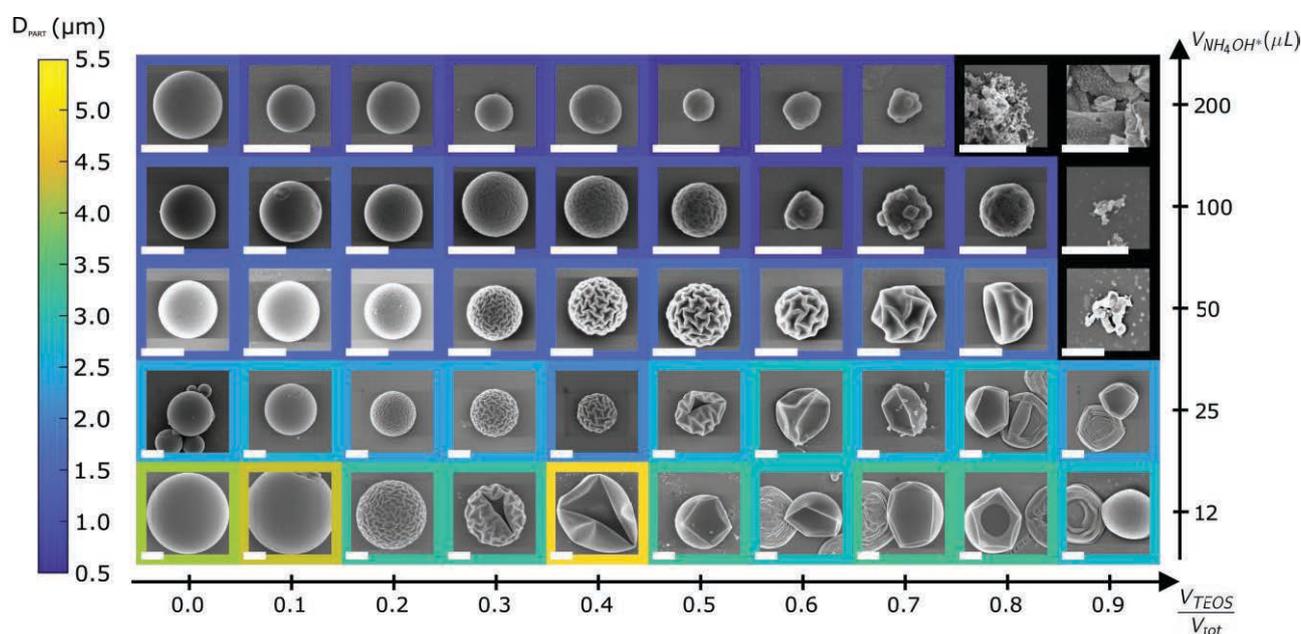


Figure 1. Different particles that can be synthesized by varying the volume of added ammonia ($V_{\text{NH}_4\text{OH}^*}$) or the ratio between the added volume of tetraethylorthosilicate (V_{TEOS}) and the total volume of silane (V_{tot}). The diameter of the particles D_{part} is represented by the colored box around the different SEM images. The white scale bar represents 1 μm .
By adding less ammonia or more TEOS, the surface of the particles buckles more easily.

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Advanced light scattering techniques for the characterization of novel materials

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Static (SLS) and Dynamic (DLS) Light Scattering are among the most powerful techniques to study nanostructures. These technologies have been widely employed for more than 30 years, and are still undergoing constant improvement.

While SLS and DLS are well-established characterization techniques, several completely new light scattering methods have gained significant traction among material scientists over the past decade. Among these, Diffusing Wave Spectroscopy (DWS) can be used to characterize the viscoelasticity of materials on a wide frequency range using low sample volumes if compared to classical mechanical rheometers. This presentation will feature a review of the scientific fundamentals of the techniques mentioned above, and take a closer look at some of the recent advancements, including Depolarized Dynamic Light Scattering (DDLS) and Modulated 3D Cross-Correlation.

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Plasmon-enhanced polymerization of conducting polymer shells on colloidal gold nanoparticles

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Noble metal nanoparticles like gold nanoparticles (AuNPs) exhibit collectively oscillating electrons when irradiated with light at their resonance wavelength, so-called localized surface plasmon resonances (LSPRs). LSPRs cause an enhanced electromagnetic near field and high energy charge carriers at the NP's surface. These phenomena affect the nature of polymerizations when polymer shells are built around the NPs. Existing synthesis routes for conducting polymer shells around colloidal AuNPs neglect this fact or synthesize only a few coated AuNPs using highly concentrated light.

We investigate the influence of the LSPR induced phenomena on the synthesis of conducting polymer around colloidal AuNPs. Commonly used polymerization methods are compared to new ones developed in our group. The obtained coated AuNPs are characterized by UV-vis spectroscopy and Transmission Electron Microscopy (TEM). An increase of 68% in polymer volume was observed for light-enhanced synthesis compared to synthesis in the dark, proving the huge influence of light on polymerization processes at AuNP surfaces.

Keywords: colloidal gold nanoparticles, LSPR, conducting polymer

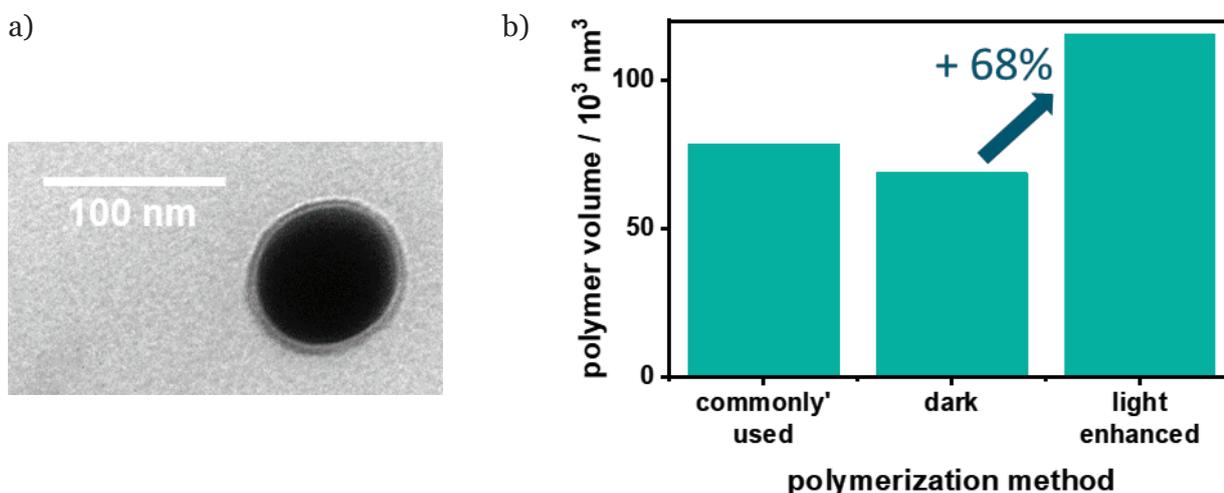


Figure 1. a) TEM image of conducting polymer coated AuNP, b) polymer volume obtained by different synthesis approaches.

EP1.22

**Safe-by-design preparation of hybrid polymer-gold
nanomaterials via self-assembly**

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Hybrid nanomaterials are focusing increased interest in different application fields [1]. Preparation methods based on supramolecular interactions are especially appealing as they imply a low energy consumption for their preparation and they do not need sophisticated equipment. In addition, the prioritization of chemical components of reduced toxicity represents a step forward, making the process of preparation and handling of these materials safer. In this context, as a proof-of-concept, hybrid polymer-gold nanomaterials of controlled features have been prepared in our group exploiting supramolecular interactions. Firstly, polymeric nanoparticles with hydrodynamic diameters between 150 and 200 nm were prepared using a low-energy emulsification-solvent evaporation approach [2]. Low toxicity materials were selected for the preparation of these polymeric nanoparticles, including ethylcellulose or poly(lactic-co-glycolic acid) (PLGA) as the polymer material, and ethylacetate as the volatile organic solvent, replacing the most frequently used and more toxic aromatic or halogenated solvents. The surface charge (zeta potential) of these polymeric nanoparticles can be tuned from positive (ca. +39 mV for ethylcellulose) to negative (ca. -40 mV for PLGA) by a proper selection of the template nano-emulsion components. In a second step, the polymeric nanoparticles were decorated with gold (Au) nanospheres or nanorods, which were attached by electrostatic interaction. The positively charged ethylcellulose nanoparticles were decorated with citrate-coated Au nanospheres of about 33 nm and a zeta potential of ca. -22 mV. The hybrid ethylcellulose-Au nanomaterial showed a mean hydrodynamic diameter of about 190 nm and a maximum absorption peak around 598 nm. By contrast, the negatively charged PLGA nanoparticles were successfully decorated with CTAB-coated Au nanorods with typical dimensions (length x width) of 31 nm x 4 nm (i.e. aspect ratio of 3.35 nm) and a zeta potential of about +30 mV. The hybrid PLGA-Au nanomaterials showed a mean hydrodynamic diameter around 250 nm and a maximum absorption band at about 800 nm. In summary, the proposed synthesis method is simple, mild and safe, and allows tuning the features of the hybrid polymer-Au nanomaterials.

Keywords: Nano-emulsions, gold nanoparticles, gold nanorods, PLGA, ethylcellulose

Acknowledgements: G. Calderó is grateful to the Serra-Hünter fellowship program.

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Preparation and characterization of biochars obtained from the wheat bran

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Economic development and an increase in the wealth of society contribute to an increase in the amount of wastes. Every year ten million tons of solid residues are disposed. These wastes are mainly of organic origin. Unfortunately, most of them are disposed on landfills where they can cause serious environmental problems. In this respect, researchers' attention is focused on finding new methods for their reuse. One of numerous possibilities of waste management is their use as precursors for the preparation of effective carbon adsorbents, due to the low price and unlimited availability [1].

Activated carbons are the materials widely applied in industry because they are characterized by a well-developed specific surface area as well as a high degree of reactivity. Physicochemical properties depend on the chemical structure and the degree of porous structure development. Due to their sorption properties, activated carbons found application, among others, in adsorption, catalysis or separation processes [2].

The aim of the presented research was to obtain effective carbon adsorbents from organic waste materials. Wheat bran was used as a precursor to prepare biochars. The pyrolysis of the starting material was conducted at different temperature variants in an oxidizing CO₂ atmosphere or in the presence of superheated steam. Moreover, the obtained biochars were modified with water assisted by the microwave energy.

On the basis of the research it was found that wheat bran is an appropriate starting material for the preparation of biochars. It was shown that the materials with good structural properties can be obtained during slow pyrolysis using CO₂ as an activating agent. In addition, pyrolysis in the presence of steam caused an additional increase in the surface and porosity. The materials were characterized by large surface areas with a well developed pore structure which makes them good prospective adsorbents for water treatment.

Keywords: organic waste materials, biochars, pyrolysis, structural properties

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Evaluation of sorption capacity of methylene blue onto biochar obtained from the wheat bran

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One of the major problems of humanity today is environmental pollution. The increase in production is forced by the increasing demands of humanity and is closely related to the increase in by-products and wastes. One of the main pollutants of the natural environment are dyes, the production of which increases every year due to the constant increase in market demand. Dyes can have a negative impact on human health that is why more and more emphasis is put on the development of technology and wastewater treatment plants.

Dyes are one of the main pollutants in sewages. Many types of dyes used in industry are toxic, showing carcinogenic, mutagenic or teratogenic effects [1, 2]. The most frequently used methods of wastewater treatment of colored dyes include adsorption, flocculation, oxidation or electrolysis [3]. Among the mentioned techniques, the most common are adsorption processes because they are conducted in an uncomplicated manner, with high efficiency and effectiveness and without too much financial expenditure [4].

In the process of adsorptive removal of dyes from wastewaters, there are used various sorbents such as: activated carbon, peat, wood sawdust, a mixture of volatile ash and fine coal dust, silica gel. Activated carbon, although expensive, is the most commonly used adsorbent for removing dyes from wastewaters. It is very effective in adsorbing cationic and acid dyes and, to a lesser extent, dispersion, direct, vat, pigments and reactive dyes [5, 6].

The aim of the research was to evaluate the adsorption capacity of biochars prepared from wheat bran assisted by physical activation. As a model impurity methylene blue was used. The carried out research allowed to state that the used biochars are characterized by high sorption capacity and can be successfully used as adsorbents in water purification processes.

Keywords: adsorption, activated carbon, effective adsorbent, water purification

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Development of Polymer/Graphene oxide nanohybrids with varying interfacial interactions

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In this work, polymer nanocomposites composed of graphene oxide (GO) and polymers of different chemical constitution and architecture were developed. Initially, the GO nanoadditives were synthesized by varying either the oxidation time or the mass of the oxidation medium to achieve different degrees of oxidation and thus alter the polymer/surface interactions; the change was quantified by X-Ray Photoelectron Spectroscopy. Subsequently, the different GOs were mixed with poly(ethylene oxide) (PEO) or hyperbranched polymers (HBPs) of different generations in a series of concentrations and the structure and morphology of the nanohybrids were investigated using X-Ray Diffraction, Scanning Electron Microscopy and Atomic Force Microscopy. In order to study the properties of the nanohybrid materials Differential Scanning Calorimetry, Thermogravimetric Analysis, FTIR & Raman Spectroscopy were utilized. For both the GO additives and the nanocomposite materials, computational models were developed to predict their properties and interpret their overall behavior.

Keywords: graphene oxide; degree of oxidation; hyperbranched polymers

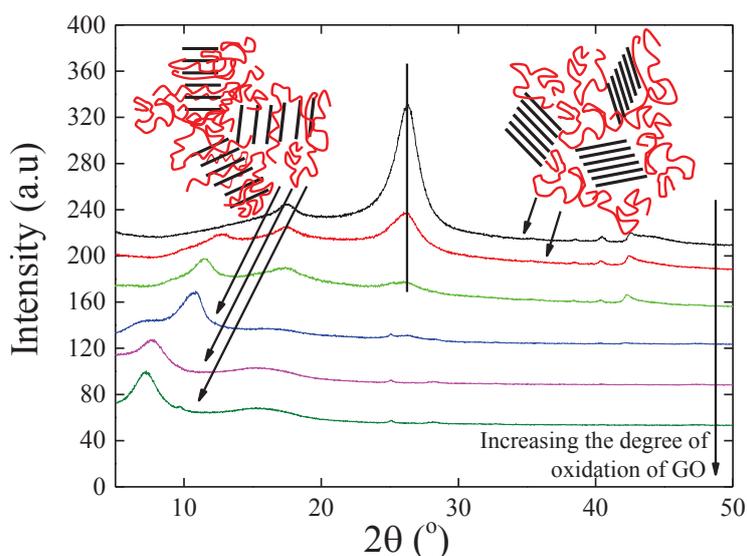


Figure 1. XRD measurements of different nanohybrids together with a schematic representation illustrating the effect of interfacial interactions of the final nanohybrid structure

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Characterization of the oil-water interfacial behaviour of chemically hardened gliadin nanoparticles

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Colloidal protein nanoparticles show promise for use as stabilizers in food emulsions and foams, although their behaviour at fluid interfaces remains largely unknown. Past studies of wheat gliadin nanoparticles (GNPs) have indicated that the deformation and interaction of GNPs at the air-water interface are partly responsible for their foam-stabilizing abilities.^[1,2] In this study, the structure-function relationship of GNPs was further explored by examining the behaviour of untreated and chemically hardened GNPs at the oil-water interface, whereby hardening stabilizes the nanoparticle matrix.^[3]

Particle size measurements showed that particles treated with glutaraldehyde demonstrated stability to disintegration in aqueous ethanol (70 v/v%), while untreated GNPs appeared to break apart into smaller particle fragments under these conditions. Oil-water interfacial tensiometry revealed that interfaces made with untreated GNP dispersions had higher dilational viscoelastic moduli than what was observed for glutaraldehyde-treated GNP dispersions. Observation of the microstructure of emulsions with cryo-scanning electron microscopy (cryo-SEM) revealed a tighter packing of oil droplets with more connections between droplet interfaces in emulsions made with untreated GNP dispersions. More and/or stronger interactions between untreated GNPs adsorbed at the interface seem to form more cohesive viscoelastic interfacial films.

These results suggest that the deformability of untreated GNPs and the increased mobility of their constituting proteins play an important role in their ability to rearrange and interact at the oil-water interface to form a strong viscoelastic film. This observation provides important insight into the mechanisms by which protein nanoparticles stabilize fluid interfaces which can aid in the design of particle stabilizers for edible emulsions and foams.

Keywords: Gliadin nanoparticles, glutaraldehyde, oil-water interface, interfacial rheology, emulsion

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***In situ* surface modification of SiO₂ nanoparticles for fabrication of bijels**

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Bicontinuous interfacially jammed emulsion gels (bijels) are a highly promising material for various applications including separation processes and fuel cells. Bijels consist of two intertwined liquid channel networks, where one channel network is composed of a water-rich phase and the other of an oil-rich phase. This bicontinuous structure is stabilized by colloidal particles that irreversibly adsorb onto the oil-water interface, ultimately forming a rigid film (Figure 1 b). [1]

In order for the colloidal particles to effectively stabilize the strongly percolating surface of the bijels, the particles should be equally wetted by both liquid phases. This requires precise control over the particle surface chemistry, which is traditionally achieved *via* covalent surface hydrophobization. However, it was recently shown that the particle surface can also be hydrophobized *in situ*, through the physisorption of oppositely charged long-chain surfactants (Figure 1 a). This strategy requires simply the mixing of particles with compatible surfactant molecules, making it a very straightforward, versatile and time-effective method. [2] The research question we address in this work is the following: can we modify the surface of SiO₂ nanoparticles *in situ* to make them neutrally wetting for the fabrication of bijels?

This work presents how we have gained control over the surface modification of Ludox TM-50 silica nanoparticles by tuning the physisorption of the positively charged surfactant cetyltrimethylammonium bromide (CTAB) on the nanoparticle surface. This tuning was done by varying pH, background salt concentration and surfactant concentration in the silica particle dispersions. The resulting dispersions could successfully be used for the preparation of bijels, thereby proving that the nanoparticles were neutrally wetting. The obtained bijels were characterized using confocal microscopy and SEM.

Keywords: silica nanoparticles, self-assembly, surface modification, bijels

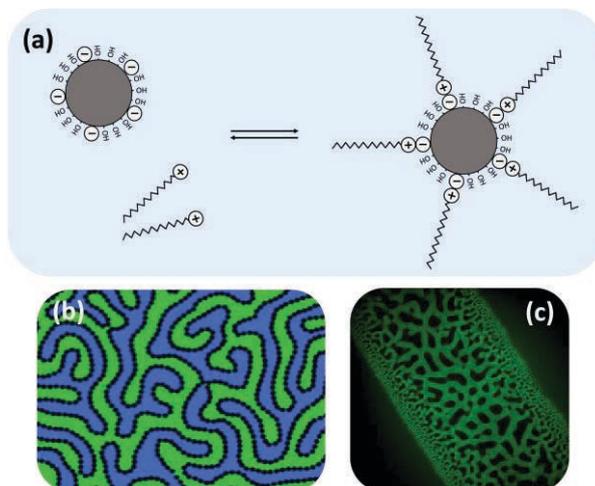


Figure 1. a) *In situ* surface modification of silica nanoparticles with CTAB molecules. b) Adsorption of nanoparticles on the oil-water interface of a bijel. c) Confocal micrograph of a bijel fabricated using surface-modified silica nanoparticles

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Synthesis of silver nanoparticles (AgNPs) in a microfluidic device

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Usage of silver nanoparticles (AgNPs) in medicine, catalysis, textile, and electronic industries has grown remarkably over the last decade due to their unique physicochemical, optical, and antibacterial properties [1]. Establishment of the routes and synthesis parameters are of great practical importance as well-defined properties are essential for many applications. The synthesis of AgNPs is usually carried out in macroscale reactors but microreactors which enable precisely control over reaction conditions as well as decrease environmental impact are currently of growing interest [2].

In this work, a T junction device is used for the synthesis AgNPs by a chemical route via the reduction of silver nitrate in the presence of tannic acid, which has weak reducing ability and trisodium citrate which has role as both a reducing and a stabilizing agent. The nucleation step in AgNPs synthesis is too fast, and therefore mass transfer is a limiting step for reaction kinetics. To enhance mixing, the outlet tube is coiled on a 3D printed rod with helical grooving. Experimental results show that helix device promotes the formation of Dean vortices within the laminar flow which enables formation of smaller particles. It was found that other operating parameters such as larger pH and increased concentration of trisodium citrate decrease the average size of AgNPs.

The reaction kinetics can be described by Finke-Watzky model considering nucleation as a first step and auto-catalytic particle growth as a second step. Kinetic constants were derived from the absorbance intensity at 400 nm, characteristic for AgNPs versus time as shown in Fig.1.

Keywords: Silver Nanoparticles, Mixing, Trisodium Citrate, pH, Microfluidics

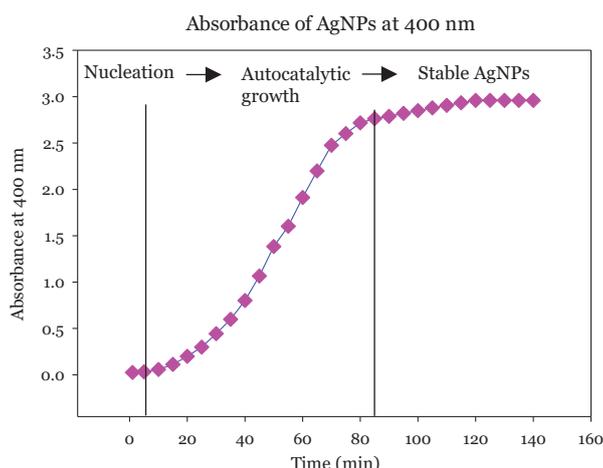


Figure 1. Sigmoidal curve for AgNPs formation. Time evolution of the absorbance at 400 nm.

Acknowledgements: This work was funded by the EPSRC Programme Grant PREMIERE EP/T000414/1.

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Brownian dynamics simulations on aggregate structures of cubic hematite particles in a rotating magnetic field

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In the present study, we have addressed a suspension composed of cubic hematite particles in a rotating magnetic field by means of Brownian dynamics simulations in order to investigate the dependence of the regime change on a variety of factors such as the magnetic particle-particle interaction strength, the magnetic particle-field interaction strength and the frequency of the rotating magnetic field. The main results that have been obtained here are summarized in the following. In the situation of a relatively weak magnetic field, the particles aggregate to form closely-packed structures shown in Fig. 1(a) as the magnetic particle-particle interaction strength is increased. Therefore, the magnetic moments of constituent particles cannot follow a change in the rotating magnetic field. As the magnetic field strength is increased, closely-packed structures collapse, and the particles tend to aggregate with an atypical face-to-face contact configuration shown in Fig. 1(b). In the situation of a strong magnetic field, the closely-packed clusters completely collapse and aggregate structures with an offset face-to-face configuration shown in Fig. 1(c) are formed in the system. In this situation, the magnetic moments of each particle are strongly restricted to the magnetic field direction, and the cluster itself rotates to follow the change in a rotating magnetic field. From these results, we conclude that a regime change in the aggregate structure of cubic particles in a rotating magnetic field may be induced by the magnetic particle-particle interaction strength and the magnetic particle-field interaction strength.

Keywords: Brownian dynamics simulation, Cubic hematite particles, Aggregation phenomena, Internal structure, Regime change, Rotating magnetic field

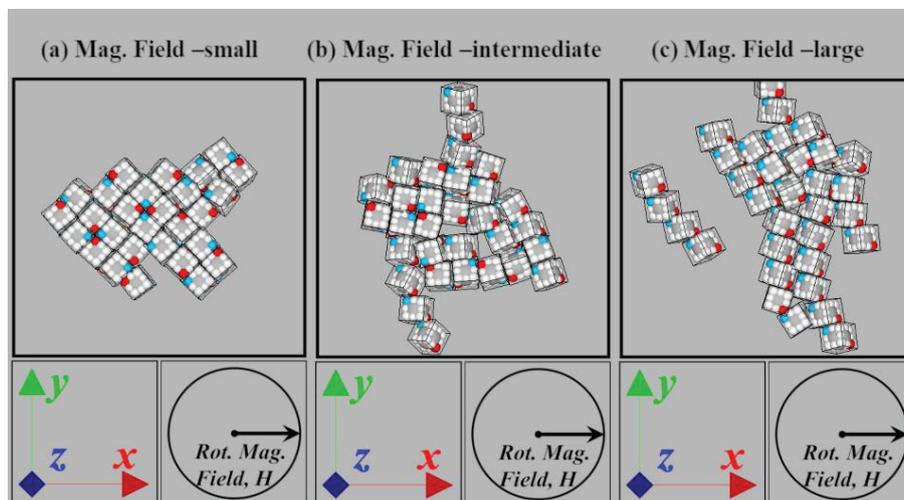


Figure 1. Dependence of the aggregate structures on the magnetic particle-field interaction strength.

EP1.30

Chitosan nanoparticles by electrostatic crosslinking: Effects of cross-linker nature and concentration

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Chitosan (CS) is an abundant cationic natural biopolymer [1] derived simply by alkaline N-deacetylation of chitin. It is biocompatible, non-toxic, has antimicrobial properties and acts as a phytostimulator (Elicitor), inducing plant defense mechanisms and preparing them for impending attack by bacteria, fungi and viruses. [2]

The purpose of this work was to prepare chitosan nanoparticles (CS-NPs) by non-covalent crosslinking, due to electrostatic interaction and / or hydrogen bonds, using three multifunctional molecules that act as crosslinkers. Bare CS-NPs were synthesized at various concentrations of CS for each crosslinker and at different crosslinker / CS mixing ratios (2% w/w, 5% w/w, 10% w/w and 15% w/w) using the following protocols. The first protocol was related to the direct addition of the crosslinker in the CS solution, while the second protocol regards the gradual addition of the crosslinking agent. The crosslinkers used were phytic acid (PA), tannic acid (TA) and tripolyphosphate (TPP). CS-NPs were studied by dynamic and electrophoretic light scattering techniques (DLS, ELS), to determine the hydrodynamic radius (R_h) and size polydispersity index (PDI), surface charge and detect possible changes in the scattered light intensity. Lastly, the mixed CS-NPs were characterized in terms of temporal stability using the DLS technique. Size and surface charge were found to depend on the nature and content of the crosslinker.

Keywords: chitosan nanoparticles, tannic acid, phytic acid, tripolyphosphate

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Synthesis of green nanoparticles utilizing agricultural wastes/natural sources: Novel nanocarriers for enzymes immobilization

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Metal nanoparticles have attracted considerable attention due to their numerous applications from biotechnology to agriculture. A novel approach regarding nanoparticles synthesis involves the utilization of biological entities as stabilizing and capping agents [1]. Plant extracts are considered environment-friendly, cost-effective, safe and stable media compared to microbial filtrates that contain intriguing phytoconstituents. For instance, agricultural wastes (olive mill or winery wastes) comprise rich sources of secondary metabolites which can catalyze the bioreduction of salt reactants. Consequently, plant-mediated synthesis of metallic nanoparticles serves the principals of both green chemistry and bioeconomy.

In this regard, aqueous olive leaf extract was utilized for the biofabrication of metal nanoparticles such as zinc oxide, iron oxide and hybrid zinc oxide-iron oxide nanoparticles. The newly synthesized nanoparticles were characterized by various techniques such as Fourier-transform infrared (FTIR) and UV-Vis spectroscopy, Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

Further, hydrolytic and oxidoreductase enzymes were immobilized on the surface of the functionalized metal nanoparticles via covalent or non-covalent approaches. The biochemical characteristics of the new nanobiocatalytic systems (NBSs) were thoroughly evaluated. Furthermore, the nanobiocatalysts were applied to synthesis of various hybrid phenolic antioxidants of high economical and scientific interest in conventional and non-conventional media [2]. Several high-added value compounds with enhanced biological activities were synthesized achieving even conversion yields of 100%.

The results of this study suggest that green nanomaterials are stable and inexpensive alternatives as nanoplatforms for enzyme's immobilization with excellent capabilities.

Keywords: green nanomaterials, synthesis, enzymes, biocatalysis, nanobiocatalysts

Acknowledgements: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH—CREATE—INNOVATE (project code: T2EDK-03599).

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Omnidirectional reflection of multi-domain spherical colloidal crystals

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Colloidal crystals with spherical shapes are called photonic balls, and their optical properties have been extensively studied because they can be applied as structurally colored pigments or colorimetric sensors[1]. Spherical colloidal crystals are prepared from water in oil emulsion by evaporating the water, in which colloidal particles are dispersed in water phase.

The photonic ball shown in Figure 1(a) was observed using an objective with a small numerical aperture (NA=0.25). The (220) planes cause the ring-like iridescent reflection in the peripheral part of the spherical crystal[2]. However, the same photonic ball appeared very differently when observed with a high NA objective (NA=0.75), as shown in Figure 1(b). The peripheral reflection formed a nearly complete ring, and the color of the ring was almost green. These observations imply that the region that appears dark under the low NA objective actually reflects light in an oblique direction, which is included in the aperture of the high-NA objective.

This study presents a detailed optical analysis of this peripheral reflection. The photonic ball consists of many small crystal domains, and the reflecting crystal planes are oriented in different directions from one domain to another. Thus, in some domains, significantly tilted planes and refraction at the spherical surface cause reflection in a highly oblique direction, such that the reflection path requires a three-dimensional description(Figure 1(c)). This study shows that such an oblique reflection significantly affects the appearance of the photonic ball. The reflection becomes omnidirectional, and this characteristic is preferred for a pigment. The analysis presented in this study will be useful for the design and analysis of similar optical systems.

Keywords: photonic ball, structural color, colloidal crystal, pigments, optical analysis

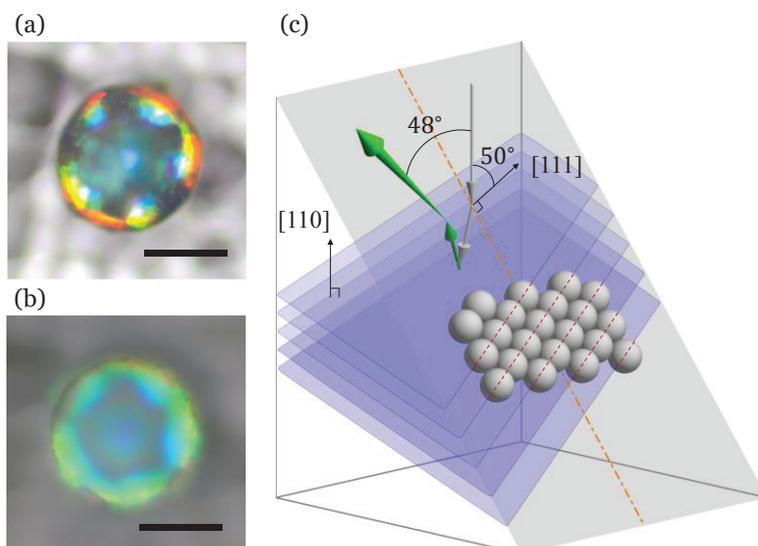


Figure 1. (a,b) Optical micrographs of the photonic ball. The same photonic ball was observed using objectives with (a) NA = 0.25 and (b) NA = 0.75. The scale bars are 50 μm . (c) Three-dimensional schematic diagram of reflection

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EP1.33

Water dynamics and structure in packed particle beds: dark field neutron imaging and NMR studies

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Microscopic detail of the transport of water and solutes through packed beds of particulate matter has the potential to enable an enhanced understanding in such diverse areas as dewatering of sludges, industrial filtration and soil physics. In this study we take experimental perspectives on the porosity and the transport of water through packed beds of CaCO₃ particles formed by gravitational sedimentation, with dark field neutron (DFI) [1] and NMR imaging [2] respectively, to provide complementary experimental views on the structure of porous material and the resulting perturbation to the dynamics of water. While both of these imaging techniques offer limited real spatial resolution the strength of these two techniques is that they are able to provide, through variable spatial averaging, of important microscopic quantities. A well-considered experiment potentially offers a basis to unify the perspectives of the Darcy and the Navier-Stokes equations in the transport of water through porous media. [3] Here we consider the experimental practice of directly comparable measurements. Pulsed gradient NMR imaging methods examine directly translational dynamics of water. DFI contains information, on a per pixel basis, on the spatial heterogeneity in water and CaCO₃. We show that smaller pore spaces result in the greatest perturbation to the free self-diffusion of water in particle beds of smaller and more finely packed particles. The addition of a commercial flocculant for equivalent sized particles results in more open structure and less restricted diffusion.

Keywords: porous media, dark field neutron imaging, NMR imaging, water self-diffusion

Acknowledgements: We acknowledge the provision of dark field imaging beamtime on the ICON beamline at the Paul Scherrer Institute. PJ thanks the Fédération Française de Diffusion Neutronique for their support. CJG acknowledges a fellowship from the Lund Institute for Advanced Neutron and X-ray Science.

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EP1.34

Dendronized oligoethylene glycols with phosphonate tweezers for cell-repellent coating of oxide surfaces.

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Dendronized oligoethylene glycols (dendron OEGs) with two phosphonate groups (phosphonate tweezers) have been drawing significant attention as a new class of coating materials for superparamagnetic iron oxide surfaces. However, despite dendron OEGs showing outstanding stability in physiological fluids in previous studies, little is understood about their structure and mechanical properties. Herein we report the surface and internal structures and mechanical properties of dendron OEGs, and quantitatively determine their ability to avoid non-specific adhesion of blood platelets. To gain insight into the interfacial force interactions, we measured the coarse-scale surface force acting on cell-sized particles and mapped the nanoscopic pinning centers by fast force mapping.

EP1.35

Tribological Performance Improvement of a Commercial Engine Oil Incorporating RGO

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The tribological behavior of commercialized, fully synthetic engine oil upon the incorporation of reduced graphene oxide (RGO) in seven different concentrations between 0.01 and 0.2 wt % was studied. The stability of the prepared samples was assessed by turbidimetry and dynamic light scattering measurements, and the tribological properties through a reciprocating tribometer, using a steel ball on special cut steel blocks. The addition of 0.02 wt % of RGO led to an improvement of the tribological behavior compared to the pristine engine oil, by significantly lowering the friction coefficient by 5% in the boundary lubrication regime. Both the surfaces and the RGO additive were thoroughly characterized by microscopic and optical spectroscopy techniques and we verified that a protective layer was formed between the worn surfaces, due to the presence of RGO. Finally, the wear scar diameter on the surface of the steel ball was lower by 3%, upon testing the engine oil sample containing RGO at concentration 0.02 wt %, compared to the control sample.

Keywords: reduced graphene oxide; engine oil additives; friction COF; tribological properties



Figure 1. The schematic representation of the study.

Acknowledgements: This research has been co-financed by EU and Greek national funds (AENAO research project, Action KRIPIS, project MIS-5002556).

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The effect of the size of Ni-Ag core-shell nanoparticles on the conductivity of ink coatings

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In the field of printed electronics, the type of components and process of inks preparation, as well as the conditions of the fabrication of conductive patterns are crucial of importance for the final properties of electronic devices. One of the most important components of conductive ink formulation are metallic nanoparticles (NPs) due to their low sintering temperature, micro-size processing capacity, and flexibility. Among them, silver NPs, due to their high conductivity and oxidation stability, have been the most commonly used so far for the fabrication of printed electronic circuits and devices. Nickel NPs have been recently considered as a replacement for Ag due to their lower price, better mechanical properties, and high electrical conductivity. However, such NPs are oxidized immediately under ambient conditions. 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 [1].

In our studies, as a result of the two-step process: (1) the formation of a dispersion of Ni nanoparticles; and (2) the transmetalation (galvanic displacement) reaction, where the surface of the Ni NPs acted as the reducing agent of silver ions, spherical Ni-Ag nanoparticles at various average diameters (100, 220, and 420 nm) were synthesized and utilized for the preparation of conductive inks composed of monodisperse NPs and their polydisperse mixtures. The shell thickness of synthesized Ni-Ag NPs was found to be in the range of 10–20 nm and to provide stability of a core metal to oxidation for at least 6 months. The conductive metallic films were obtained by thermal sintering, which is the most favored method to transform nonconductive coatings to conductive one.

The conductivity of metallic coatings formed by inks with monodisperse Ni-Ag NPs was compared with those formed by a mixture of them with different average size (model polydisperse) inks. In all cases, the optimal conditions for the formation of conductive patterns (weight ratio of monodisperse NPs for polydisperse composition, the concentration of the wetting agent, sintering temperature, and duration) were determined. It was found that metallic films formed by polydisperse ink containing 100, 220, and 420 nm Ni-Ag NPs with a mass ratio of 1:1.5:0.5, respectively, are characterized by the lowest resistivity, 10.9 $\mu\Omega\cdot\text{cm}$, after their thermal post-coating sintering at 300°C for 30 min that is only 1.6 higher than that of bulk nickel. We believe that such ink coatings composed mainly of low-cost non-noble metals with high electrical conductivity can have great potential applications in the printed electronics industry and will contribute to developing an efficient and low-cost manufacturing route for electronic devices.

Keywords: core-shell nanoparticles, thermal sintering, conductive coatings

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Simple Characterization of Colloidal Anisotropic Nanocrystals by Analytical Ultracentrifugation

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Analytical ultracentrifugation (AUC) is a powerful technique to characterize colloidal nanocrystals (NCs) in solution and obtain critical information about their mass distribution, heterogeneity, colloidal stability, solvation degree and diffusion properties [1,2]. These AUC abilities are especially beneficial to investigate unstable colloidal NCs with small dimensions, stabilized by thick surface ligand shells, and difficult to capture by electron microscopy techniques [3]. Although AUC was developed by T. Svedberg (Nobel Prize Chemistry 1926) for the analysis of gold NCs, it has been primarily applied to the characterization of (bio)polymers [4]. The utilization of AUC for the analysis of nanocrystalline colloids has been traditionally limited to spherical NCs [1,3,5]. The entangled effects of the NC morphology and the nature of the surface stabilizing ligands on the sedimentation and diffusion behaviour of NC colloids represent a tremendous obstacle towards the exploitation of AUC to investigate anisotropic NCs.

We propose a methodology for AUC analysis of anisotropic NCs based on matching the density of the solvent with that of the stabilizing ligands. Thereby, it is possible to separate the effect of the surface ligands on the sedimentation and diffusion properties of the NCs, which eventually enables precise characterization of NCs with complex morphologies. The simplicity and reliability of the method are evaluated with different NCs such as gold nanorods, palladium nanodendrites or nickel oxide nanoplates. Moreover, the proposed method is further exploited to analyze core-shell NCs, regardless of their shape or composition. Thus, under the condition that the density of the solvent matches that of the stabilizing surface ligands, AUC displays great potential for studying an array of anisotropic colloidal NCs of different nature directly in solution.

Keywords: Analytical Ultracentrifugation; Anisotropic Nanocrystals; Characterization.

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Separation of biomolecules from model and biotechnological mixtures using iron oxide nanoparticles

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Over the past years, magnetic nanoparticles have demonstrated the ability to adsorb different molecules. These promising materials have unique physicochemical characteristics, allowing fast processing due to their superparamagnetism and making them ideal for large-scale production. The major challenge to exploit this technology in the downstream process area is to control the selective adsorption of molecules, mainly from complex environments such as lysates, where there is a mosaic of several biomolecules and ions.

The binding dynamics of molecules to nanoparticles in mixture solutions, generally physiological environments, was initially discussed for proteins. However, binding competition studies of proteins, lipids, carbohydrates, and nucleic acids are yet to be developed [1].

To have a controlled reference, we develop model mixtures by including materials that represent each molecule type. Said models have established concentration profiles, assuring “fair play” conditions between adsorbing macromolecules. Sodium oleate, BSA, dextran, and plasmid DNA are selected to portray the four main macromolecules, while microalgae lysate is used as a case of study for biotechnological mixtures.

Here we undertake studies to determine the dynamics of the different biomolecules when binding to inexpensive iron oxide nanoparticles. Preliminary findings showed that BSA is not adsorbed in presence of sodium oleate, suggesting an inhibitory effect that could lead to selective separation processes.

From model multi-component systems to biotechnological mixtures, we develop strategies to control the adsorption sequence, with the final goal to exploit the whole biomass through fractionation and to obtain sustainable downstream processes.

Keywords: magnetic separation, biomolecules, mixtures, nanoparticles.

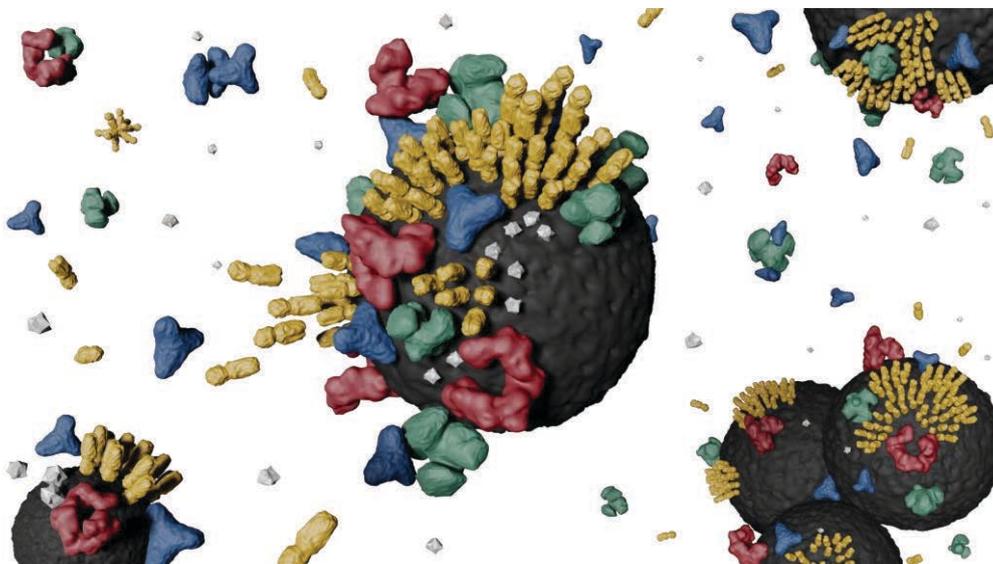


Figure 1. Interaction of biomolecules with magnetic nanoparticles [1].

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EP1.39

The Preparation of Mono- and Multicomponent Nanoparticle Aggregates Using Emulsion Templating Method in Microfluidics

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Gold nanoparticles (Au NPs) have unique optical-electrical properties, iron oxide nanoparticles (IO NPs) are magnetic and polycaprolactone nanoparticles (PCL NPs) are biocompatible and biodegradable, which are all useful properties for medicinal applications. Whereas mono- and bicomponent nanoparticle aggregates were reported in literature, multicomponent aggregates are quite rare.

Thus, we assembled the three types of NPs to combine the mentioned favorable properties within this work. We prepared hollow layer-by-layer structured aggregates with the inner inorganic shell composed of IO+Au NPs and with PCL NPs covering the outer surface. Such arrangement, with biocompatible outside layer, facilitate the potential contact with tissues. Core space enables a cargo loading.

The aggregates were produced with water in n-butanol two phase laminar flow generated by microfluidic channels. Using partially miscible system, we employed so-called emulsion templating method, which does not require any additional chemical or physical treatments. The NPs adsorb onto the aqueous droplet interface, acting as a template, to stabilize the emulsion. Due to the diffusion of the aqueous phase into the n-butanol environment, the NPs are compressed into the form of spherical solid aggregates by the time leaving the microfluidic channel. That enabled us to significantly reduce the aggregate size, being in the range of $3.2 \pm 0.3 \mu\text{m}$ to $22.0 \pm 1.7 \mu\text{m}$, compared to droplet microfluidics using immiscible phases.

The flow regime description was necessary part of the work since the data describing water in n-butanol two phase flow in microfluidics were missing in literature. The computational fluid dynamics (CFD) model was created and verified against experimental data proving its very good predictive power and providing us with results unavailable from experiments, which were important for the NPs aggregation process.

Keywords: nanoparticle aggregate, colloidosome, emulsion templating method, microfluidic channel, CFD, n-butanol

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EP1.40

Incorporation of Fluorescent Silver Nanoclusters into PEGDA Hydrogel for Lead Sensing

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Heavy metal ions pose a significant threat to human and environmental health, for this reason, the ability to sense and quantify the presence of these contaminants is of paramount importance [1]. The techniques commonly used for this purpose, such as atomic absorption spectroscopy or mass spectrometry are expensive, time-consuming and require experienced analysts. Optical sensors offer a sensitive, low-cost alternative to the forementioned techniques [2]. Furthermore, solid-state sensors are easy to handle, can simplify the sampling process and can also be exploited as filters. In this study, we employ silver nanoclusters (AgNCs) stabilized with poly methacrylic acid (PMAA) as a probe for Pb(II) ions. The AgNCs present a strong emission at 660 nm which is selectively enhanced in the presence of lead [3]. In order to fabricate a solid state sensor, we introduced them in a hydrogel material formed by poly(ethylene glycol) diacrylate (PEGDA) with low molecular weight. The precursor solution was poured into plastic cuvettes and through a photo-polymerization reaction the PEGDA chains trap the AgNCs-PMAA within the polymer network, forming a hydrogel-based device. The use of the PEGDA matrix does not prevent Pb(II) detection, however, the sensitivity and limit of detection of the system can be affected by the composition of the matrix and the parameters of the measurements. Here, we evaluated the performance of systems containing different concentrations of AgNCs, polymerized with the aid of different photoinitiators and excited at different wavelengths.

Keywords: Fluorometric sensor, Silver nanoclusters, Hydrogel

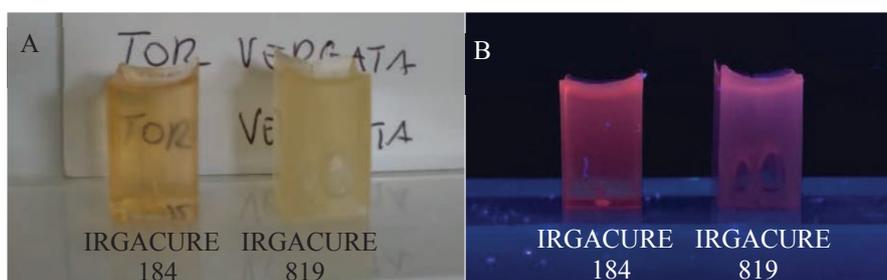


Figure 1. PEGDA matrices containing AgNCs with different photoinitiators under daylight (A) and UV (B) illumination.

Acknowledgements: The authors gratefully acknowledge the funding of Regione Lazio, through Progetto di ricerca 85-2017-15125, according to L.R.13/08 and the financial support of the University of Rome Tor Vergata through the project “Beyond the borders” n. E84I19002280005.

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Capillary imbibition of binary fluid mixtures in nano-channels

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Many-body Dissipative Particle Dynamics (MDPD) simulations of binary fluid mixtures imbibing cylindrical nano-channels reveal a strong segregation of fluids differing in their affinities to the pore walls. Surprisingly, the imbibition front furthest into the channel is highly enriched in the fluid with the lower affinity for the walls, i.e., the fluid less prone to enter the pore. This effect is caused by the more-wetting fluid forming a monolayer covering the walls of the pore, while the lesser-wetting fluid is expelled from the walls to the interior of the pore where the higher axial flow velocity carries it to the front. The fluids remix after cessation of the flow.

Non wetting fluids can be made to enter a pore by mixing with a small amount of wetting fluid. The imbibition depth of the mixtures scales with the square root of time, in agreement with Bell–Cameron–Lucas–Washburn theory for pure fluids.

Keywords: Binary mixtures, Bell-Cameron-Lucas-Washburn, Imbibition, MDPD simulations

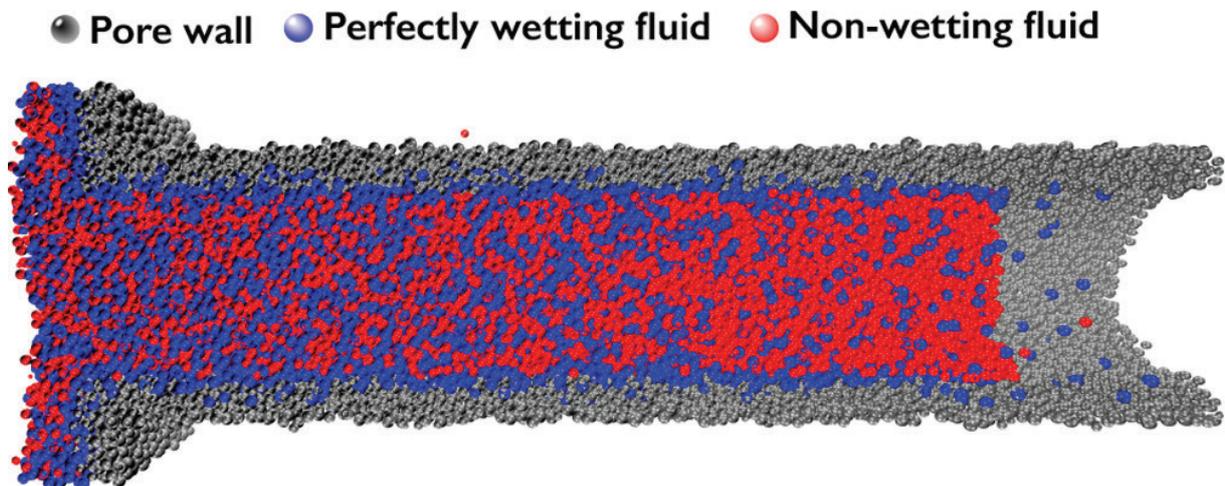


Figure 1. Simulation snapshot of the enrichment of the non-wetting fluid at the wetting front during the binary fluid imbibition.

Acknowledgements: This work is part of an Industrial Partnership Programme of the Foundation for Fundamental Research on Matter (FOM), which is financially supported by The Netherlands Organisation for Scientific Research (NWO). This research program was co-financed by Canon Production Printing (Venlo, The Netherlands). We thank Stefan Luding (UT), Herman Wijshoff (Canon), and Nicolae Tomozeiu (Canon) for stimulating discussions.

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Silver nanoparticles functionalized with a dye bound to the capping agent: influence on optical properties

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Nanotechnologies are now widely used in various fields, such as energy, catalysis and sensors, where the high surface/volume ratio makes them highly attractive [1].

In particular, in the last decade silver nanoparticles (AgNPs) are arousing great interest both for their possible applications in environmental protection/monitoring and for their antibacterial activity [2, 3].

This work presents the synthesis of new hydrophilic silver nanoparticles (AgNPs), which have 2 capping agents, L cysteine (Lcys) and a dye, rhodamine B isothiocyanate (RITC) or fluorescein isothiocyanate (FITC). The optical and structural properties of these new plasmonic materials are compared and discussed with respect to those of AgNPs that have only Lcys as a capping agent, studying in particular the interaction between surface plasmon resonance band (PRSB) and dye absorption.

Keywords: silver nanoparticles; rhodamine B isothiocyanate; fluorescein isothiocyanate; plasmonic materials.

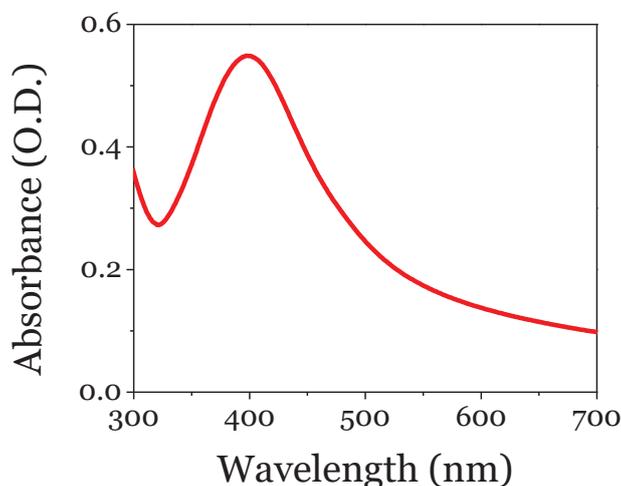


Figure 1. UV-Vis absorption spectrum of AgNPs-Lcys in water.

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Colloidal Silica: A Versatile Material for a Broad Range of Applications

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Colloidal silica is an aqueous dispersion of non-porous, non-crystalline nanoscale particles [1]. It is an important industrial product that is manufactured from the simplest of ingredients, sand and water. However, its useful properties are far from commonplace.

In addition to being extremely durable, stable, and heat-tolerant, these particles can be tailor-made and chemically customized to yield enormous potential. For example, these tiny silica particles offer excellent chemical reactivity and high surface area, which make them highly effective as a binder to stabilize a wide range of products, including chemical catalysts, ceramics, and high-temperature insulators. Silica nanoparticles can also act as an abrasive to achieve a fine polish on electronic components or, conversely, be applied as a coating to add traction to surfaces to prevent skidding and slipping. Colloidal silica can bolster the strength of cement, introduce a corrosion-proof outer layer onto metal surfaces, and can act as a flocculant during papermaking and beverage production, among other processes [2]. Despite this abundance of applications, colloidal silicas still have considerable untapped potential, for example in food packaging and encapsulation technologies.

In this contribution, existing and promising applications of colloidal silica are summarized. In addition, W. R. Grace & Co.'s production process for LUDOX® Colloidal Silica is outlined and colloidal stability of these silica dispersions is discussed.

Keywords: Colloidal silica; silica nanoparticles; nanoparticle dispersions; industrial applications; colloidal stability

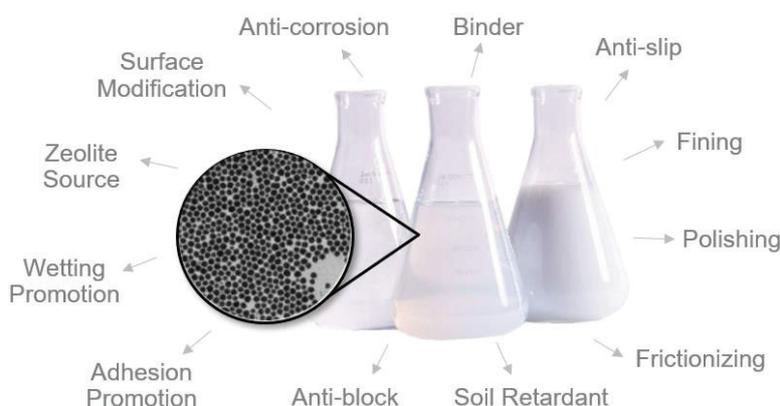


Figure 1. LUDOX® Colloidal Silicas are made by a process of nucleation and growth which results in particles with well controlled size distributions. These nanoparticle dispersions have a broad range of industrial applications.

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EP1.44

Cross-linked porous gelatin microparticles with tunable shape, size and porosity

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Gelatin particles are relevant to many applications in the biomedical field (*e.g.*, as drug delivery vehicles [1] or as scaffolds for the adhesion and proliferation of anchorage-dependent cells [2]), due to their excellent biocompatibility and versatility. The preparation of porous gelatin microparticles through double emulsion methods has been previously reported in the literature [3-5]; nevertheless, the effect of preparation parameters has not been yet addressed up. In particular, tailoring shape, size and surface features of gelatin microparticles is of utmost importance to many applications, as well as enhancing stability against dissolution through a cross-linking treatment, especially when the application takes place in aqueous environments at physiological temperature.

We prepared porous gelatin microparticles from oil-in-water-in-oil (O/W/O) emulsions, modifying the gelatin/surfactant ratio and the stirring speed. The effect on structural properties, including surface and inner porosities, was assessed by multiple microscopy techniques (optical, electron and confocal Raman). Three selected samples were cross-linked with glutaraldehyde or glycerinaldehyde and their swelling properties and stability against dissolution was evaluated, while the influence of the cross-linking at the nanoscale was studied by scattering of X-rays. Depending on the preparation parameters, particles with different shapes (irregular or spherical), radii (ca. 40-90 μm), and porosities ($>10 \mu\text{m}$) were successfully obtained. The cross-linking treatment extends their stability in water from a few minutes up to several days, while the swelling ability and the mesh size at the nanoscale of the gelatin network are preserved. The analysis of the experimental results as a function of the preparation parameters demonstrates that microparticles with tunable architectures can be designed using a double emulsion method.

Keywords: Gelatin; microparticles; porous; double emulsions; cross-linking; swelling.

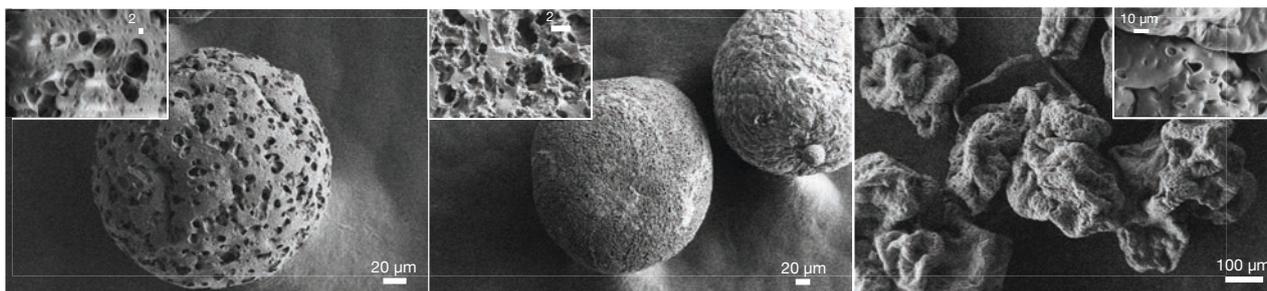


Figure 1. FE-SEM micrographs of the porous gelatin microparticles prepared with a O/W/O method changing the gelatin/surfactant ratio and the stirring speed.

Acknowledgement

CSGI and Fondazione Cassa di Risparmio di Firenze are acknowledged for financial support. This work benefited from the use of the SasView application.

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Static and dynamic control of magnetic microgels

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Microscale anisotropic building blocks have been receiving increasing attention in respect to their use as model systems to study complex phase diagrams, dynamics and self-assembly processes and for their biomedical applications. Tissue engineering is one of them, where rod-like magnetic microgels loaded with superparamagnetic iron oxide nanoparticles (SPIONs) were found to direct cell growth when aligned under a homogeneous magnetic field [1].

We are currently aiming at controlling the magnetic orientation and actuation of such microgels using ferrimagnetic maghemite spindles as anisotropic magnetic fillers instead of SPIONs [2]. Polyethyleneglycol microgels of various shapes were designed through two different synthesis methods. Rod-like microgels were produced using particle replication in non-wetting templates (PRINT), and “any-shaped” microgels via stop-flow projection lithography [3]. The maghemite spindles were pre-aligned and self-assembled into dipolar chains during the microgel synthesis as evidenced by the examination of the resulting composite microgels by scanning electron microscopy (SEM) (Figure 1A). This procedure allows us to pre-program the orientation of the composite microgels parallel or perpendicular to the applied magnetic field as shown in Fig. 1B,C. The actuation of these systems by an external rotating magnetic field further offers the possibility to dynamically align the microgels rods with an orthogonal magnetic moment in the third dimension (Figure 1D). We conclude with the extension of this strategy to more complex shapes and its application for the design of magnetic micro-actuators (Figure 1E).

Keywords: anisotropic magnetic microgels, composite materials, micro-actuators

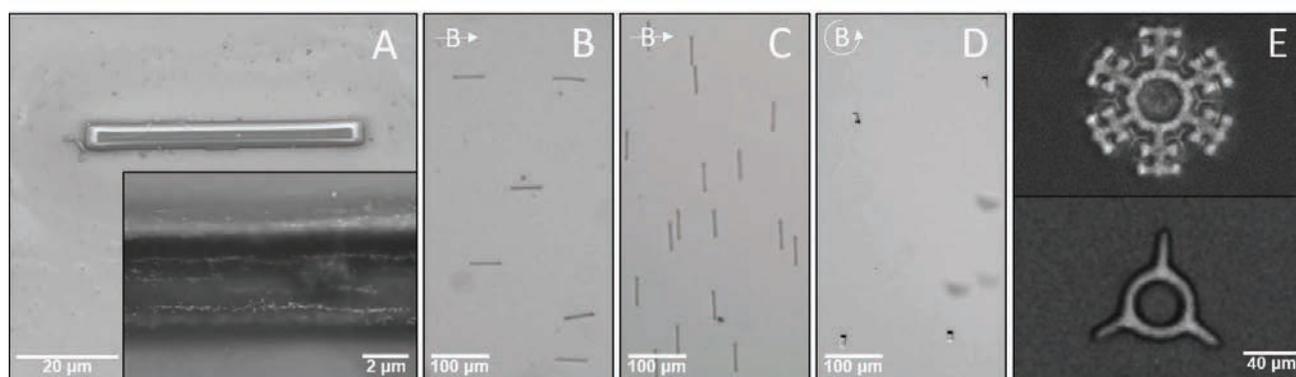


Figure 1. (A) SEM image of incorporated maghemite nanoparticles inside a rod-like microgel. (B,C) Bright field micrographs of the composite microgel alignment parallel and perpendicular to the applied magnetic field. (D) Vertical alignment of the composite microgels with an orthogonal magnetic moment under rotating field (70 mT, 10 rpm). (E) Snowflake and impeller geometries obtained by stop-flow projection lithography for the design of magnetic actuators.

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Adsorption of polyoxometalate nanoclusters on the alumina surface

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Polyoxometalate complexes are of considerable interest in many areas, including drug transport, modern hybrid materials and catalysis. Molybdenum oxide nanoclusters have shown high catalytic activity in liquid-phase oxidation of various organic compounds [1]. In addition, toroidal molybdenum oxide nanoclusters in the form of dispersions of molybdenum blue are successfully used as a precursor for highly dispersed molybdenum carbide [2]. For the controlled synthesis of supported catalysts, it is necessary to study the interaction of nanoclusters with the support surface. The aim was to investigate adsorption of molybdenum oxide nanoclusters on the alumina surface.

Stable dispersions of molybdenum oxide nanoclusters were obtained by reducing a solution of molybdate ions with glucose in the presence of hydrochloric acid. A membrane made of $\alpha\text{-Al}_2\text{O}_3$ was used as a support. Molybdenum blue dispersions were investigated using UV/Vis spectroscopy and electrophoretic light scattering.

The interaction was studied using adsorption; Gibbs adsorption was chosen as a quantitative parameter. Based on the results, we found the monolayer adsorption of molybdenum oxide nanoclusters in the stability region of molybdenum blue dispersions ($\text{pH} \approx 2.0$). At this pH value the molybdenum blue nanoparticles are negatively charged and have the maximum absolute value of ζ -potential.

In the range of pH values, which are characterized by the loss of long-term stability of dispersions ($\text{pH} < 1.0$ or $\text{pH} > 2.8$), monolayer heteroadagulation is observed, followed by nanocluster coagulation. The processing of adsorption data using the Langmuir theory made it possible to estimate the value of the monolayer capacity (A_∞), the adsorption equilibrium constant (K) and surface which is occupied by 1 molybdenum oxide nanocluster (s_0).

Keywords: polyoxometalate, molybdenum blue, nanoparticle adsorption, alumina, supported catalyst, sol-gel method

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Hybrid supramolecular/plasmonic switches based on stimuli responsive host/guest interactions

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Since many years, efforts have been made in the design of stimuli-responsive materials for different analytical and biological applications. One of the strategies developed takes advantage of the stimuli-responsive supramolecular interactions between β -cyclodextrin (β -CD) and its guests such as ferrocene (Fc) to achieve controllable surface binding.

This strategy enables to trigger electrochemically the adsorption and the release of polymers on self-assembled monolayers (SAMs) (Figure 1) [1]. Several levels of control are achievable thanks to supramolecular interactions such as reversibility under electrochemical stimulus, strong binding due to multivalency and high selectivity [1,2]. The strategy was also used with bifunctional linkers (Fc-biotin) to give access to biospecific and reversible immobilization of biomolecules. [3] Finally, the strategy has been extended to the capture and the release of cells using the combination of RGD ligand and β -CD/Fc redox switchable system [4].

The goal of this project is to extend this strategy from surfaces onto nanostructures such as gold nanoparticles or patterned nanoarchitectures. As an example, we propose to use fluorescent probes in combination with host/guest strategy to synthesize hybrid supramolecular/plasmonic switches (Figure 1). By taking advantages of stimuli responsive host/guest interactions as well as strong dependence of fluorescence with the fluorophore/particle distance, we aim to develop luminescent switches allowing wide and reversible fluorescence modulation. The developed switches have potential applications as renewable sensors, multifunctional nanoprobe and mechanofluorochromic materials.

Keywords: Supramolecular chemistry, Host/guest, Hybrid materials, Stimuli responsive materials, Plasmonic switches

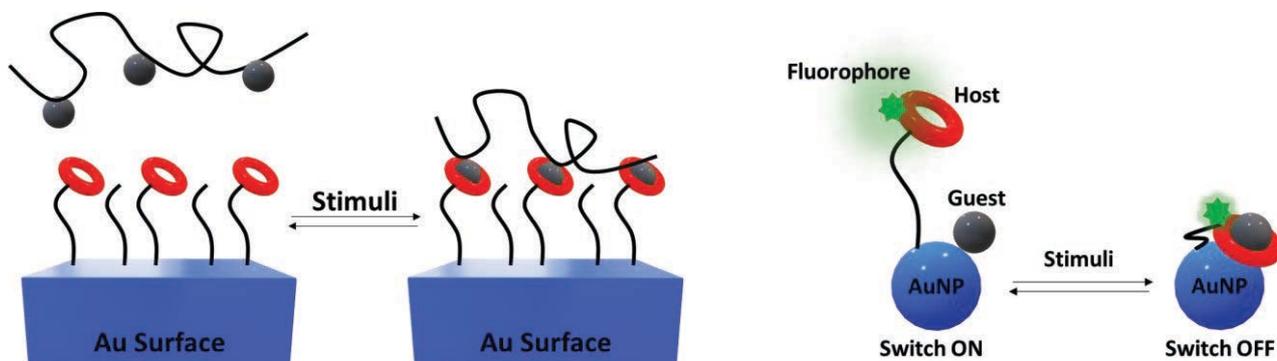


Figure 1: From functional surfaces to multifunctional nanostructures

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Carbon nanodisks decorated with guanidinylated hyperbranched polyethyleneimine derivatives with enhanced antibacterial performance

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It is known that nanostructured carbon-based nanomaterials as well as polymers bearing suitable positively charged groups, such as quaternary ammonium, guanidine groups, arginine groups, etc., exhibit enhanced antibacterial properties [1,2]. Combining the above-mentioned categories, new nanomaterials with excellent antibacterial activities are expected to be obtained. Carbon nanodisks represent an interesting alternative to bulk graphite, produced through the so-called pyrolytic Kvaerner Carbon Black & H₂ (CB&H) process [3].

In this study, acid-treated carbon nanodisks (oxCNDs) were interacted both electrostatically and van der Waals attraction forces as well as through hydrogen bonding with guanidinylated derivatives of 5000 and 25000Da molecular weight hyperbranched polyethyleneimine (GPEI5K and GPEI25K), affording the nanohybrids oxCNDs@GPEI5K and oxCNDs@GPEI25K. Chemical characterization of these GPEI-functionalized oxCNDs revealed successful and homogenous anchoring of GPEIs on the oxCNDs surface which, due to the presence of guanidinium groups, offered them aqueous compatibility, thus exceptional colloidal stability. Moreover, the antibacterial activity of oxCNDs@GPEIs was evaluated against gram- and gram+ bacteria. It was found that both hybrids exhibited an enhanced, dose-dependent antibacterial activity against both test organisms. The obtained IC-50 values were lower compared to oxCNDs, revealing that the attachment of GPEIs strongly induces the antibacterial properties of the hybrids. These improved properties were attributed to the polycationic character of the oxCNDs@GPEIs, which enables the effective interaction of the hybrids with the bacteria membranes, leading to the cell envelope (wall and membrane) damages and finally to the cell lysis as revealed by SEM microscopy (Fig. 1). These results suggest that oxCNDs@GPEIs can be very attractive candidates as antibacterial agents, able to be used for applications in the disinfection industry.

Keywords: carbon disks, guanidinium, hyperbranched polyethyleneimine, antibacterial agents.

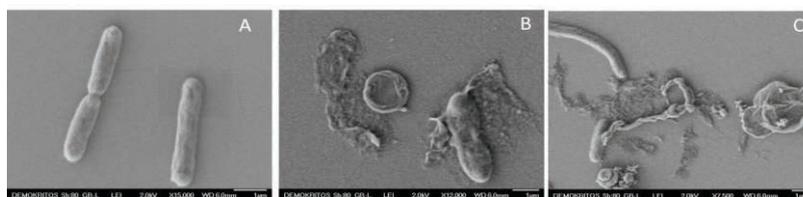


Figure 1. SEM images of *Escherichia coli* bacteria: untreated cells (A) and cells after incubation with oxCNDs@GPEI5K (B) and oxCNDs@GPEI25K (C) at 50% inhibitory concentrations. The scale bar is 1 µm.

Acknowledgements: This research was partially co-financed by Greece and the European Union (ESF) in the context of the project “Strengthening Human Resources Research Potential via Doctorate Research” (MIS-5000432), implemented by the State Scholarships Foundation (IKY) and by GSRT, under the frame of EuroNanoMed III, ANNAFIB project (MIS 5053890).

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EP1.51

Hybrid soft magnetic micro-actuators with thermo-programmable response to external magnetic field

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Hybrid materials that can respond to multiple stimuli are promising materials with the potential to be employed as carrier materials in biological systems [1]. Poly(N-isopropylacrylamide) PNIPAM hydrogels are an excellent option to achieve such systems. Their thermo-responsive nature allows a reversible switch from a swollen to a shrunken state. By adding maghemite nanoparticles and pre-programming their alignment in the matrix of those hydrogels, thermo- and magneto-responsive systems can be designed.

Different microgel shapes with embedded maghemites were synthesized using Particle Replication in non-wetting template (PRINT). Their thermo- and magneto- responsivity were determined through swelling experiments and through the investigation of their response under rotating magnetic fields of different strengths. These systems were characterized by a maximum rotation speed ω_c marking their transition from a synchronous to an asynchronous rotation. ω_c showed to be strongly varying with the temperature (Figure 1a).

When the hydrogels were additionally coated with a metal layer, the restricted swelling of the soft layer enabled the creation of more complex shapes [2-3]. The conformations and polarizability to the applied magnetic field of such shapes can be controlled with the temperature (Figure 1 b). These properties were further utilized to create diverse actuations combining the response to temperature, magnetic field, and light.

Keywords: thermo-responsive, magnetic, actuators, PRINT, smart polymers.

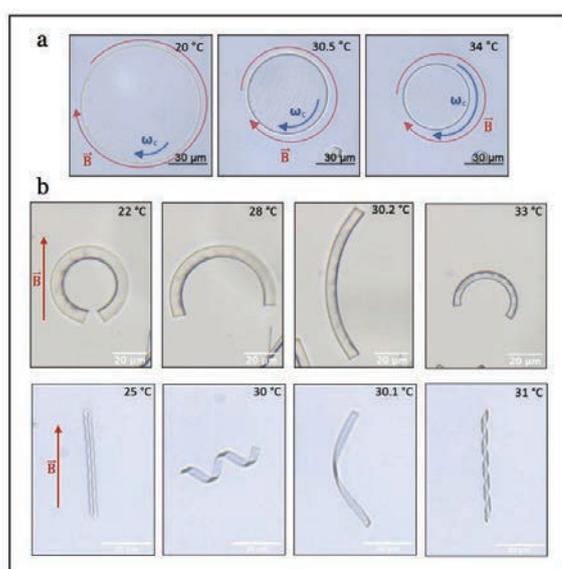


Figure 1: Thermo-responsive and magnetic microgels a) Hybrid disks with tunable response under an applied rotating field b) Loop and helix bilayer structures that change their alignment to the field when the temperature is varied.

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Heteroaggregation of alumina and silica colloids: an experimental and numerical study

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In this study, an original approach coupling experiments and Brownian dynamics simulations was followed to study the heteroaggregation in binary mixtures of alumina and silica colloids, with a high size ratio of 8.5 ($\text{Al}_2\text{O}_3 \sim 200\text{nm}$; $\text{SiO}_2 \sim 24\text{nm}$). The first original target is to bridge the gap between coagulation and dispersion, by examining systematically the effect of the relative concentrations of silica and alumina, in a very wide range, much larger than those previously published. The second one is to study the effect of the volume fraction of solid, which impacts strongly the aggregation mechanism. These two parameters (relative concentration, and solid fractions), are essential for environmental applications such as flocculation of nanomaterials for water treatments processes, or colloidal structuration in suspension for new materials developments. The coagulation or the dispersion are evidenced by sedimentation tests, granulometry, and rheological measurements, supported by zeta potential measurements. Heteroaggregates could be observed by transmission electron microscopy. Thanks to Brownian dynamics simulations, an insight into the very first moments of the heteroaggregation process is proposed, to predict with an extremely good accuracy the heteroaggregates structure obtained in these different conditions.

Keywords: Heteroaggregation; Brownian dynamics simulation; Colloidal suspension; Al_2O_3 ; SiO_2

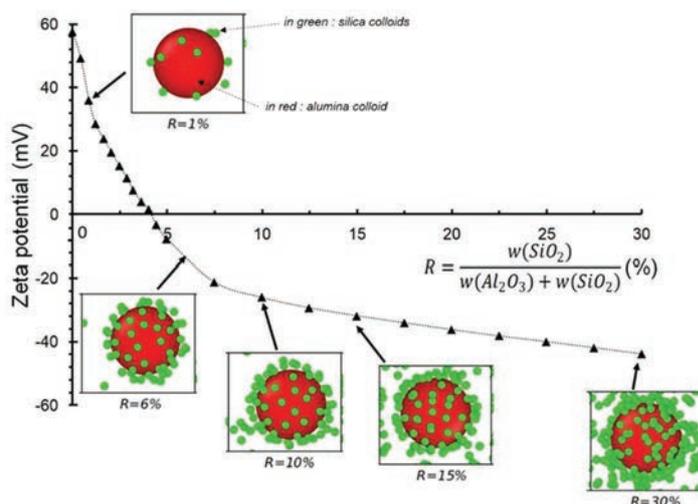


Figure 1. Heteroaggregation of silica and alumina colloids as a function of silica [1].

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EP1.53

Control of Gold Nanoparticle Aggregation by Ion-specific Effects, Concentration and Aging

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Composite materials of inorganic nanoparticles in polymer matrices are employed in various fields: medical technology, catalysis, material engineering, and many more. The combination of both materials offers great versatility in mechanical, optical and chemical properties. The materials can increase each other's strength or cover their drawbacks depending on the situational need, e.g. by structuring or stabilization of the nanoparticles by the matrix.

Gold nanoparticles AuNPs are a prominent and extensively studied representative based on multiple advantages. Firstly, AuNPs exhibit a localized surface plasmon resonance in the visible spectrum, which is sensitive to particle specific parameters (size, shape) and the surrounding (solvent properties, particle distance). Thereby, even small changes of a AuNPs suspension or composite can be monitored optically. Secondly, AuNPs are easily synthesized in different sizes and the shape can be controlled. Thirdly, the gold-sulfur affinity allows covalently bound capping of AuNPs, with the opportunity to control the solubility through the capping molecule.

The long-term goal of our project is the control of particle formation in composite materials by utilizing a stimulus. The assembly of AuNPs in polymer brushes is expected to be influenced by the addition of salt. Controlling the composite formation requires knowledge of the response of the components to the stimulus. Thus, here we investigate the behavior of AuNPs suspensions with two sizes (5 nm, 13 nm) by systematically varying the anion of sodium salts and monitoring the optical response. Figure 1 demonstrates the effect of salt on AuNP suspensions and indicates deviations from the Hofmeister series.

Keywords: gold nanoparticles, ion specific effects, composite formation

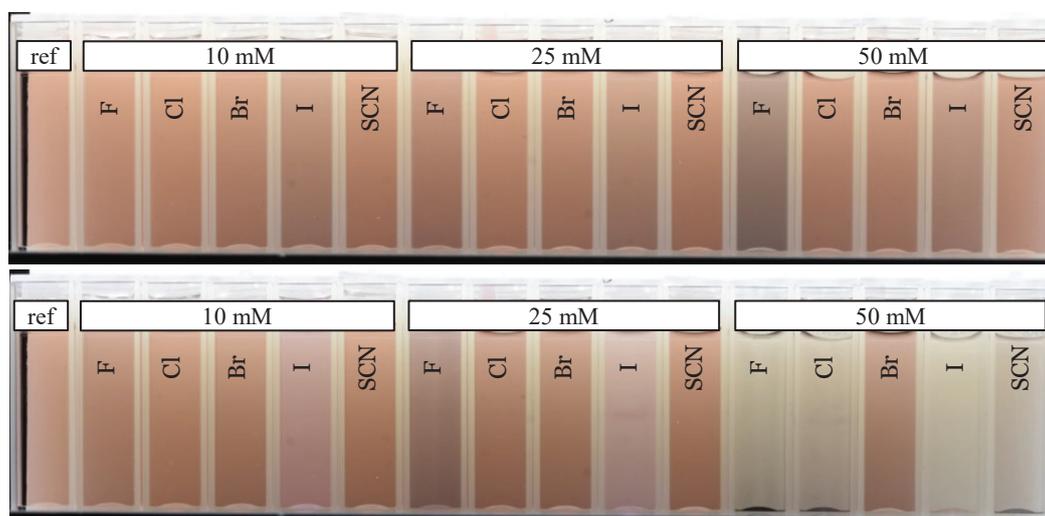


Figure 1. AuNP suspensions with varying salt type and concentration: after mixing (upper) and 12 h later (lower). The samples are ordered with increasing concentration and ion size of the sodium salt (F, Cl, Br, I, SCN).

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EP1.54

Mechanics of Colloidal Supraparticles under Compression

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In recent years, colloidal supraparticles have arisen as an exciting new material platform. They exhibit emergent properties arising from structural arrangement of primary colloidal particles, not found in the individual building blocks. Yet, they also show discrete and size-dependent features inaccessible to bulk colloidal assemblies. However, the mechanical stability of colloidal supraparticle has received little attention, even though it is the key prerequisite for any potential applications.

Here, we provide a comprehensive understanding of the mechanical properties of colloidal supraparticles with well-defined structural features. We provide a predictive scaling theory relating the fracture stress, the deformation resistance and the work of deformation to the relevant geometrical parameters of the colloidal supraparticles. We then demonstrate how the mechanical response depends on – and can be controlled by – the interplay between primary particle material and cohesive interparticle forces by in-situ measurements in vacuum inside an SEM chamber and by replacing polymeric particles with silica particles.

Keywords: supraparticles, nanomechanics, nanoindentation, fracture, deformation

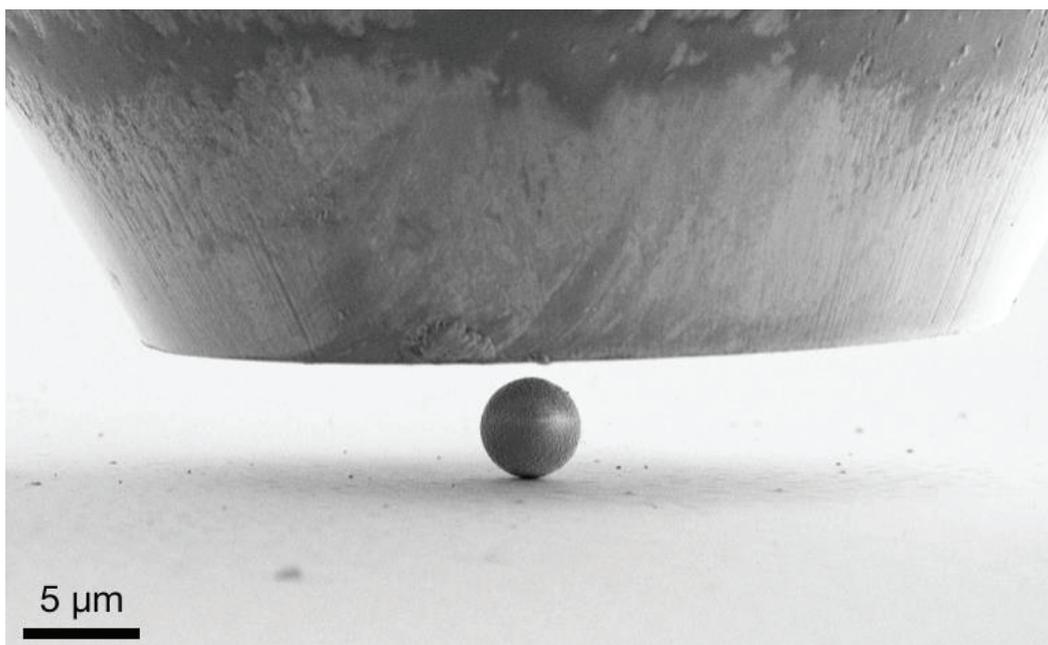


Figure 1. Colloidal supraparticles under compression.

Surface-driven green synthesis of polyaniline-oxide nanocomposites for environmental remediation

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PANI-materials were recently applied to pollutant abatement owing to PANI environmental stability and sorption capabilities [1]. However, the conventional PANI synthesis involves toxic reagents, hazardous by-products and large amounts of inorganic waste. As an alternative, we developed a two-step green procedure starting from benign reactants ((N-(4-aminophenyl)aniline and H₂O₂) and initiated by UV-irradiated semiconductors [2] (Figure 1a). The prepared PANI-composites presented a nanorod morphology yielding a large surface area and a crystallinity degree higher than the PANI-materials reported in the literature. These features were shown to be related to a surface reaction mechanism. ATR-FTIR, XPS and ζ -potential measurements (Figure 1b-1c) highlighted the formation and slow growth of PANI-oligomeric chains at the photocatalyst surface upon UV-irradiation. The ensuing addition of H₂O₂ in stoichiometric amounts promotes the polymer chains growth at the oxide surface, leading to highly porous and large surface area nanocomposites. Conversely, when H₂O₂ is adopted in excess, homogenous phase reactions take place, overshadowing the surface-driven pathway, and giving rise to composites more amorphous and with compact morphology [3]. The role of the oxide material was investigated by adopting photocatalysts of different nature and surface areas. The tailored morphology of the nanocomposites resulted in a fast and complete removal of both organic dyes and heavy metals, also in complex water matrices. The adsorption mechanism was investigated also via adsorption isotherms and kinetics studies. Consecutive tests without regeneration treatments showed promising results even in simulated drinking water. The recovery of the adsorbed molecule was obtained upon eco-friendly conditions, opening the door to its reusage in a circular economy perspective.

Keywords: polymer, nanostructured material, environmental remediation

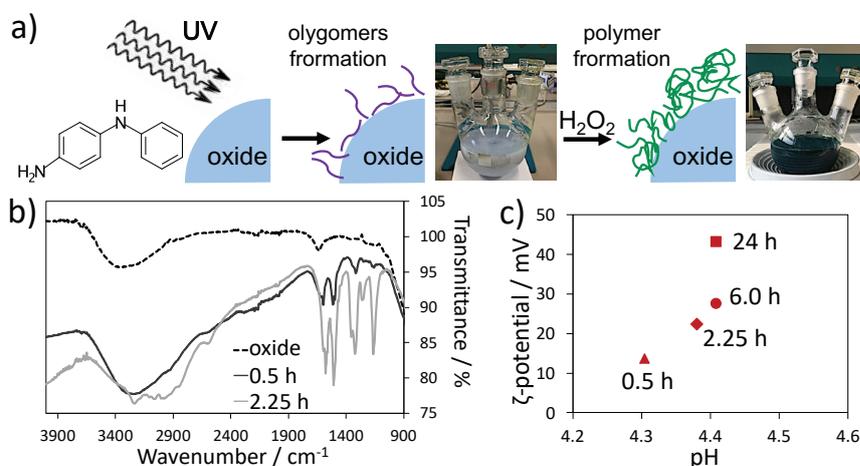


Figure 1. a) Scheme of the two-step synthesis of PANI nanocomposites, b) ATR-FTIR spectra and c) ζ -potential at spontaneous pH of the product isolated upon irradiation for different time lengths, before H₂O₂ addition.

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Synthesis of Inverse Patchy Particles

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Colloidal structures prepared by self-assembly find applications in photonic devices, nanoscale electronics and miniature diagnostic systems. This colloidal self-assembly enables easier and cost-effective fabrication compared to standard fabrication methods based on top-down approaches such as optical lithography. However, this bottom-up approach is limited by the available building blocks that are mostly spherical and by the interactions between them, which are mostly isotropic. To expand the range of building units, one emerging approach is to engineer the surface of the colloidal particles with “patches” to confer particles predetermined “instructions” for assembly [1].

In this work, we focus on the synthesis of inverse patchy particles [2], that consist of charged patches that repel each other and that are attracted by the rest of the particle. We will first show that binary bipods, which consist in a silica particle surrounded by two polystyrene nodules, can be produced with a yield higher than 70% by seeded dispersion polymerization. The dissolution of the PS nodules followed by the regioselective functionalization of the patches allowed us to produce Inverse Patchy Particles in large quantities (See Figure 1.a). By tuning the experimental conditions, particles with three well-positioned patches were also obtained (See Figure 1.b).

Keywords: Colloids, Charge, Patches, Seeded Polymerization

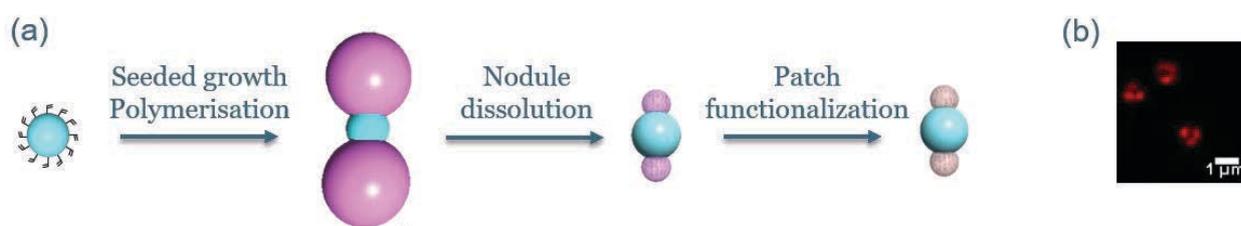


Figure 1. (a) Scheme of the synthesis of Inverse Patchy Particles through seeded dispersion polymerisation, (b) Confocal image of three-patch particles.

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Sideways propelled micro-rods in 2D confinements: cargo transport

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Manipulation of micron-sized objects is a challenging but necessary task for a range of applications, such as sensing, moving microscopic cargo, or transporting active pharmaceutical ingredients in the human body. A promising approach is to exploit self-propelling micron-sized particles, which are capable of moving without an applied external force due to self-generated field gradients. The efficiency of collection and transport of cargo by such self-propelled particles can be drastically increased by using specific Janus geometries away from those achieved for classical spherical particles. In this paper, we present an example of a Janus coating that allows a micro-rod to propel perpendicular to its long axis, vastly increasing the area swept from a model cargo [1,2]. The dynamics of micro-rod motion and cargo transport in 2D confinements have been studied for two specific cases: close to a solid wall, and trapped at the interface between two immiscible fluids. Our findings reveal the possibility of a one-by-one collection of model spherical cargo that at the same time reduces the rod velocity, while the drag force on the eventually pyramidal shaped micro-rod-cargo aggregate remains unaffected by the attached particles.

Keywords: Janus particles, self-propulsion, active matter, interfaces

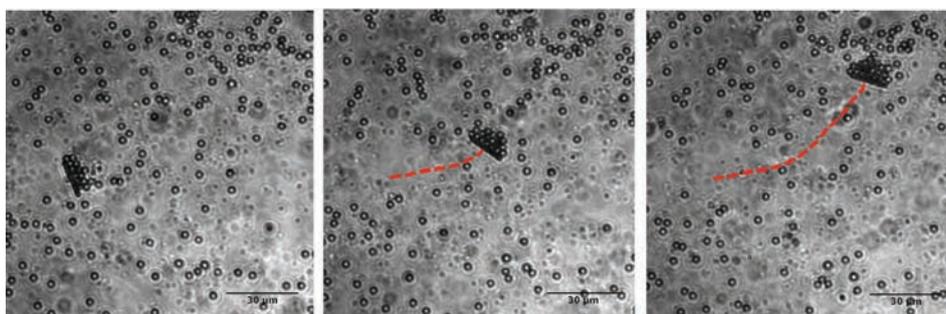


Figure 1. Sideways propelled Pt/Au rod collecting polystyrene cargo particles ($\sim 0.02w/v\%$) in aqueous hydrogen peroxide (2.8 wt.%), scale bar is 30 μm [2].

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EP1.58

Copper oxide nanocubes wrapping metals by microwave synthesis

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Copper (I) oxide (Cu_2O , cuprite) is one of the most interesting copper oxide phases for photocatalysis. However, fast recombination and stability remain an obstacle, as Cu_2O can be easily oxidized or reduced by the photogenerated carriers. By doping Cu_2O with ions or combining it with metal or semiconductor nanoparticles (NPs), higher photocatalytic activities have been achieved. Here we report for the first time on noble metal- Cu_2O heterostructures using a microwave-assisted synthesis.

Microwave-assisted chemistry is becoming attractive in all areas of synthetic chemistry; it is fast, efficient in terms of energy consumption and environmentally friendly. Microwave-synthetic routes are also gaining importance in colloidal chemistry, including the fabrication of multimaterial or metastable alloy nanoparticles. I will report on a universal microwave-assisted two-step synthesis to fabricate noble metals [Au, Ag, Pd, Pt]/ Cu_2O heterostructures in a short time. By using Au, Ag or Pd, nanoparticles as seeds, the final material consist of Cu_2O nanocubes wrapping those metal particles. This was achieved by benefiting from the MW selective heating, the metal nanoparticles in the reaction media act as a nucleation sites for the Cu_2O to grow. Interestingly, no size refining step was introduced before size analysis of the obtained monodispersed nanocubes. Moreover, the reproducibility and scalability of the process could be demonstrated. Furthermore, we have proposed the synthetic parameters that key to good quality final material such as the molar ratio of metal nanoparticles to copper precursor, the molar weight of the polymer-stabilizer, the two-step order and the size of the metal particle. In fact, when smaller metal particles ($< 5 \text{ nm}$) were used as in the case of Pt, the metal NPs decorated the Cu_2O nanocubes sides.

Keywords: copper oxide nanocubes, metal nanoparticles, core-shell heterostructures, microwave-assisted chemistry

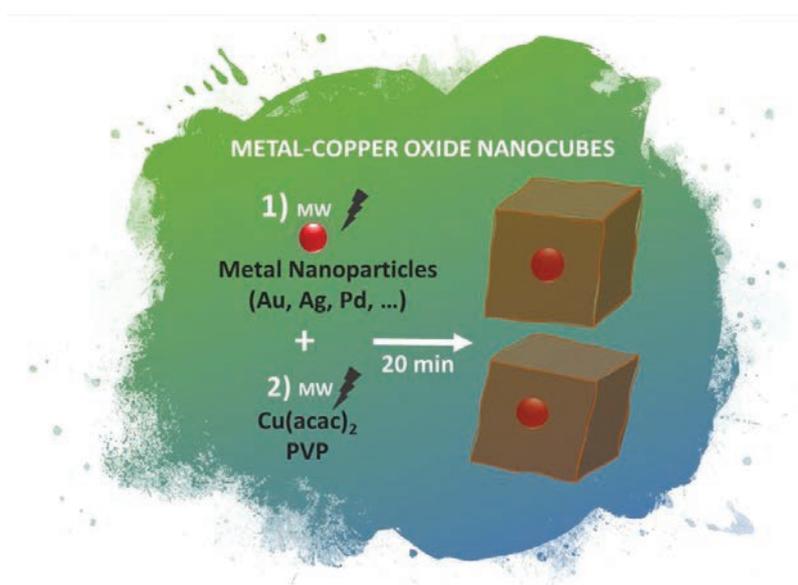


Figure 1. Schematic representation of the two-step microwave-assisted synthesis of the noble metal- Cu_2O heterostructures.

EP1.59

Single and camera-based method to determine the amplitude and phase of electrophoretic mobility of individual particles

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Electrophoresis is a frequently used technique to characterize the surface charge of colloidal particles. In the last decade, applications in colloidal science increasingly rely on measurements on a particle-to-particle basis to complement the traditional ensemble-based methods. Advantages of such a particle-to-particle approach are that polydisperse samples can be accurately characterized and that individual particles and interactions with their environment can be studied in detail. A limiting factor in the accuracy of such measurements is the measurement error due to electroosmosis. In different techniques, either a theoretical model or pre-calibration is used to compensate for electroosmosis, or measures are taken to reduce the electroosmosis [1].

In this work we present a method to accurately measure the electrophoretic mobility, including its phase, of individual microparticles. In our approach, electroosmosis is suppressed by applying an AC voltage with a high frequency while measuring at the mid-plane of the microfluidic channel. The method enables to extract the amplitude and phase of individual particles in a single experiment. A sinusoidal electric field is generated across the microchannel and the resulting motion of individual particles is recorded with a high-speed CMOS camera. In post processing, a tracking algorithm is used to determine particle trajectories. Next, mobilities are estimated by performing a Fourier analysis of the resulting non-uniformly sampled particle positions.

The accuracy of this method is experimentally evaluated and compared with a commercial apparatus for polystyrene microspheres in water. The method is further demonstrated on a range of particle materials and particle sizes, and for a mixture of positively and negatively charged particles. Lastly, a streptavidin-biotin system, representing a model system for a receptor/ligand binding, is studied to give an indication of the feasibility of our technique to investigate binding events.

Keywords: electrophoresis, electroosmosis, mobility, zeta potential, particle tracking.

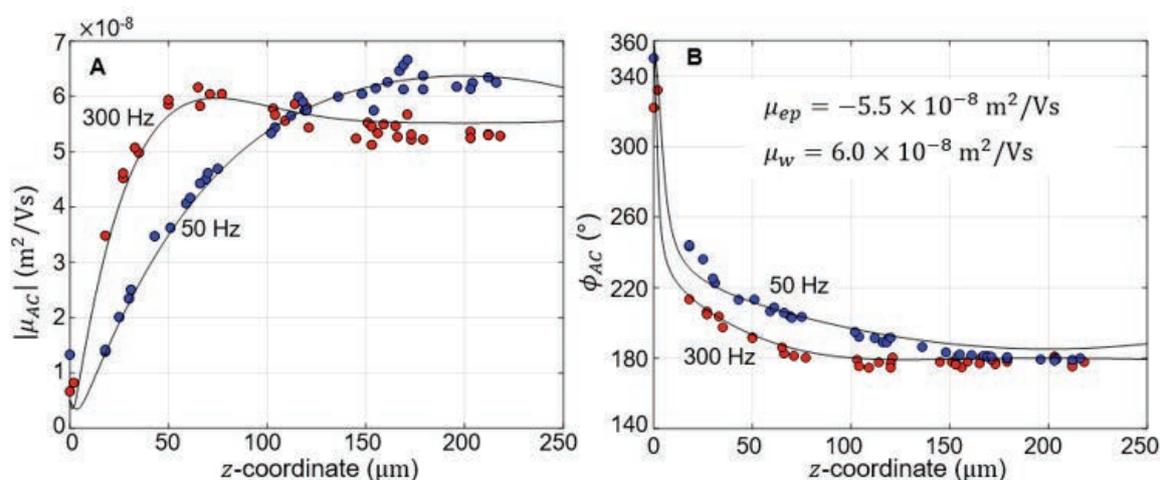


Figure 1. Amplitude $|\mu_{AC}|$ and phase ϕ_{AC} of the AC mobility of 1.9 μm polystyrene microspheres as function of the position (z-axis) in the 400 μm high channel.

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Ultra-Enhanced Antibacterial Action of Copper Oxide Nanoparticles with Self-Grafting Surface Functionality

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Copper oxide nanoparticles (CuONPs) have been widely recognized as good antimicrobial agents but are heavily regulated due to environmental concerns of their post use. In this work, we have developed and tested a novel type of formulation for copper oxide (CuONPs) which have been functionalized with (3-Glycidyloxypropyl)trimethoxysilane (GLYMO) to allow further covalent coupling of 4-hydroxyphenylboronic acid (4-HPBA). As the boronic acid (BA) groups on the surface of CuONPs/GLYMO/4-HPBA can form reversible covalent bonds with the diols groups of glycoproteins on the bacterial cell surface, they can strongly bind to the cells walls resulting in a very strong enhancement of their antibacterial action which is not based on electrostatic adhesion [1]. We demonstrate that the CuONPs with BA surface functionality are far superior antibacterial agents compared to bare CuONPs. Marked increase of the CuONPs/GLYMO/4-HPBA antibacterial action was observed compared with the bare CuONPs [2]. We demonstrated that the cytotoxicity of CuONPs/GLYMO/4-HPBA can be controlled by adding glucose in the media which competes for the BA-groups on CuONPs.

We also fabricated surface-rough mesoporous silica nanoparticles ('ghost' SiO₂NPs) by using composite mesoporous copper oxide nanoparticles ('host' CuONPs) as templates which allowed to copy their surface morphology [3]. The 'host' CuONPs used as templates, had a very high antibacterial effect, with or without functionalization. The BA-functionalized 'ghost' SiO₂NPs showed significant antibacterial effect compared to smooth SiO₂NPs of the same surface coating and size. We attribute this to the 'ghost' SiO₂NPs mesoporous surface morphology which mimics those of the original mesoporous CuONPs used as templates for their preparation. We envisage that the 'ghost' SiO₂NPs effectively acquires some of the antibacterial properties of the 'host' CuONPs, with the same functionality, despite being completely free of copper.

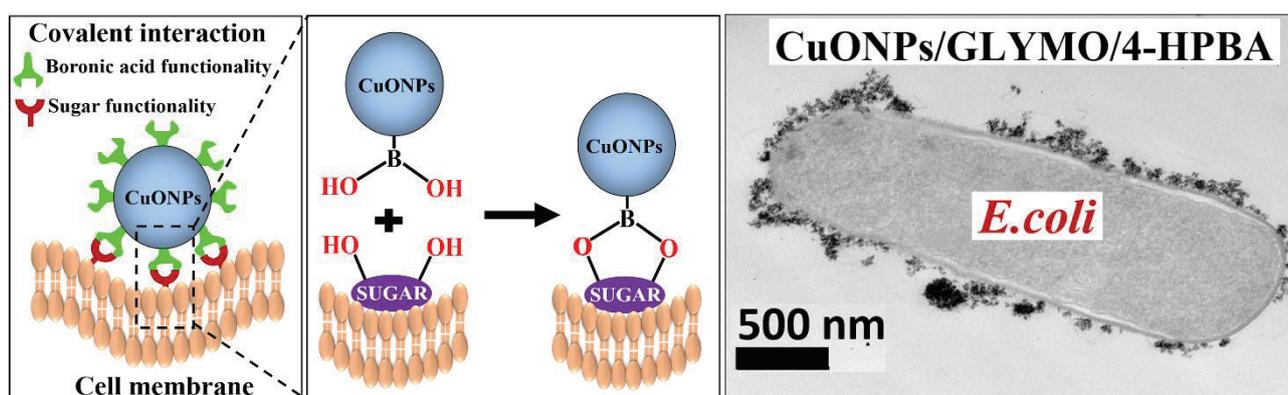


Figure 1: Self-grafting CuONPs with HPBA surface functionality attach covalently to bacterial cells.

Keywords: antibacterial nanoparticles, copper oxide, E. coli, R. rhodochrous, hydroxyphenylboronic acid, carbohydrates

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EP1.61

Mesoporous foams and ZnO inverse opals obtained from polystyrene nanoparticles with adjustable size and polydispersity

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Using polymer particle templates to prepare porous materials is not only a cost-efficient strategy but offers the possibility of pore size and morphology control by the particle size and polydispersity. In this study, we investigated the influence of the sodium dodecyl sulfate (SDS) concentration utilized in the emulsion polymerization of styrene on both the properties of the obtained polystyrene (PS) nanoparticles and the morphology of the closed-packed arrangements formed by these particles. Combining dynamic light scattering, small-angle neutron scattering and scanning electron microscopy (SEM), we found a strong decrease of the particle radius with increasing SDS concentration (Fig.1 left) which levels off at the same concentration where the polydispersity increases suddenly. Studying the interfacial tension between aqueous SDS solutions and styrene allowed us to link this increase to the critical micelle concentration (CMC). The closed packed arrangement of PS nanoparticles obtained via drying were investigated by small-angle X-ray (SAXS) and SEM. Both techniques show that the increase in particle polydispersity induces a loss in packing order, while the SAXS analysis confirmed that polydisperse particles allow for a more densely packing. Subsequently, these templates were used for the preparation of novel mesoporous PS and ZnO inverse opals, which are promising tailor-made supports for catalytic applications. The mesoporous PS was obtained by an optimized NF-CID-procedure yielding a highly porous material with micrometer-sized spherical pores surrounded by extended open-cellular regions of mesopores ($R_{\text{pore}} \approx 25$ nm) (Fig. 1, right, top) [1]. Mesoporous ZnO inverse opals were obtained through mineralization of closed-packed PS particle templates via chemical bath deposition (CBD) method, followed by solvent extraction of the template particles to obtain the inverse replica of the closed-packed PS nanoparticle arrangement (Fig. 1, right, bottom) [2].

Keywords: Emulsion polymerization, Porous polystyrene, Inverse opals

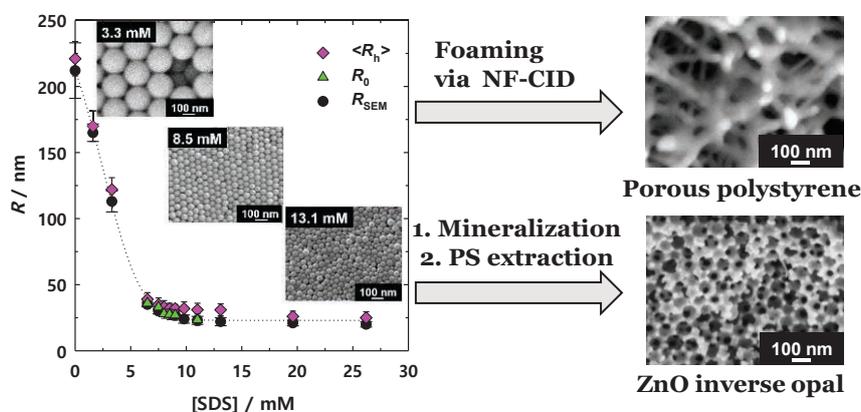


Figure 1. Varying the SDS concentration in the emulsion polymerization of styrene, the particle properties and their close-packed assemblies can be adjusted (left). The latter can be utilized to produce porous polymers following the NF-CID principle (right, top) [1] or ZnO inverse opals via the CBD method (right, bottom) [2].

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Investigating Emulsion Destabilisation and Dynamics under Microgravity Conditions by Diffusion Wave Spectroscopy

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Diffusion Wave Spectroscopy (DWS) is a powerful optical technique providing information on the dynamics of disperse phase in colloidal systems. Its application to emulsions allows investigating structural properties and their time evolution as a consequence of the aging and destabilisation. Experiments performed under microgravity conditions allows decoupling the single mechanism responsible for the emulsion destabilisation from creaming, which can be therefore investigated and characterised with a superior accuracy. Within the international project EDDI (Emulsion Dynamics and Droplet Interface), in a first set of experiments to be performed onboard the International Space Station, we are going to investigate the coalescence of droplets in semi-concentrate and concentrate emulsions and of its effects on the aging and on the dynamics of droplets.

Here we will describe the concept of these experiments and of the utilisation of DWS in the experimental apparatus (the Soft Matter Dynamics facility) purposely developed by the European Space Agency. Results from the ground preparation of these experiments will also be presented.

Keywords: emulsions, Diffusion Wave Spectroscopy, microgravity

Acknowledgements: European Space Agency: MAP project “Emulsion Dynamics and Droplet Interfaces – EDDI”.

EP2.2

Synthesis of Multicomponent Polymer Nanoparticles in Microfluidic Emulsion Droplets

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Microfluidic devices with microchannels from tens to hundreds of micrometers are becoming more and more popular for performing complex reactions with supramolecular components in microemulsion droplets of confined multiphase flows [1,2]. Such an approach allows for controlling reaction conditions by varying operation parameters of microfluidic devices and, thus, sizes of droplets and their residence times in microchannels.

In this work, we used microfluidic flow focusing and T-sensor devices to generate ordered microemulsions and use the emulsion droplets as the reactors for synthesis of polymer nanoparticles in varying conditions of microfluidic flows. The polymers we used in this work were polydiallyldimethylammonium chloride (synthetic polymer) and hydroxyethyl cellulose (natural polysaccharide).

The first step was to generate emulsion droplets of different sizes. The key dimensionless parameter to evaluate droplet formation in microchannel was the capillary number; its values were changed by using microchips with different geometries, varying flowrates and changing organic solvents. The reproducible droplets were generated in the size range of 40-200 μm . Fig. 1 demonstrates formation of a microfluidic droplet inside a 50 μm wide channel.

The next step was to perform complexation of the synthetic polymer with the oppositely charged surfactant and cross-linking of polysaccharide with calcium chloride in microemulsion droplets. Polymer aggregates in the size range of 10-200 nm were synthesized in microfluidic multiphase flows. A correlation between the flow parameters and the sizes of polymer aggregates was revealed.

Synthesized polymer nanoparticles can be used as containers for drug delivery systems or photosensitive agents such as quantum dots.

Keywords: microfluidics, complexation, polyelectrolyte, microdroplets

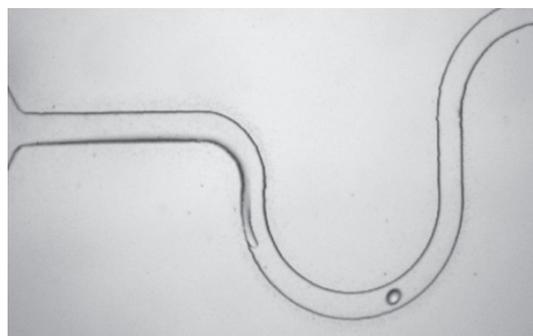


Figure 1. Formation of a 40 μm aqueous container for the hydroxyethylcellulose cross-linking reaction.

Acknowledgements: the project is performed with the financial support of the UMNIK grant awarded by the Russian Foundation to Assistance of Small Innovative Enterprises, Agreement 0064673.

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EP2.3

Controlled Destabilization of Pickering Emulsions

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In this contribution, we present experimental study of formation of highly stable emulsions and their controlled destabilization. We first use a mixture of oppositely charged colloidal particles and polyelectrolytes to obtain emulsions with outstanding storage stability. We show that it is possible to tune (i) the mean diameter of the emulsions and (ii) arrangement of particles on the surface of the drops by manipulating the concentration of polyelectrolyte and other process variables. Further, our experiments revealed that polyelectrolyte can also be used for controlled de- stabilization of already formed emulsions. We discuss results of in-situ video microscopy observation of the micro-structural changes during de-stabilization. The generality of this approach and the mechanism of destabilization are presented.

Keywords: Pickering Emulsion, De-stabilization, Polyelectrolyte, Microstructure

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EP2.4

Investigation of nano-structure and thermoreversibility of microemulsions using small angle neutron scattering

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Due to their ability to form diverse structures via self-assembly at appropriate conditions, microemulsions (MEs) are a subject of investigation for various applications in addition to immense fundamental interest. The motivation to study MEs of aliphatic, aromatic and a mixture of oils (surrogates) comes from designing and understanding multi-component model systems. We present small angle neutron scattering (SANS) investigation of thermally induced microstructural changes in the water-in-oil microemulsions (MEs) at fixed water to surfactant ratio and various volume fractions of dispersed phase. The core structure of the MEs was studied by substituting water with D₂O and enhancing the contrast between the dispersed and the continuous phase. The SANS data was recorded at six different temperatures ranging from 20 °C to 50 °C and volume fractions from 5 to 20% for all the samples. Furthermore, MEs were prepared by considering three different oils (aliphatic, aromatic and a surrogate which is a mixture of the two in the ratio of 9:1) to understand the effect of oil structure on the microstructure and interactions. Analysis of the SANS data from dilute systems showed the presence of spherical or cylindrical structures depending on the type of oil used in ME formulations. For all three systems, the size of the spherical micelles for aromatic MEs and the long axis of the cylindrical micelles of aliphatic and surrogate MEs, is found to increase with temperature, consistent with previous works [1]. For the MEs with aromatic oil phase, inclusion of hard sphere structure factor for low volume fraction (~5%) was necessary in addition to that at higher volume fractions. Finally, the thermoreversibility of the ME formulations will also be discussed.

Keywords: microemulsions, small angle neutron scattering (SANS), microstructure, hard-sphere interactions

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EP2.5

Enzymatic modification of triglycerides in conventional and surfactant-free microemulsions and in olive oil

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Dietary triglycerides (TAGs) and their stereospecific structure play a decisive role in human lipid metabolism. TAGs are hydrolyzed into 2-monoacylglycerol and free fatty acids by pancreatic lipase in the intestine, and the resulting products are absorbed via the intestinal lumen. sn-2 palmitic glycerides affect the amount of fat and minerals absorbed. Moreover, the position of fatty acids on triglycerides plays a major role in the functionality of fats in food products.

Vegetable oils such as palm and coconut oil, commonly used in the food industry, contain palmitic acid located predominantly at sn-1,3 positions. Unlike other vegetable oils, olive oil is rich in oleic and palmitic acids which makes it an ideal raw material for TAGs synthesis with palmitic acid at sn-2 position.

In the fat and oil industry, numerous enzyme-based processes are applied and among them lipases are used to replace conventional procedures. With respect to positional specificity towards triglycerides, lipases vary from completely non-specific, to 1,3-specific or weakly specific. Interestingly, very few lipases have been reported to hydrolyse the 2-positioned ester bond of triglycerides.

In this study, TAGs rich in 1,3-dioleoyl-2-palmitoylglycerol (OPO) were synthesized through a top-down process. As a first step, interesterification reaction was conducted with the use of a variety of commercial available lipases (free and immobilized) and triolein and palmitic acid as substrates in order to confirm the enzyme's activity and stereoselectivity. Different parameters were tested while special attention was given to the environment including conventional and surfactant-free microemulsions.

The use of olive oil as the substrate is the final step of the present study, since it affects the properties, the nutritional value and the cost of a wide range of food products.

Keywords: Triglycerides, Olive oil, Lipase, Monopalmitate

Acknowledgements: We acknowledge support of this work by the project "ELAION" MIS 5040301), which is co-financed by the European Union and national funds through OP. WESTERN GREECE 2014-2020 in the framework of Action "Supporting Businesses for Research Projects" (project code: ΔEP6-0021436)

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EP2.6

Surfactant – solvent Chemical Optimization

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The discussion of thermodynamic stability and packing of self-assembled surfactant films often focuses on the air-water surface. For aqueous solutions, surfactant- monolayer efficiency can be understood in terms of the extent of lowering of air-water surface tension. Surfactants with sufficiently long and significantly branched hydrophobic fragment(s) are found to stabilize air-water interface to a greater extent [1]. Can surfactant-film stability be similarly generalized at more complex nonpolar solvent (or oil)-water interfaces - considering air to be a nonpolar solvent with zero dielectricity and polarizability? In systems of surfactant molecules at oil-water interfaces, chemical structural variation can now be explored for both the surfactants and oils (ex. hydrocarbon solvents) and there have been indications that the extent of maximum interfacial film stability might be linked to surfactant-solvent chemical structure matching [2-4]. This work investigates the underlying principles inherent to surfactant-solvent chemical structures that lead to optimization of such systems for highly efficient interface-films. The fundamental understanding will benefit designing thermodynamically stable, high performance additive-solvent systems.

Keywords: Chemical Structures, Colloids, Microemulsions, Interface, Surfactants

Acknowledgements: Commonwealth Scholarship Commission, FCDO, UK

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EP2.7

High Temperature Surfactancy for Cleanliness in Modern Engines

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Multicomponent water/oil/surfactant mixtures display complex phase behaviour and variations in structure upon changes in thermodynamic conditions and in system compositions. Stable single-phase microemulsions can be formed when these components are mixed at the right ratios, alongside appropriate thermodynamic conditions. Since their stability is influenced by temperature and pressure, the effects of these parameters need to be explored and understood to develop systems suitable for certain industrial applications; such as engine oil additives, where they are used for cleanliness and lubrication inside modern internal combustion engines (ICEs), which operate under extreme temperature and pressure (approximately 250°C and 100 bar).

Two approaches for normalising for the effects of thermodynamic conditions are being explored. Studies report systems with reduced temperature sensitivity composed of mixed non-ionic and ionic surfactants - due to their opposite behaviour as a function of temperature [1-4]. Phase behaviour experiments have been performed on model anionic AOT and non-ionic C_iE_j surfactants; mixed systems have been prepared and their temperature sensitivity examined.

Interest has also been shown in the role density plays in phase behaviour of complex systems [5-6]. It has been reported that linear hydrocarbons exhibit similar densities at extreme temperature and pressure and at RTP [7], which suggests T and P offset one another. The question arises – to what extent does the chemical structure of the components affect the system behaviour, and whether density can be used as a universal factor for its normalisation.

This research aims to gain a deeper understanding of how surfactants self-assemble in non-aqueous media (dry reversed micelles and water-in-oil microemulsions); and how their behaviour is affected by changes in temperature and pressure (separately and combined), particularly when they reach values found in ICEs.

Keywords: surfactants, microemulsions, temperature, pressure

Acknowledgements : The researcher thanks Infineum for PhD sponsorship and Professor Julian Eastoe for his advice and support throughout the project.

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EP2.8

Origin of the extremely high elasticity of bulk emulsions, stabilized by Yucca Schidigera saponins

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We found experimentally that the elasticity of sunflower oil-in-water emulsions (SFO-in-W) stabilized by Yucca Schidigera Roezl saponin extract, is by >50 times higher as compared to the elasticity of common emulsions [1]. We revealed that strong specific interactions between the phytosterols from the non-purified oil and the saponins from the Yucca extract lead to the formation of nanostructured adsorption layers which are responsible for the very high elasticity of the oil-water interface. This elastic layer, combined with strong attraction between the neighboring emulsion drops, leads to synergistic effect with resulting extremely high emulsion elasticity. Remarkably, this extra high emulsion elasticity inhibits the emulsion syneresis even at 65 vol% of the oil drops – these emulsions remain homogeneous and stable even after 30 days of shelf-storage. These results demonstrate that the combination of saponin and phytosterols is a powerful new approach to structure oil-in-water emulsions with potential applications for formulating healthier functional food. The clearly shown in the current study synergism between high interfacial elasticity and drop-drop adhesion is rather general and can be used as a universal approach to produce highly elastic emulsions and foams [1-2].

Keywords: Saponin, Phytosterols, Non-purified oil, Emulsion, Emulsion elasticity, Drop aggregation, Drop-drop adhesion, Interfacial elasticity

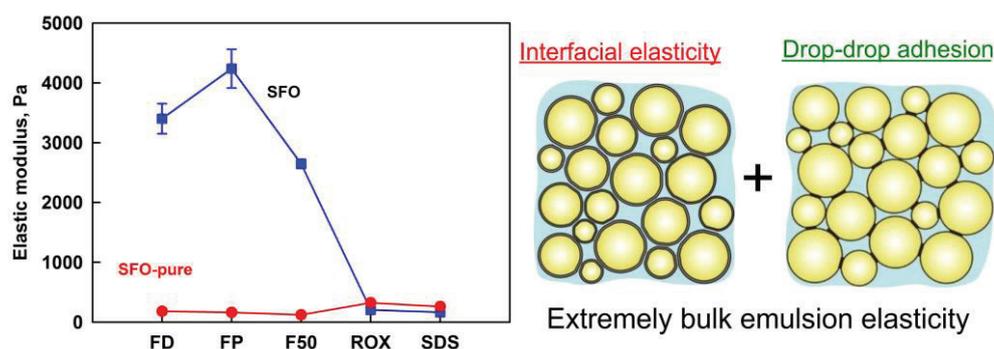


Figure 1. Bulk elasticity of emulsion stabilized with Yucca saponins.

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EP2.9

Foamability and foam stability of mineral oils

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Lubricating oils find applications in numerous industries. They consist of main oil and modifying components which ensure the application purposes of the system. Some of the used additives could stabilize bubbles, causing serious problems for engines and gearboxes, like oxidative and thermal oil degradation. From this point of view, it is important to control the process of foam stabilization in such non-aqueous systems.

The non-aqueous foams properties are harder to be analysed compared to the aqueous foams, due to the low values of the oil-air interfacial tension, thus leading to weak effect of surfactants on surface tension. Also, there is no electrostatic stabilization in foam films, meaning that other factors, such as steric interactions and surface rheology, are important for foam stabilization. The aim of the current study is to analyse the effect of several additives on the foaming properties of model mineral oils which could represent the main trends for more complicated systems of lubricating oils. We analysed the systems' foamability and foam stability at several temperatures and also performed model experiments with single foam films.

We found that the foamability increases in the order hexadecane < light oil < heavy oil and this order is explained by two effects: (1) much lower viscosity of hexadecane as compared to light and heavy oils which leads to faster foam film thinning for hexadecane and (2) the presence of long chain alkanes in light and heavy oils which might create steric repulsion between the foam film surfaces, as seen in the foam film experiments. Two of the tested additives are able to improve foamability and foam stability of heavy and light oils, without changing the foamability and foam stability of hexadecane. Good correlation between the foam stability and the stability of vertical foam films is observed with all systems studied.

Keywords: foaming, foam stability, model experiments

EP2.10

A Green Tattoo Ink in Asia and in Europe: a comparative analysis

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Tattoo practice is on the rise worldwide, including eastern countries [1]. In terms of regulations, only a few countries in Europe have issued a legislation on tattoo and permanent make-up inks composition, whereas Asian regulations, to the extent where we had access, are more focused on the practice of tattoos, rather than on ink composition [2]. In this framework, it appears that the same producers (such as Eternal Ink) has bottles of the same ink with different labels, for European and Asian markets, and more specifically with the indication *For Asia Market only* on the one destined to the Asiatic market. This triggered our comparative study of a green tattoo ink, the *Green Concentrate* by the *Eternal Ink*, to determine potential differences (Figure 1). The investigation has been carried out in order to explore all components of a tattoo ink, i.e. the pigment(s) and the vehicle, including additives and possible metal pollutants.

It turns out that the major pigment is, in both cases, the PG7, i.e. the hexadecachloro copper phthalocyanine, C.I. 74260, restricted in Europe [3], though it is reported to be PG36, i.e. the hexabromodecachloro copper phthalocyanine C.I. 74265 on the EU bottle. Toxic cyclic siloxanes are also present [4] as well as hydrocarbons. In both cases carcinogenic components have been detected and metals above the allowed threshold. Some differences are detected in the type of hydrocarbons present, sometimes characterized by different toxicity. Furthermore, an additional yellow ink is suspected to be mostly present in the Asian ink.

Keywords: tattoo ink, composition, regulations, Asia vs. European markets

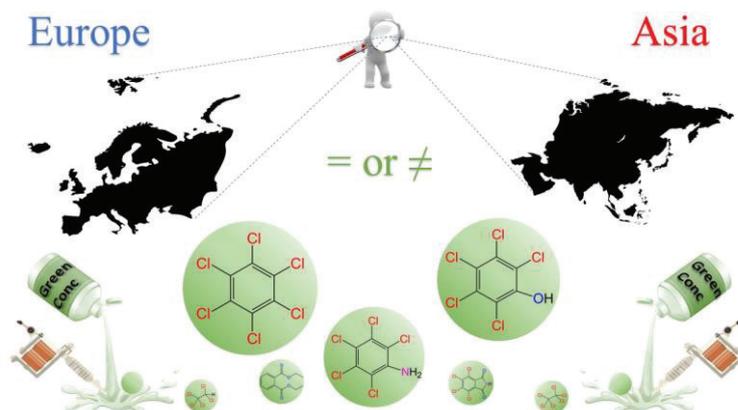


Figure 1. A comparative investigation of a green tattoo ink for Asian and European markets by the same producer

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The role of oscillating piston geometrical features on the performance of a miniature emulsification device

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An innovative miniature emulsification device in which shear is generated by periodic movement of a piston up and down inside a rectangular cell, has been developed. The aim of this study is to test five different piston plate geometries, dictating different width and height of the gap between the plate and the cell walls. Emulsification experiments have been conducted and a wide range of piston stroke frequency and emulsification time has been tested. The oil volume fraction and the surfactant concentration are kept the same for all experiments and they are such that the phenomenon of coalescence between oil droplets is eliminated. Emulsion stability is registered by two methods. Microscopy images analysis and phase separation observations have been used to estimate the resulting droplet size distribution. The combined information from these techniques is necessary in order to register the broad size range of droplets. A semiquantitative analysis of the flow field in the gap reveals that droplet breakage occurs at the laminar boundary layers developed between the piston and the cell walls and allows characterization of this field. The analysis of experimental results demonstrates that four of the five tested piston plates are appropriate for emulsification regarding the generated droplet size distribution. The final choice among them requires additional criteria, e.g. input energy requirements.

Keywords: oscillating piston, small volume, droplet size distribution, droplets breakage

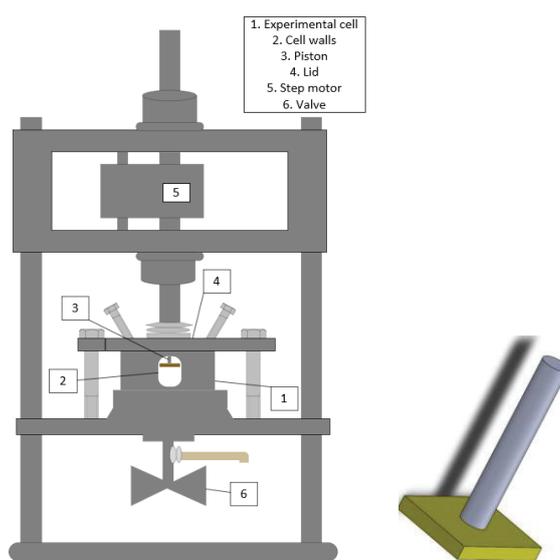


Figure 1. Schematic representation of the miniature emulsification device and of the oscillating piston

Acknowledgements: This research was supported by the European Space Agency (ESA) MAP PROJECT “Emulsion Dynamics and Droplet Interfaces (EDDI)” – Contract No.: 4000128643/19/NL/PG.

Spherical vs cylindrical micelles for advanced lubricant development

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In a typical passenger car approximately 33% of fuel energy is wasted trying to overcome friction. Efficient and optimized lubricants are key to reducing friction within engines, and the associated CO₂ emissions that are produced because of these frictional losses. [1]

Reverse micelles in oily media are known lubricating agents, and this raises a question about the effects of micellar structure (size, spherical vs cylindrical/wormlike vs disc-like) on friction reduction. [2-4] Non-spherical micelles (e.g. Wormlike) are often highly viscous fluids, acting akin to covalent polymeric systems but with the added relaxation mechanism of micellar scission [5]

The focus of this talk will be on the methods that were utilized to drive the formation of non-spherical reverse micelles i.e. changing the surfactant identity, water content, and with the addition of hydrotropes (essentially a primitive surfactant) to the systems. Techniques such as viscometry and small-angle neutron scattering were used to aid the tracking of micellar transitions and to help discern whether tuneability of micellar sizes and lengths is possible through a combination of these methods.

Keywords: Micelles, surfactants, SANS, lubrication

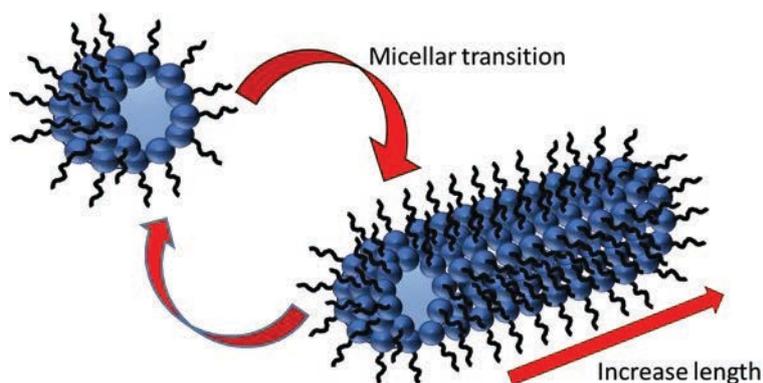


Figure 1. Transition and tuning of reverse micellar shape, and length.

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EP2.13

Essential oil-in-water microemulsions: A structural study

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Essential oils (EOs) are complex volatile natural mixtures formed by aromatic plants as secondary metabolites. EOs possess numerous biological activities including antioxidant, anti-inflammatory, antimicrobial and insecticidal. As a result, EOs are of great interest in food and cosmetic industries, human health, and sustainable agriculture. Direct application of EOs often presents rapid volatilization of their ingredients thus reducing their effectiveness. To address this issue, nanoencapsulation by means of emulsification has emerged as a method that could provide protection, duration and controlled release [1,2].

In this study, oil-in-water (O/W) microemulsions containing up to 23% w/w geraniol or citrepele (75% PMD) were formulated. The aqueous phase was a 1:1 mixture of water and diethylene glycol monoethyl ether (DEGEE). Labrasol was used to emulsify the immiscible liquids. All microemulsions were structurally characterized using advanced analytical techniques.

Dynamic light scattering (DLS) analysis showed low polydispersity ($PdI < 0.3$) and average droplet diameter ranging from 13.7 ± 0.7 to 35.2 ± 2.7 nm. Mean viscosity was from 15.7 ± 0.3 cP to 23.8 ± 0.2 cP indicating that all preparations were suitable for different application methods. Electron paramagnetic resonance (EPR) spin probing spectroscopy gave information about the rigidity of the surfactants' monolayer. In all cases an outer compact configuration and a more flexible inner one was observed. SAXS measurements revealed significant changes in the low q values related to the impact of the EOs on the microemulsions. Looking at the high q region of the spectra, the curves were affected by the presence of the EOs in a concentration depended manner.

Keywords: geraniol, citrepele, DLS, EPR, SAXS

Acknowledgements: European Regional Development Fund of the EU and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation-call RESEARCH, CREATE, INNOVATE (QFytoTera, T1EDK-00996)

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Effect of butanol on the bubble formation hysteresis in flow-focusing devices

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The formation of microfoam in a flow-focusing device is an important topic of microfluidics. The injection of gas (N₂ in our experiment) and liquid (water with Tween 20 at 1wt%, with or without 7wt% of butanol) can either result -depending of the flow parameters of the co-injection- in only a liquid flow, in a foam, or in a stream of gas flowing in the middle of the channel [1-2].

Working at constant gas pressure, we observe an hysteretic behavior when increasing the liquid flow (and so the capillary number) or decreasing it: as shown as in Fig.1, the jet-foam transition and the foam-jet transitions occur at different experimental conditions.

We herein study the effect of a short alcohol on this phenomenon. We show that butanol strongly affects in microfluidic devices both the formation and destabilization of bubbles.

Keywords: Foam - Microfluidic - Hysteresis

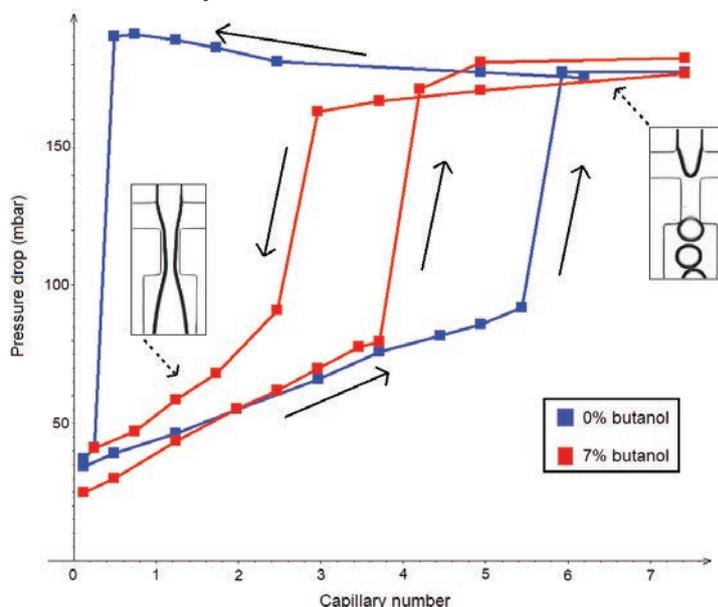


Figure 1. Pressure drop evolution when decreasing or increasing (indicated by the black arrows) the capillary number in water, without butanol (blue squares) or with 7% of butanol (red squares).

Acknowledgements: We thank Total S.A. for giving permission to publish this work.

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Encapsulation of fragrances and oils by core-shell structures from silica nanoparticles, surfactant and polymer: Experiment

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Colloidosomes provide a possibility to encapsulate oily substances in water in the form of core-shell structures. In this study [1], we obtained microcapsules with composite shell from nano-sized colloidal particles, polymer and surfactant (carboxylate). For this goal, we used hydrophilic silica particles (spherical and agglomerated) which were hydrophobized by the adsorption of potassium oleate. The used polymer is Carbopol 971 NF which was used in a previous study of ours and produced the best results [2]. The procedure of encapsulation is simple and includes single homogenization by ultrasound of the formulation that contains all ingredients together. The produced capsules have mean radius in the range between 2 and 11 microns. The produced microcapsules are stable when rinsed with pure water of pH in the range 3 – 10. However, if dispersed in water of pH > 11, the microcapsules are destabilized and release their cargo, i.e., they are pH-responsive. Various fragrances and oils, such as limonene, citronellol, benzyl acetate, and sunflower seed oil were encapsulated.

Keywords: Encapsulation, Colloidosomes, Fragrances

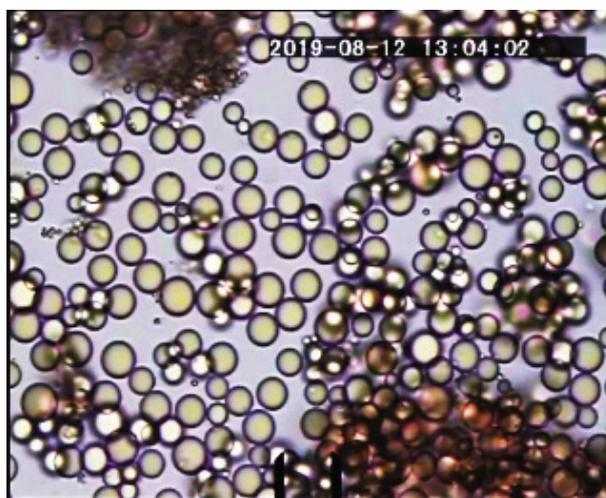


Figure 1. Microcapsules containing limonene in water; scale mark = 20 mm.

Acknowledgements: The authors gratefully acknowledge the support from the National Science Fund of Bulgaria, Grant No. KP-06-PN 49/5/2020.

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CO₂-Switchable Foaming Agents

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In industry, foams are often required for part of a process but can be detrimental in downstream processes. Traditionally to control undesired foam, antifoaming and/or defoaming agents are used. Unfortunately, these additives change the composition of the foaming solution preventing the recovery and reuse of the foaming agent [1]. A solution to having foam control without additional chemicals is using a molecule that can be switched between being a surfactant and being a defoaming agent. Such molecules are called switchable surfactants [2], they can be switched between a form that has significant surface activity (the “on” form) and a form that has less surface activity or less capability of stabilizing a foam (the “off” form). CO₂ is an advantageous pH trigger for this process as it is non-toxic, inexpensive, and does not lead to salt buildup as can occur with acids and bases [3].

While the bulk of attention has been on CO₂-switchable surfactants with switchable head groups, we have designed CO₂-switchable surfactants where the surfactant head group is permanently anionic, cationic, or nonionic and the CO₂-responsive group is placed in the middle of the hydrocarbon tail. Under air, the CO₂-responsive group is neutral and acts as part of the hydrophobic tail. When this form of the molecule is added to water and energy is applied, a stable foam is produced. In the presence of CO₂, the CO₂-responsive group in the tail becomes protonated and reduces or disrupts the amphiphilic nature of the molecule, which in turn, disables the molecule's ability to stabilize a foam.

These surfactants are advantageous in industrial applications where foam is needed under air. When the foam is no longer desirable, CO₂ can be added to the system, thus providing easier post-processing and recycling of the surfactant solution.

Keywords: CO₂-switchable surfactant, foaming agent, defoaming agent

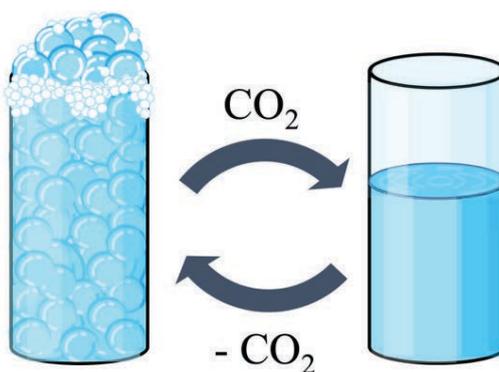


Figure 1. Scheme for CO₂-responsive foam stability.

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Role of surfactant adsorption and surface properties for the efficiency of PDMS-silica antifoams

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We study how the composition of various surfactant mixtures affects the efficiency of mixed PDMS–silica antifoam in foamed surfactant solutions. First, systematic experiments are performed to characterize the surface and foam film properties of the studied surfactant solutions. The spreading, bridging and entry coefficients are calculated and the spreading ability of the antifoam is characterized by microscopy observations and by surface tension measurements. Next, the initial antifoam activity and the antifoam durability are characterized in foam tests. The obtained results reveal that the antifoam efficiency in solutions of low-molecular mass surfactants with low surface dilatational modulus depends strongly on the density (area-per-molecule) of the respective adsorption layer. The addition of nonionic surfactants, which increase the mean area-per-molecule in the mixed adsorption layer, enhances significantly the antifoam activity and durability. In contrast, the addition of surfactants, which decrease the mean area-per-molecule, suppresses the antifoam activity. Furthermore, we found that surfactant mixtures which form condensed adsorption layers on the solution surface suppress strongly the antifoam activity. As an extreme, the condensed adsorption layer formed from the natural surfactant Quillaja saponin suppresses the antifoam spreading even at highly positive spreading coefficient which results also in very poor AF efficiency. The obtained results rationalize in a coherent way the observed differences in the AF activity and durability in mixed solutions of various ionic, nonionic and zwitterionic surfactants.

Keywords: antifoams, surfactant adsorption, surface modulus, spreading, saponin

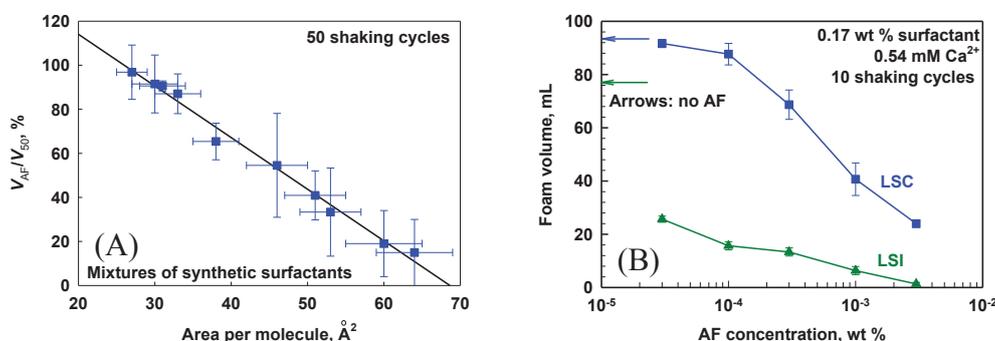


Figure 1. (A) Ratio between the foam formed in the presence of AF, V_{AF} , and in the absence of AF, after 50 shaking cycles, as a function of the area-permolecule in the adsorption layers. (B) Foam volume vs antifoam concentration at fixed surfactant concentration.

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Encapsulated BSA/alginate water-in-water emulsions based on polyelectrolyte complexation

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Encapsulation of emulsions is a suitable technique to protect, transport and control the delivery of active compounds. In addition, the use of water-in-water (W/W) emulsions, based on biopolymers and proteins, has focused a great interest in potential applications like cosmetics, foods and biomedicine. In our previous works, W/W emulsions have been used to successfully encapsulate active ingredients, like the β -galactosidase enzyme [1]. However, the stability of this encapsulated enzyme, in a simulated gastric fluid, was not sufficient. Therefore, the encapsulation process should be improved to protect and release possible active ingredients in the optimal conditions. For this reason, the present work proposes an alternative encapsulation of W/W emulsions, based on aqueous mixtures of an anionic polyelectrolyte (sodium alginate, NaAlg) with a globular protein (bovine serum albumin, BSA), by polyelectrolyte complexation [2]. With this purpose, the phase behavior BSA/NaAlg aqueous mixtures was studied, finding the region that showed a two-phase region, which was used to prepare W/W emulsions. The emulsion formation was investigated as a function of pH and the complexation of the BSA-in-NaAlg emulsions was performed with three different solutions, CaCl_2 , FeCl_3 or chitosan.

The results have demonstrated the feasibility of encapsulating BSA-in-NaAlg emulsions by polyelectrolyte complexation with CaCl_2 , FeCl_3 or chitosan, obtaining capsules with diameter around 2–4 mm. By using CaCl_2 or FeCl_3 , it is possible to obtain capsules with a short immersion time (5 min). Nonetheless, the use of CaCl_2 produces a shrinkage of BSA-in-NaAlg capsules, during freeze-drying. This shrinkage was not observed with FeCl_3 (Figure 1). The results obtained with the biopolymer chitosan are quite interesting because the emulsions capsules do not present any shrinkage after freeze-drying and they show an inner porous structures, probably due to the emulsion templating effect.

Keywords: water-in-water emulsion, polyelectrolyte complexation, chitosan

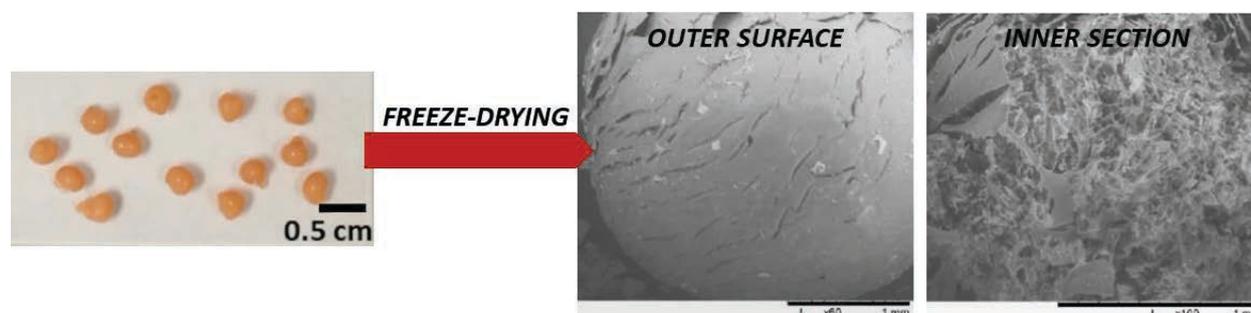


Figure 1. Encapsulated BSA-in-NaAlg emulsion after FeCl_3 complexation (left) and texture of freeze-dried capsules by Scanning Electron Microscopy, SEM (right).

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Thermal properties of lipid nanocapsules and solid lipid nanoparticles

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Nanocapsules (NC), i.e. nanoemulsion droplets with the liquid core and solid shell formed by surfactants, and solid lipid nanoparticles (SLN), are promising carriers for drug delivery. Incorporation of a lipophilic drug into lipid particles increases if the lipid core is liquid or in a supercooled melt state. The presence of a solid shell on the surface of the lipid particles provides an additional advantage, as it protects the incorporated drug from external influences and increases the physical stability of the lipid particles.

The system we designed includes lipid nanoparticles of 25-50 nm in diameter that are very resistant to aggregation and sedimentation at the ambient temperature. NC withstood at least two heating cycles to 60 °C and subsequent cooling to 5 °C without signs of degradation. SLN could only withstand temperatures up to 50 °C. These temperatures were higher than the melting point of the surfactant shell; however, SLN and NC remained stable.

The NC structure involved a liquid core of paraffin oil, coated with a solid shell of Tween 60 and Span 60 surfactants. After preparation, the SLN consisted of a semi-liquid core formed by a supercooled melt of stearic acid and also coated with a solid shell of surfactants with minor stearic acid inclusions.

Keywords: nanoemulsion, nanocapsule, solid lipid nanoparticle, lipid crystallization

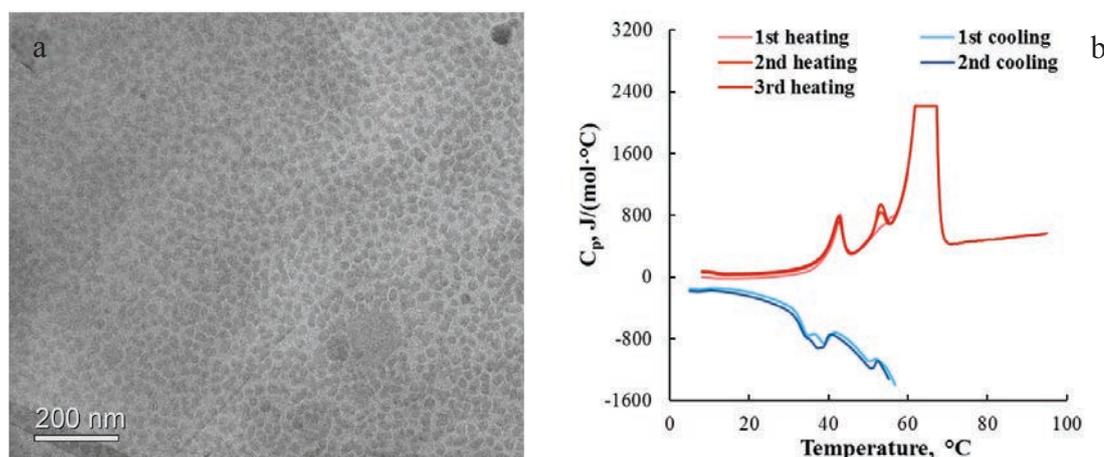


Figure 1. a - Microphotographs of SLN; b - SLN thermograms with two heating-cooling cycles from 5 to 60 °C and the third heating from 5 to 95 °C

Acknowledgements: This work was supported by the Russian Foundation for Basic Research and MOST (grants 19-53-06014 and 3-16496).

Foam formation using soft porous media

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Foams are a common occurrence in many industries and many of these applications require the foam to interact with porous materials. For the first-time interaction of foams with porous media has been investigated both experimentally and theoretically by A. Bureiko et al [1].

However, foam formation using soft porous media has only been investigated recently. The foam was made using a compression device with soft porous media containing surfactant solution. Amount and quality of foam produced by compression/decompression cycles of a porous media with surfactant solution and surfactant-polymer mixture was investigated.

The theory of the foam formation using compression/decompression cycles of soft porous material was develop and validated experimentally. It was found that the maximum amount of foam is produced when the concentration of the foaming agent (dishwashing surfactant) is in the range of 60-80% m/m (see figure 1). The amount of foam produced was independent of the pore size of the media in the investigated range of pore sizes [2].

Keywords: foam, soft porous material, compression

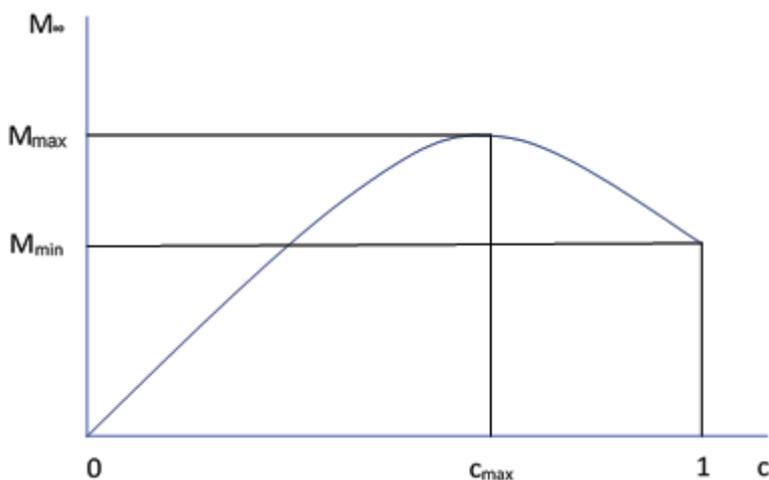


Figure 1. Schematic presentation of dependency of mass of foam (M_s) of the total surfactant concentration during foam formation within soft porous material.

Acknowledgements: This research was supported by Proctor & Gamble, Brussels; MAP EVAPORATION project, European Space Agency.

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Formation and interaction of foams with porous materials

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Foams are a common occurrence in industry where many applications require the foam to interact with porous materials including dishwashing. In this investigation a compression device for foam generation has been developed, which allows standardisation of the process of foam generation using sponges. The foam mass generated as a function of the concentration of surfactant solution was obtained for each of the three porous sponges investigated.

The porosity and pore size of the dishwasher and car sponge were found to be very similar whilst the audio sponge was found to have the same porosity but a significantly smaller pore size. It was found that the maximum amount of foam is generated with a 70% w/w% concentration of commercial dishwashing solution in water solution for all the sponges. The dishwasher and audio sponge foamability was found to be independent of the hardness of water i.e. concentration of salt in water, whereas the car sponge foamability increases as hardness increases. The average amount of foam produced for the audio sponge and dishwasher sponge is similar indicating that pore size has no significant effect on the amount of foam produced.

To provide a comparison with the commercial surfactant a pure surfactant, sodium dodecyl sulphate (SDS) was used, which has the same critical micelle concentration as the commercial dishwashing surfactant. During the investigation, it was found that the amount of foam generated increases up to 10 times the critical micelle concentration (CMC) after 10 CMC any further increase in concentration resulted in no further increase in the mass of foam being generated. The results for SDS and commercial dishwashing solutions have been used in the development of a model determining the amount of foam produced during the compression/decompression cycle of sponges.

Keywords: Foams, Porous Media, Compression, Dishwashing, Quality of foam

Controlling oil emulsions to improve deposition profile and sensorial characteristics of fabrics

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Using polydimethylsiloxane (PDMS) as a model system, we studied the synergistic effect of oil viscosity and resulting droplet size on the deposition profile of PDMS on cotton fabrics in a lab-based washing process. Low viscosity PDMS produced emulsions containing small droplets, under the same preparation conditions, which generated a uniform and thin film after the treatment, whilst high viscosity PDMS resulted in a localised deposition profile. The wicking and penetration characteristics of PDMS into cotton fabrics were found viscosity-dependent, which agrees with the deposition data. Both mechanical properties characterisation (Friction, Compression, Stiffness) and consumer evaluation confirm that the fabrics treated by the emulsion containing low viscosity PDMS was preferred, suggesting that homogeneous deposition and thorough penetration of PDMS are critical for maximising tactile sensorial benefits, which could be accomplished by optimising the emulsion design using oil of low viscosity and small droplet size that matches the porosity of the fabrics.

Keywords: polydimethylsiloxane, deposition, fabric, sensorial, wicking

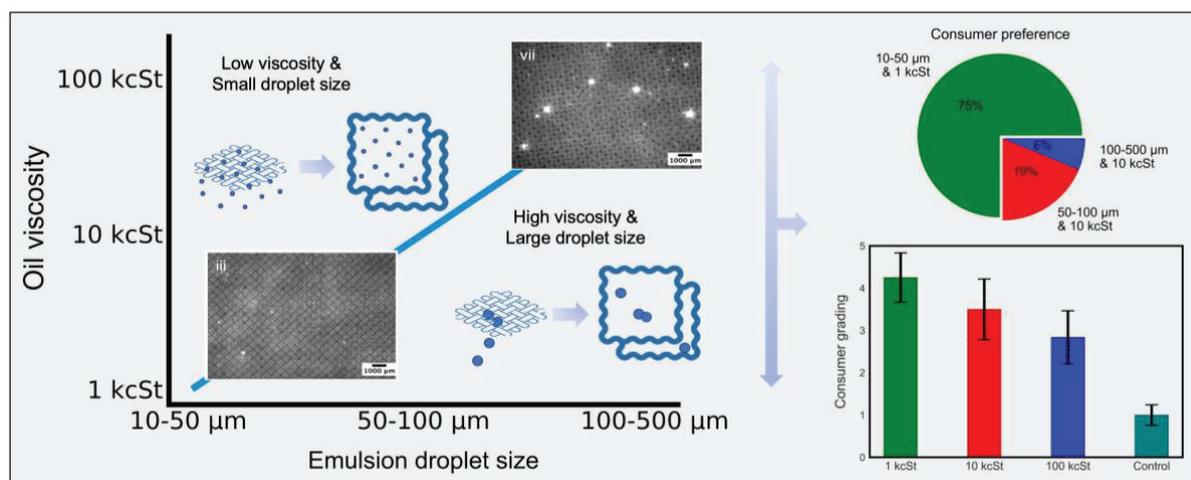


Figure 1. Graphical abstract of oil droplet size effect on deposition profile and consumer response

Interfacial behaviour and partitioning of partially neutralized naphthenic acids: experiments versus HLD-NAC predictions

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Recent studies have shown that naphthenic acids (NAs) and sodium naphthenates, more than asphaltenes, dominate the interfacial activity of crude oils, and the formation of crude oil emulsions. NAs are naturally occurring mixtures of carboxylic acids present in crude oil, and they can represent up to 4 wt% in some crude oils and bitumen. Previous work has used adsorption isotherms to predict interfacial tension changes due to the presence of NAs and sodium naphthenates. However, this adsorption approach does not explain low to ultralow interfacial tensions reported with other partially neutralized fatty acids. To explain low or ultralow interfacial tensions, a curvature model, the combined HLD (Hydrophilic Lipophilic Difference) + NAC (net-average curvature) model was considered. The HLD-NAC model predicts that at a specific degree of neutralization of the NAs, low (<0.1 mN/m) to ultralow (<0.01 mN/m) tensions can be obtained. The experimental tensions of pre-equilibrated systems show that although the low tensions correspond to HLD-NAC predictions, ultralow tensions are not obtained experimentally. Liquid chromatography measurements of the concentration of naphthenates in water reveal that not all the naphthenates produced due to neutralization end up in the aqueous phase. The HLD-NAC model can explain some of these observations, except for the region of expected ultralow tension where the lack of a middle phase suggests a failure to form bicontinuous systems. Potential explanations for this failure are offered along with the potential implications for crude oil production.

Keywords: Emulsions, Naphthenic Acid, HLD, HLD-NAC, interfacial tension, Spinning drop tensiometer

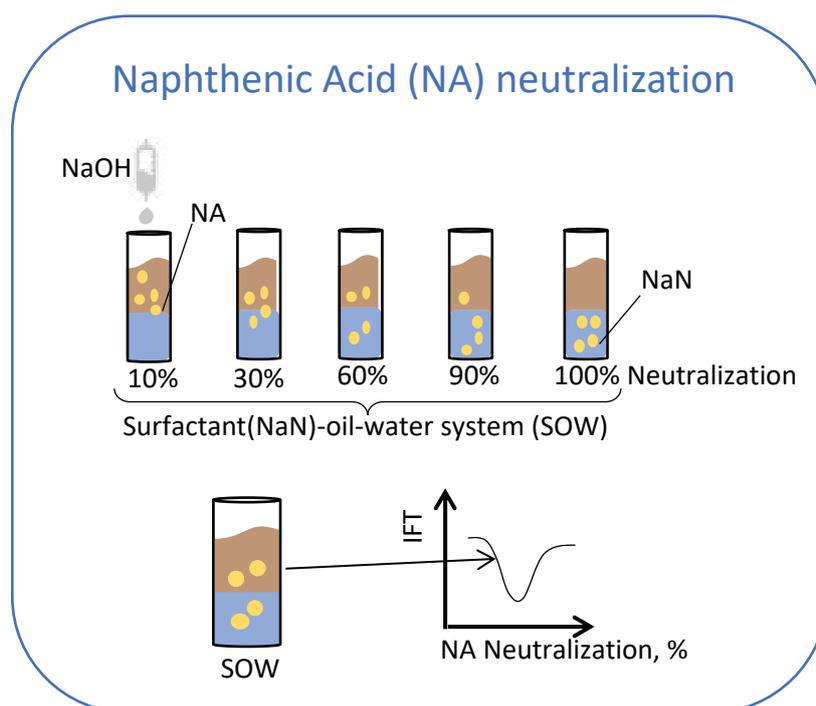


Figure 1. Schematic representation of the neutralization of naphthenic acids (NAs) to sodium naphthenates (NaNs) and its role in obtaining low to ultralow interfacial tensions.

The Characteristic curvature (Cc) of surfactants

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Curvature is a defining thermodynamic property of surfactants at oil-water interfaces. The curvature depends on a set of state conditions: temperature, pressure, the composition of the oil and aqueous phases, and the hydrophilic-lipophilic nature of the surfactant. The HLB (1949), the packing factor, the phase inversion temperature (PIT), among others, quantify the hydrophilic-lipophilic nature of the surfactant, but without a full set of state conditions. A lesser-known term, sigma (1977), was introduced in an empirical correlation equation that predicted the state conditions (salinity, oil composition) that led to optimal (net zero curvature) formulations of surfactant-oil-water (SOW) systems. In 2003, a form of this empirical correlation, the hydrophilic-lipophilic difference (HLD), was linked to a net-average curvature (NAC) model that interpreted the HLD as the net curvature normalized by the surfactant tail length. In 2009, the curvature interpretation of HLD led to the renaming of sigma as the characteristic curvature or Cc. The Cc was defined as the net curvature of the surfactant, normalized by its tail length, under a set of characteristic conditions: T=25C, a salinity of 1 g NaCl/100 mL, without additives or co-surfactants, and in the presence of an oil with an equivalent alkane number (EACN) of zero. Finding a suitable EACN=0 oil phase, and palisade layer solubilization issues prevented the use of the definition to assess Cc. Cc is often determined using surfactant mixtures, involving dozens of test tubes. This work shows how a recent discovery of an oil mixture with EACN=0, and methods for estimating the palisade layer solubilization term, has enabled the use of the Cc definition to develop a single test tube determination of Cc employing solubilization and SAXS techniques.

Keywords: microemulsions, surfactant, curvature, characterization.

Building up an HLD framework for cationic surfactants

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Cationic surfactants are primary ingredients in hundreds of home and personal care products. Quaternary ammonium compounds (QUACs) are active ingredients in disinfectants formulation because of their capability of disrupt biological membranes [1].

The introduction of these ingredients in several formulation became a priority during SARS-CoV-2 pandemic when people changed their cleaning habits all over the world [2]. Formulators and industries faced this challenge using classic approaches such as the design of experiments (DoE) or exploiting AI through Machine Learning algorithms [3]. In the present work, we used the hydrophilic-lipophilic deviation model (HLD) as rationale to handle cationic surfactant mixtures.

In the last twenty years, the HLD has proven to be a powerful tool for wisely formulating microemulsions [4], however HLD model was never extended to cationic surfactants. For the first time we built up an HLD framework for cationic surfactants: salinity scans have been conducted for several binary mixture of QUACs to determine dependence upon salinity and oil type.

Eventually, the HLD-titration experiment is here proposed as a fast and novel way to assess hydrophilic-lipophilic tendencies of surfactants exploiting noticeable changings in viscosity of emulsified systems induced by adjustments of surfactant composition. This titration approach has been used to measure characteristic values (Cc) for many cationic surfactants of strategic relevance: alkyl trimethyl ammonium bromides (C12-16TABs), benzalkonium chloride (BAC), 1-alkyl-3-imidazolium chloride and cetyl pyridinium chloride (CPC).

Keywords: cationic surfactants, microemulsions, hydrophilic-lipophilic deviation, HLD

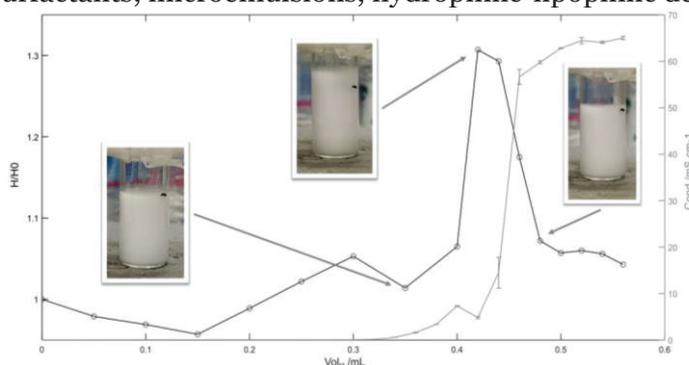


Figure 1. The titration of a DDAB/brine/nonane at $S = 10\%$ is monitored by a camera and a conductometer. The titrant is a solution of LTAB 2%, NaCl 10%. Conductivity and height of stirred fluid are plotted against added titrant volume.

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Diffusing Wave Spectroscopy characterization of emulsions: going beyond average values

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We report here a novel analysis scheme for Diffusing Wave Spectroscopy (DWS) experiments on creaming or sedimenting emulsions, allowing to extract not only average values for drop size and drop dynamics - as usual in DWS - but also properties related to the width of the distributions governing these quantities [1]. This analysis scheme starts from a realistic Monte Carlo simulation of light diffusing in the volume of the sample and reaching the detector. This simulation is more accurate than the analytical expressions available for the idealized geometries normally used in DWS interpretation. By disentangling Brownian and ballistic motions we directly access the variance of velocity distribution, σ_v . In relatively unstable emulsions σ_v governs the frequency of drop-drop collisions and subsequent coalescence events. Furthermore, when gravity dominates dynamics, as in emulsions subject to sedimentation or creaming, σ_v is strongly related to the 2nd and 4th moments of drop size distribution.

This novel analysis scheme is exemplified investigating freshly formed model emulsions. Results are validated by comparison with microscopy imaging. This analysis is then extended to emulsions with a much broader drop size distribution, resembling those that are planned to be investigated in microgravity by the Soft Matter Dynamics facility onboard the International Space Station (ISS). We conclude by discussing similarities and differences in terms of additional information accessible by introducing a local oscillator in the correlation (aka heterodyning) between single scattering (DLS) and multiple scattering regimes (DWS).

Keywords: Emulsion; sedimentation; Diffusing Wave Spectroscopy – DWS

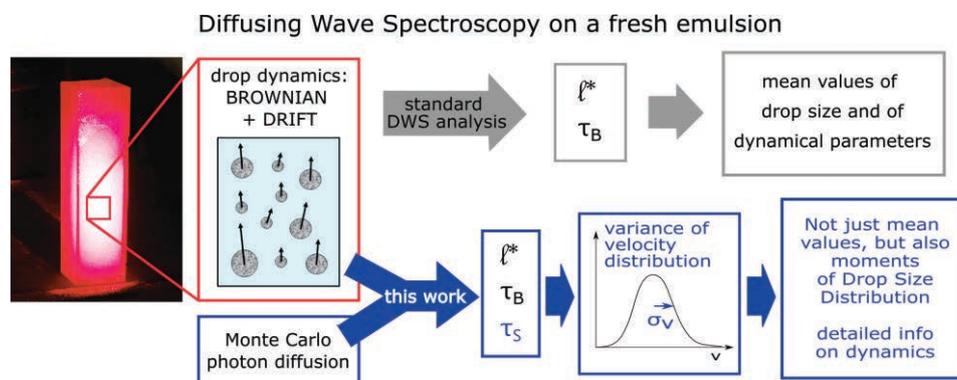


Figure 1. Sketch of the novel analysis scheme proposed for DWS on emulsions.

Acknowledgements: European Space Agency, MAP project “Emulsion Dynamics and Droplet Interfaces” (4000128643/19/NL/PG) and Topical Team “Foams and Emulsions Technology”.

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Emulsion Stabilized with Alumina-Functionalized Mesoporous Silica Particles

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The Pickering emulsions have attracted considerable interest due to their superior stability compared to surfactant-stabilized emulsion. The Pickering emulsions have been used for various applications including the preparation of porous materials or microcapsules, the stabilization of food-based emulsions or catalysis. The wettability and surface charge of the particles are among the key parameters allowing to control the type and the stability of the emulsions. The wettability of the particles can be adjusted by using different methods: surface functionalization (silanes, polymer), addition of electrolyte, change of pH, addition of surfactant, etc.

Ordered mesoporous materials are widely used in different fields (catalysis, separation, and adsorption). The most used are silica-based materials (M41-S, SBA, MSU) due to atypical properties such as: i) high surface area; ii) tunable pore size; iii) good hydrothermal stability and iv) surface enriched in silanols. This last characteristic affords easy surface modification by grafting, impregnation or precipitation. Acidic surface groups can then be obtained by insertion of heteroatoms of lower valence, as aluminum, on the silica surface to create negative charges in the framework.

In this work we report the use of aluminum-functionalized SBA-15 particles for stabilizing water/toluene-based Pickering emulsions. The solid particles have been synthesized with controlled content of aluminum species within the silica framework in order to evaluate their capability to stabilize Pickering emulsions. The physico-chemical properties of the materials and also the characteristics of the emulsions formed were determined in order to associate the properties of the materials with the stabilization of the Pickering emulsions.

Keywords: Pickering emulsion, Mesoporous particles, Alumina, Silica, Surface roughness,

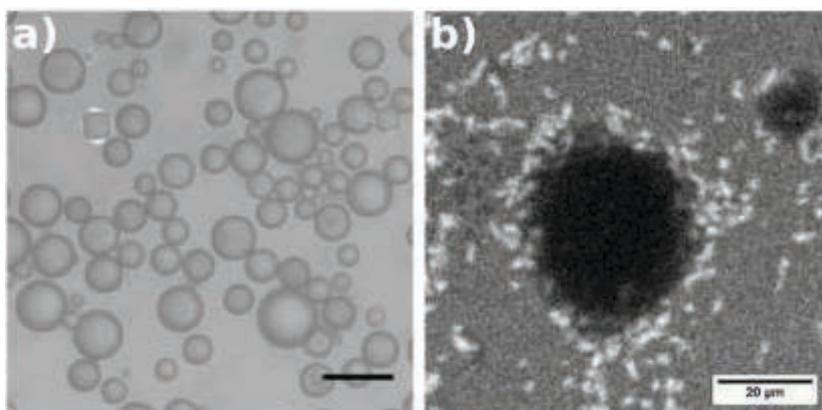


Figure 1. a) Optical microscope picture and SEM micrographs of emulsion stabilized by Al₃O/SBA particles (1 wt %).

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Ethyl cellulose nanoparticles as stabilizers for Pickering emulsions

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Pickering emulsions stabilized by biobased nanoparticles have recently received great attention for their remarkable stability and industrial applications [1,2]. An example of these biobased materials are ethyl cellulose nanoparticles. Despite the great potential of these emulsions, the exact stabilization mechanism of Pickering emulsions stabilized solely by ethyl cellulose nanoparticles (ECNPs) is yet not fully known. Both the stabilization of emulsions by particle adsorption and via network formation in the continuous phase are suggested [3,4].

In this work we prepare soybean oil-in-water emulsions stabilized by ECNPs and investigate them using confocal microscopy and interfacial tension measurements. We find that the main stabilization mechanism of ECNPs-stabilized emulsions is the adsorption of particles at the interface causing a reduction of the interfacial energy. At the same time, oscillatory rheology measurements show yield stress behavior in the emulsions well below the jamming transition, suggesting short-range interactions between the oil droplets caused by the presence of particles at the oil/water interface. The identification of the stabilization mechanism by ethyl cellulose nanoparticles provides a means toward the ability to further use these emulsions on a larger scale.

Keywords: Pickering emulsions, confocal microscopy, rheology

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Propolis nanoparticles offering Pickering stabilisation and antimicrobial activity onto O/W emulsions

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A clear consumer preference towards formulated products that utilise natural active species over synthetic, has been generating significant industrial interest. As a result, a range of natural species possessing a magnitude of functionalities have been investigated. One such natural component is propolis which is made by honeybees for healing and antiseptic purposes and has been associated with antibacterial, antifungal and antioxidant functionalities. However, propolis has limited aqueous solubility which restricts its use in industrial formulations.

The present study demonstrates that aqueous dispersions of propolis nanoparticles (formed by sonication of propolis extracts in water) possess enhanced antimicrobial activity. This functionality can be 'transferred' into oil-in-water (O/W) emulsions, by using the propolis dispersions as the continuous phase in these systems. It was revealed that antimicrobial activity is linked to the mass fraction/concentration of propolis, the duration of sonication and the final dimensions of the formed nanoparticles. Emulsion droplet size and stability were also investigated, for different oil and surfactant fractions. The role of the propolis nanoparticles in the interfacial stabilisation emulsions was studied via dynamic interfacial tension measurements and imaged using fluorescent microscopy. It was revealed that propolis nanoparticles exhibit some affinity for the emulsion interface (Pickering-like functionality) which can provide complete emulsion stabilisation either by itself (at low oil contents) or synergistically in tandem with low concentrations of small molecular weight surfactants. Future research efforts will focus on the mechanism by which the Pickering functionality of the propolis nanoparticles arises and enhancing its magnitude. The ultimate goal would be to utilise these propolis colloidal species as natural ingredients offering both stability and antimicrobial activity to industrially relevant emulsion formulations.

Keywords: antimicrobial activity, interfacial behavior, oil-in-water emulsions, Pickering particles, propolis

Destabilization of concentrated emulsion: theoretical predictions of bottle test behavior

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Coalescence is an important problem in emulsions and foams. Classical bottle test experiments are often used to study emulsion stability. Several series of experiments have been carefully performed on a model W/O emulsion system (containing two surfactants in various proportions) in order to model the destabilization kinetics. We observe two regimes for emulsion separation. After a first regime in which water droplets sedimentate, a very dense and stable emulsion forms. At the beginning of the second regime, we predict the thickness of this dense emulsion zone as a function of the composition of the surfactant mixture and of the mean droplet diameter. A simple model is introduced to quantitatively describe this effect. From the assumption that the coalescence rate only depends on the area of the thin film that separates two droplets in contact [1], we quantitatively model the separation kinetics of the dense emulsion zone with only one fitting parameter that is the coalescence frequency per unit area, ω [2]. Lastly, we show that thermodynamical arguments allow to one to quantitatively estimate ω in terms of the physico-chemical parameters at play.

Keywords: Emulsion – Coalescence – Bottle test

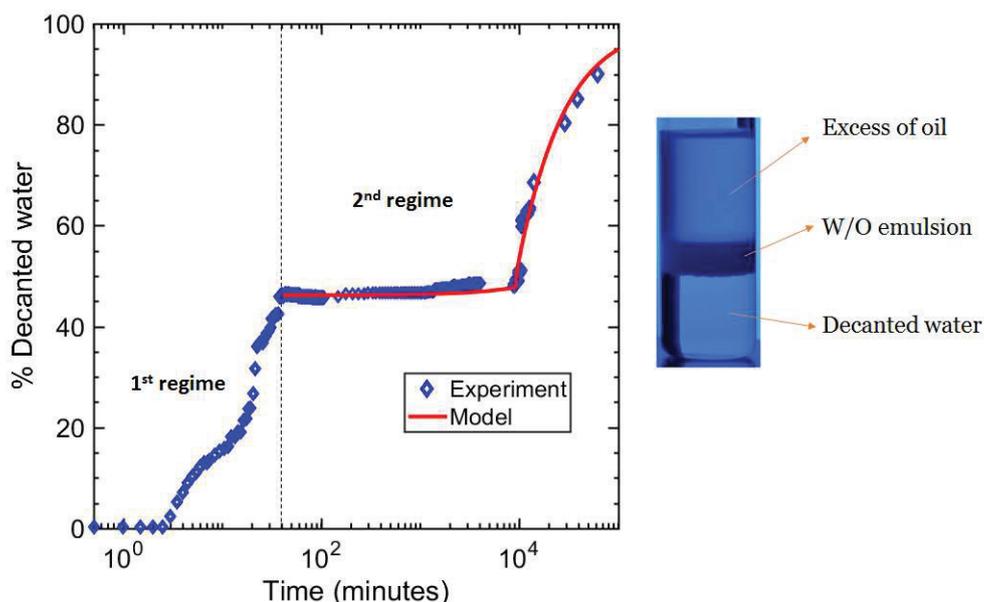


Figure: (Blue diamond): Time evolution of decanted water volume, normalized by original amount of water volume | (Red line): our model to determine the coalescence frequency ω

Acknowledgements: We thank Total S.A. for giving permission to publish this work.

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EP2.34

**Surface-tension gradient in thin films:
why foams form in liquid mixtures**

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Foams do not form in pure liquids because of the very short life time of liquid films, whose interfaces are submitted to van der Waals interactions. On the other hand, froth formation in mixtures of different liquids is extensively described in the literature, especially in oil mixtures. Based on the non-linear variations of the surface tension of a mixture with its composition, we suggest a mechanism that stabilizes the thin films of liquid mixtures. The effect can be described by the dependency of mixture surface tension on its thickness. By examining experimental lifetimes of foams in binary mixtures, we demonstrate that their variations are reliably forecasted by the proposed mechanism. Finally, we calculate the thickness reached by the liquid films in the foam before drainage occurs from the experimental surface tensions of the mixtures, and demonstrate a significant correlation between the thickness and foam lifetime for polar and non-polar liquids.

Keywords: Foamability; Thin liquid films; Bubble lifetime; Oil foam formation; Surface tension

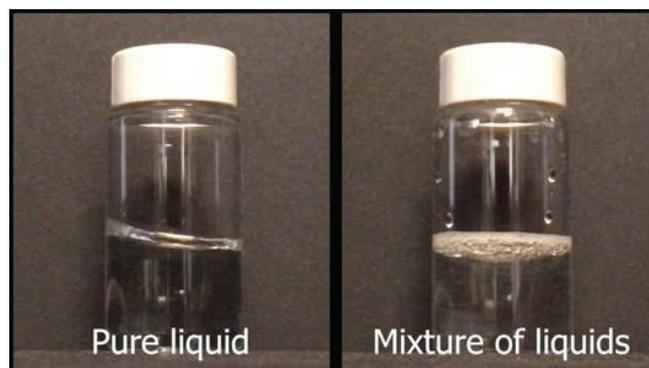


Figure 1. Photograph of a pure liquid (left - decane) and a mixture of liquids (right - decane/toluene) after manual stirring. The formation of froth is observed in the mixture of liquids.

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Self-perturbation of the salt partition at a liquid/liquid interface

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Open circuit potential (OCP) measurements of the partition of tetrapentylammonium chloride (TPeACl) at the water/1,2-dichloroethane (DCE) interface reveal two remarkable processes. First one is characterized by a substantial drop and further decay of the OCP from its expected equilibrium value. This process has been previously investigated and ascribed to the anomalous extraction of the salt driven by its accumulation in the hydrated salt clusters in the DCE phase [1]. The second process, which has been observed for the first time in the study [2], is characterized by the short-term potential spikes, cf. Fig. 1, overlapping the long-term OCP records. These spikes are assumed to be associated with the collision and fusion of the hydrated salt clusters or their aggregates produced by the former process with the water/DCE interface. The impact of the hydrated salt clusters can be treated as a self-perturbation of the salt partition at a liquid/liquid interface. Self-perturbation of the steady-state salt partition by a single cluster or aggregate impact offers a new approach to study kinetics and the mechanism of the hydrated salt cluster formation.

In principle, this approach has all advantages of the traditional electrochemical perturbation techniques and, moreover, this kind of perturbation is introduced by the electrochemical process itself. In contrast to the perturbation signal from an external source, this perturbation is caused by a small electrically neutral particle, the impact of which does not induce any measurable mechanical instability of the interface. An analysis of the potential response of the electrochemical system to the perturbation of the steady-state process provides a unique possibility to infer the kinetic and equilibrium data from single cluster impact measurements.

Keywords: Salt partition; Potential spike; Hydrated salt cluster

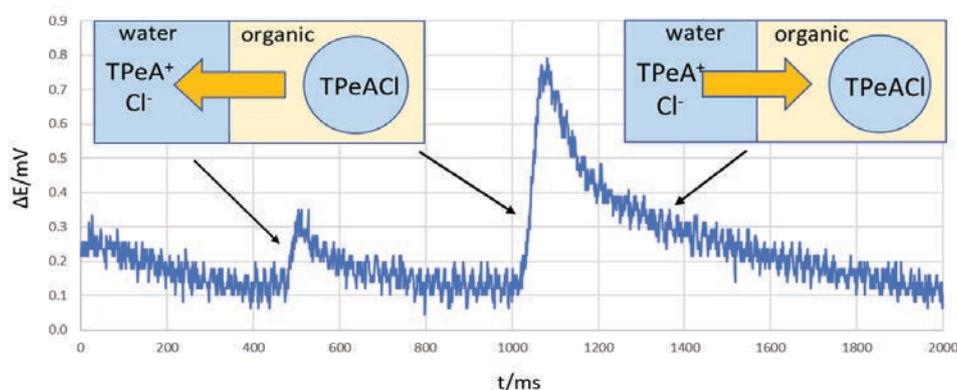


Figure 1. Potential spikes overlapping the OCP records. Time resolution 1 point/ms.

Acknowledgements: Financial support from the J. Heyrovský Institute of Physical Chemistry of the CAS is gratefully acknowledged.

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Controlling rheology of a solid emulsion with phase-changing droplets

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Emulsions are interesting systems whose rheological properties depend on the continuous and dispersed phases and the interface between them. By solidifying the continuous phase around the dispersed phase, we can create a composite viscoelastic material that can be tuned by changing the moduli of both the dispersed phase and the continuous phase, and/or the surface properties. [1-3]

We study such a "solid emulsion" with a crosslinked PDMS (poly(dimethyl) siloxane) continuous phase. The dispersed phase is PEG (poly(ethylene) glycol) with an average molar mass of 600 g.mol⁻¹, which crystallizes at room temperature. This phase change was used to vary the moduli of the dispersed phase. Previous theoretical work [4,5] has shown that we can expect to see different rheological responses depending on the dispersed phase moduli, the size of the inclusions in the solid matrix and the volume fraction of dispersed phase (see Figure 1).

The aim of this work is to show the feasibility of a composite system whose storage and loss moduli can be controlled independently, as opposed to the commonly used viscoelastic materials such as adhesives and gels, and study the mechanisms for such a decoupling. For our system, we have observed a decoupling of the storage and loss modulus in the rheological response for low volume fractions whatever the temperature. We will show that this decoupling only occurs below a critical volume fraction, above which the two moduli start to diverge for low temperatures.

Keywords: rheology, emulsion, polymer

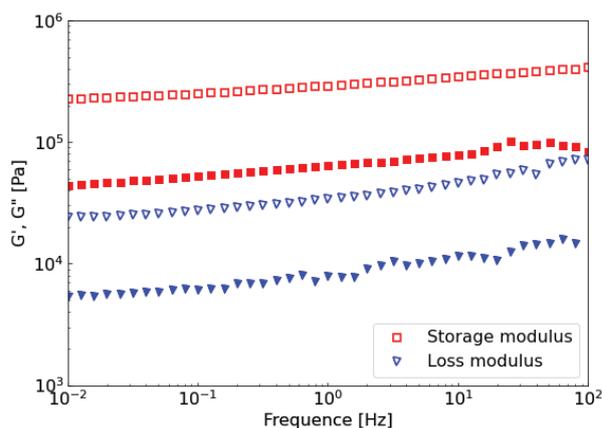
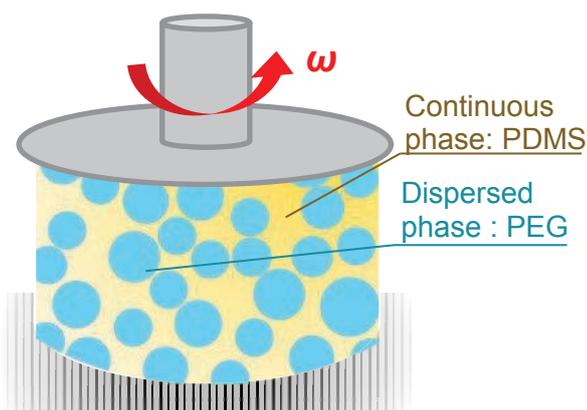


Figure 1. *Left:* Schematic representation of a sample undergoing oscillatory shear to derive its moduli. *Right:* Typical rheology curves for our systems, at 0°C (empty markers) and 25°C (full markers).

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Emulsion stabilization or texturizing agent: possibilities in microgel particles, oil, and water systems

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Ternary systems of two immiscible liquids and a solid can form different microstructures depending on the concentration of each component: Pickering emulsions, capillary suspensions, agglomerates, granulates, emulsion gels or bijels are found in these systems. These conformations depend on many factors, such as particle wettability and surface properties. Microgel particles (MGP) can also act as particles in ternary systems. However, in contrast to solid particles, MGP are deformable, can undergo volume changes, do not have clear contours, and might interact with each other in a different manner than solid particles do. In this study, we investigated whether previously found conformations and relations for solid particles also apply for pectin-based MGP in oil-water-systems. It is the first time that such solid particle concepts are applied to soft, polysaccharide-based microgel particles. By varying pectin-based MGP concentration, and oil concentration, we evaluated the conformation of all components in the samples, measured the rheological properties of the samples and their oil droplet size distributions.

We found concentration regimes for a microgel-stabilised, free-flowing emulsion or a microstructured ternary system: Whilst an increase in the oil concentration did not affect the structure of the investigated formulation, an increase in microgel concentration led to the formation of agglomerates. A further increase in this concentration favoured the formation of a continuous particle-oil network throughout the aqueous phase. The change of state due to rearrangement of the components in other structures was visible in the flow behaviour of the samples. We also showed the influence of the microgel and oil concentration on the oil droplet size in the emulsion state. The obtained information was summarised in a ternary diagram. The study highlights the potential of pectin-based microgel particles for texture modulation and simultaneous oil stabilisation in, e.g. food applications.

Keywords: Microgel particles; Pectin; Emulsions; Droplet size; Ternary systems

EP2.38

Electrophoretic mobility of Ag and Au nanoparticles in AOT solutions in a mixture of n-hexadecane-chloroform

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The electrophoretic mobility values obtained in experiment and the ζ -potentials calculated from these values under various models are the fundamental characteristics of nanoparticles in liquid media [1]. Recent studies [2-3] were devoted to the causes of charge generation and electrophoretic mobility of nanoparticles in the media with a low dielectric permittivity (<10). This is related to the application of low-polar organic solvents (oils) in such modern devices as electrophoretic displays (e-books) [4-5] metal-containing solvent ink for 2 and 3D printing, heat removing nanoliquids, electrorheological fluids. The goal of our work was to investigate electrophoretic mobility of Ag and Au nanoparticles in n-hexadecane–chloroform mixtures at low concentrations of anionic AOT.

Silver and gold nanoparticles were obtained by microemulsion synthesis. The obtained nanoparticle solutions were concentrated, and the dried concentrates were dissolved in mixtures of AOT solution in n-hexadecane-chloroform. The nanoparticles were stabilized by sodium bis-(2-ethylhexyl) sulfosuccinate. Electrophoretic mobility of Ag and Au nanoparticles in n-hexadecane–chloroform mixtures was studied in dependence on the chloroform content (from 0 to 100 vol.%).

The obtained organosols were characterized by phase analysis light scattering (mobility and electrokinetic potential), dynamic light scattering (hydrodynamic diameter), transmission electron microscopy (diameter), spectrophotometry (wavelength) and conductometry (conductivity). Electrophoretic mobility of the nanoparticles sharply increased from 0 to $3.6 \times 10^{-9} \text{ m}^2/(\text{V}\cdot\text{s})$ with increasing chloroform content. The growth of mobility was caused by an increase in the concentration of solvated AOT ions, which formed by the disproportionation reaction from uncharged molecules. The zeta potential of silver and gold nanoparticles was in the range of 60-90 mV, which indicates the stability of the obtained organosols. The hydrodynamic diameter of nanoparticles increased slightly (from 10 to 17 nm) with increasing chloroform content in n-hexadecane-chloroform mixture. Low concentrations of AOT and a considerable zeta potential (up to ~ 100 mV) made it possible to use the obtained organosols for the formation of electrostatically bound aggregates of Ag and Au with negatively charged nanoparticles (such as SiO_2 , TiO_2), which is a promising task for the development of work.

Keywords: Micelle, nanoparticles, electrophoretic mobility, PALS, electrokinetic potential, dynamic light scattering

Acknowledgements: The reported study was funded by RFBR, project number 19-33-90022.

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EP2.39

**Structure and rheology of water-in-oil emulsions
stabilized by asphaltenes**

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The problem with production and transportation of heavy crude oils is their high viscosity, which can be reduced through deasphalting. However, the result is asphaltenes that have to be disposed of somehow. Asphaltenes are natural surfactants that are part of crude oils and stabilizing water-in-oil emulsion extracted during oil production. This hints at the opportunity for rational utilization of asphaltenes.

This research examines the possibility of obtaining water-in-oil emulsions stabilized only with asphaltenes. Asphaltenes were dissolved in ester oil in which water or aqueous solutions of various substances were then emulsified. Several series of emulsions was prepared, differing in asphaltene concentration as well as disperse phase content and its type. In addition, solutions of asphaltenes were prepared in order to understand the role of viscosity of continuous phase in determination of emulsion rheology. For both asphaltene solutions and water-in-oil emulsions, their rheology was studied in detail: flow curves and frequency dependences of storage and loss moduli were obtained and analyzed.

As it turns out, about 3% of asphaltenes is sufficient to make water-in-oil emulsions resistant to coalescence of droplets. However, water droplets form spatial agglomerates, which lead to the viscoelastic and viscoplastic behavior of these emulsions. An increase in the concentration of asphaltenes and/or the water phase result in an increase in the effective viscosity of the emulsions and their yield stress. At the same time, replacing water with aqueous solutions of various substances does not cause the emulsions to lose their resistance to coalescence and fundamental changes in their rheology. This opens up the possibility of using such emulsions as well as utilizing asphaltenes.

Keywords: emulsions, asphaltenes, rheology, morphology

Acknowledgements: This research was supported by the Russian Science Foundation (project 19-79-10283, the study of asphaltene solutions) and the Council for Grants of the President of the Russian Federation (project MK-1557.2019.3, the study of emulsions).

OP3.1

Study on Microstructure Changes and Ion Fluctuation by Excess Inorganic Salt of Phosphatidylcholine Aqueous Dispersions

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Addition of excess CaCl_2 to phospholipid aqueous dispersions affects dispersion stability, inducing membrane fusion and growth of vesicles [1]. We have studied effects of ionic strength and cation species on static structure of phosphatidylcholine (PC) aqueous dispersions, focusing on the salt-induced modulation of intermembrane interactions as the underlying mechanism.

SAXS intensities exhibit reflection peaks, arising from the membrane-membrane correlations. These peaks become markedly broader by adding inorganic salt. Applying the modified Caillé theory [2], we analyzed static structure factor, $S(q)$, of the PC dispersions, taking undulation fluctuation disorder (UFD) into account. The analysis reveals that salt addition destabilizes the long-range order of the membranes.

We also measured dielectric spectra of the PC dispersions. The major contributions to the dielectric spectrum of the sample without salt are rotational diffusion of the zwitterionic headgroups of PC molecules and the cooperative rearrangement of the hydrogen-bond network of bulk water. We observed that additional low-frequency dispersions emerge upon addition of CaCl_2 which are assigned to the interfacial polarization (the Maxwell-Wagner (MW) relaxation) and ion fluctuations into two different directions at the membrane interface [3].

After adding CaCl_2 , the apparent dielectric loss peak in the MHz frequency region becomes significantly marked with time. At the same time, bulk conductivity showed a steep decrease. These phenomena monitor time-dependent growth of the interface that blocks ion transport. These phenomena should be closely linked to a decrease of the outer aqueous phase volume observed by scanning electron-assisted dielectric microscopy [4].

Keywords: phospholipid, vesicle, intermembrane interaction, interface formation

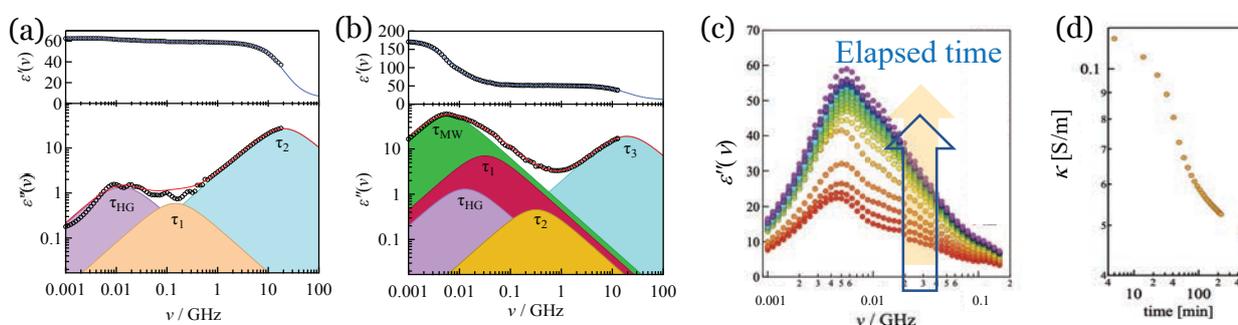


Figure 1. (a), (b) Dielectric relaxation spectra of PC aqueous dispersions at 298K. Time evolution of (c) dielectric loss and (d) bulk conductivity of the aqueous dispersions of 10 wt% PC at 298K. CaCl_2 concentration is fixed to (a) 0 mM and (b), (c), (d) 10 mM.

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OP3.2

Structure, Immunogenicity, and Causing Factors of Peptide Aggregation – A Small Angle Scattering Approach*Ellen Brunzell*¹¹*Uppsala University, dept. medicinal chemistry*Presenting author e-mail: ellen.brunzell@ilk.uu.se

Self-assembly of peptides into larger, insoluble aggregates can cause a number of problems. Aggregation of peptides is part of the pathology of many common degenerative diseases, such as type 2 diabetes mellitus (T2DM), and Alzheimer's disease, in which deposition of fibrillated peptides in pancreatic tissue or brain, respectively, is seen. The causes behind peptide aggregation and the mechanism behind their cytotoxicity is currently unknown [1-2]. Increasing the knowledge of aggregate structure, and the mechanisms behind aggregation is the key to better understanding of diseases in which aggregation plays a major role. By learning more about the self-assembly properties of peptides, we can learn how to predict and prevent aggregation. In the quickly growing field of biopharmaceutics, this can provide insights in how to create optimized formulations for biopharmaceutical drugs.

Aggregation of peptides has been studied with various types of microscopy and fluorescent techniques [3], among other methods, but characterization by small angle scattering analysis is a relatively unexplored field. At early stages of self-assembly, when the aggregates are in the submicron size range, they can be investigated with scattering techniques. With SANS (small-angle neutron scattering), SAXS (small-angle x-ray scattering), and SLS/DLS (static/dynamic light scattering) the size, shape, and inter-particle interactions can be investigated. By varying the conditions, e.g. temperature, pH, metal ions, we can investigate the environment's impact on the peptide self-assembly behavior.

By including phospholipids to the peptide system, we can assess the interactions between self-assembled peptide structures and cellular membranes. This can shed some light on the mechanism behind the cytotoxicity of aggregated peptides [4].

With SAXS and SANS it is possible to characterize the size and structure of aggregate particles in nano-size range. Using contrast-matching SANS, it is possible to localize different components in an aggregate or formulation, for instance aggregated peptides in a phospholipid membrane [5].

Keywords: peptides, aggregation, scattering.

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OP3.3

Cubic phases as a model biomimetic membrane for reconstitution of transmembrane proteins

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Self-assembled lipid-liquid crystalline nanostructures, which are stable in excess of water, are shown to be a promising matrix for the reconstitution of membrane protein. Membrane proteins, generally not stable outside the cell membranes, can be stabilized by entrapment in a matrix that resembles natural environment. A chloride-conducting ion channel from *Escherichia coli* (EcCLC) was incorporated into the MO based cubic phase LCP and was studied with electrochemical methods. The chloride channel proteins constitute a superfamily of membrane transport proteins ubiquitous across species ranging from bacteria to mammals, where they play central roles in a broad range of fundamental biological processes. The CLC catalyze the transmembrane exchange of Cl^- with $2\text{Cl}^-/1\text{H}^+$ stoichiometry. Structural characterization of the lipidic mesoscopic systems with and without incorporated EcCLC was carried out by means of small-angle X-ray scattering (SAXS). The structural symmetry of the ecCLC modified LCPP showed Ia3d symmetry as revealed by the SAXS. Electrochemical methods were applied to study the transport functions of ecCLC reconstituted into the protein into MO derived cubic phase. Our results demonstrate that the presence of the ecCLC in the bilayer has a clear influence on the transport of Cl^- through the mesophase. The ecCLC membrane proteins transports chlorides more efficiently at more acidic pH, the resistance of the film (measured from the slope of I/V curve), decreases at pH5. 4,4-Diisothiocyanatostilbene-2,2'-disulfonic acid (DIDS) used as an ecCLC inhibitor was shown to decrease transport efficiency either at pH 5 or pH 7.

Keywords: cubic phase, membrane protein

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OP3.4

Temperature effect on the properties of aqueous solutions of Kolliphor ELP

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Many different excipients are necessary for effective drug dissolution and for their transport across biological barriers in the pharmaceutical industry. These excipients are used as fillers, disintegrants in the conventional forms such as capsules and tablets to enhance overall drug absorption [1]. Surfactants are used as excipients for poorly water soluble drugs. In general, they increase the drug absorption by increasing its concentration in the gastrointestinal tract. In the pharmaceutical industry mostly nonionic surfactants such as Kolliphors are used to improve dissolution and delivery of drugs [2]. Kolliphor ELP (ELP) is commonly used in pharmaceutical formulations to improve the bioavailability of poorly water soluble drugs. ELP has been used as an excipient for solubilization of cyclosporin A, diazepam, propofol and paclitaxel [3-5].

The aim of the presented studies was to determine some volumetric, adsorption and thermoacoustic properties of aqueous solutions of Kolliphor ELP by the surface tension, viscosity and density measurements at T=293-318K (with 5K interval). Based on the results, the analysis was applied to study molecular interactions in the solutions taking into account the impact of temperature and concentration on these properties.

Keywords: surfactant, surface tension, viscosity, density

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Interaction of DPPC/DOPC/Cholesterol system vesicle with amphiphilic peptide

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Amphiphilic peptides are known to interact with lipid bilayers, causing channel formation, membrane deformation and disintegration [1]. These phenomena have been linked to functions such as substance transport, uptake, release, and signal transduction in heterogeneous structures of biomembranes called raft. Therefore, elucidating the effects of amphiphilic peptides on bilayer membrane structure is a very important to understand the process and regulation of biomembrane functions. In this study, the morphological changes of lipid vesicles by adding amphiphilic peptide were observed to consider the effect of peptide on deformation mechanism and the interaction between peptide and lipids.

The model biomembrane was prepared by electroformation method using saturated phospholipid (DPPC), unsaturated phospholipid (DOPC), and cholesterol (Chol), and Alamethicin was employed as amphiphilic peptide. The morphological changes of the vesicles upon addition of Alamethicin (concentration 0-50 μM) were observed using a fluorescence microscope (OLYMPUS LX73) with lipid compositions (DPPC/DOPC/Chol = 15/75/10, 55/10/35) in liquid disordered (Ld) and liquid ordered (Lo) phases at 25°C.

Addition of Alamethicin to circular Ld phase vesicles (10-20 μm in diameter) induces various morphological changes as shown in Figure. 1. As the concentration of Alamethicin increased, the size of vesicles increases, and various morphologies such as disc and string-shaped vesicles were observed. An expected scenario for this is that Alamethicin aggregates in the bilayer to form pores (channels), which promotes the fusion of vesicles. The morphological change of the Lo-phase vesicles was much smaller than that of the Ld-phase ones (Figure. 2), suggesting that Alamethicin has a higher affinity for DOPC than for DPPC and is significantly more likely to cause deformation in Ld phase vesicles, which contain a larger fraction of DOPC than DPPC.

Keywords: lipid vesicle, amphiphilic peptide, vesicle deformation, peptide-lipid interaction

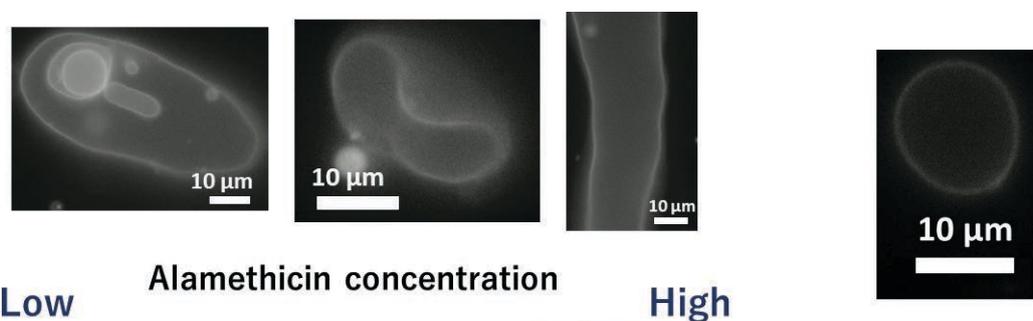


Figure 1. Morphological changes of Ld phase vesicles with increasing Alamethicin concentration.

Figure 2. Lo phase vesicle at Alamethicin concentration.

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OP3.6

Structure and function investigation on membrane-binding proteins: a neutron reflectometry study

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Clathrin-mediated endocytosis (CME) is the main mechanism by which eukaryotic cells internalize and recycle most membrane proteins. Mutations affecting endocytosis have been directly linked to cancer as well as to Alzheimer¹ and Stiff-man² diseases. The CME is driven by different Adaptor and Modulator Proteins, which solely interact with the inner leaflet of the cell membrane.

By exploiting techniques such as ellipsometry, pressure–area isotherms and Neutron Reflectometry (NR), the aim of this work has been to investigate the binding and resultant structures formed by the adaptor protein CALM and by the modulator FCHo2 on association with lipid monolayers enriched in either phosphatidyl-inositol-4,5-diphosphate (PIP₂), or 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (POPS). In particular, Neutron Reflectometry allowed us to determine the position and orientation of both CALM and truncated versions of FCHo2 with respect to the membrane. The resultant position of the CALM atomic structure³ on the membrane made biological sense. Regarding FCHo2, a 4-layer-model, which fit well to the NR data, allowed the general orientation of the protein as well as the relative positions of the protein’s individual domains to be determined.

Keywords: model membranes; protein-lipid interaction; endocytosis; neutron reflectometry; structural biology.

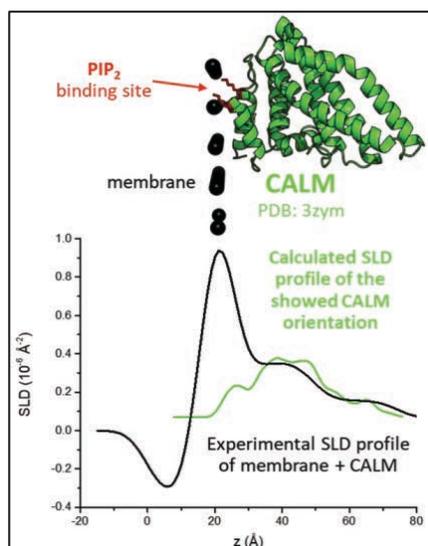


Figure 1. Best orientation of CALM obtained from Neutron Reflectometry. The experimental SLD profile obtained from the fitting and the calculated SLD profile of CALM are shown.

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Effect of tiny amounts of surfactants on the zeta potential of phosphatidylcholine liposomes

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In recent years, the number of research on model biological membranes shows an increasing trend, and this growing interest was the first motivation to conduct the research presented here. Moreover, this approach is used now by scientists from various fields of science, starting from molecular biology, through medicine, and ending on environmental science. This indicates a great usefulness of liposomes and Langmuir monolayers in the development of science and exploring the world. But, do all scientists know how easily the properties of model systems change under the influence of substances so ubiquitous in today's world as surfactants? This seems to be particularly important when measuring the zeta potential of liposomes.

In view of liposomes advantages, for example biocompatibility, biodegradability and non-toxicity, they are designed as carriers to deliver bioactive compounds into cells, immunological adjuvants, contrast agents for molecular imaging, nutritional additives or preservatives [1], and thus they are a subject of numerous studies including electrokinetic potential measurements. It is directly related to the fact that this parameter is crucial in prediction of vesicles stability, as well as, their fate and behaviour in vivo [2]. Although there are many studies related to the measurement of the zeta potential of liposomes, the research on its changes under the surfactants presence remains limited. Therefore, we conducted a systematic study in which the effect of various surfactants on the properties of liposomes with different lipid composition were verified. More precisely, the anionic SDS, cationic DTAB and nonionic Triton X-100 were examined in order to explain the influence of the surfactant charge on the value of the zeta potential of DPPC liposomes, and also two more cationic surfactants: TTAB and CTAB were investigated to specify the impact of the surfactant carbon chain length on the zeta potential of the liposomes. Finally, cholesterol was included into the study as it had a chance to affect the DPPC–surfactants interactions. The results obtained for the bilayer model were correlated with the surfactants influence on the Langmuir monolayers properties. Our research confirms the incorporation of tiny amounts of surfactants into the lipid layers, which in the case of lipid bilayers leads to significant changes in the zeta potential of DPPC and DPPC_Chol liposomes.

Keywords: surfactants, liposomes, zeta potential, biological model membranes

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OP3.8

Growth of a multilayer film composed of alternating protein-polysaccharide layers on gold surface. A Surface Plasmon Resonance Study.

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In this work the responsiveness of a biomolecular multilayer film of alternating Bovine Serum Albumin (BSA) and Chondroitin Sulfate (CS) layers upon pH changes is examined with Surface Plasmon Resonance Spectroscopy. Bovine serum albumin is one of the most important blood proteins and it has significant ability to bind reversibly a variety of ligands, a fact that ranks it as a multifunctional transport protein. Chondroitin sulfate is a highly sulfated polysaccharide that is normally found in cartilage around joints in the human skeleton and it can bind to a large variety of proteins. The layer by layer adsorption is investigated with Surface Plasmon Resonance Spectroscopy, a method which allows the observation of adsorption on surfaces due to its high sensitivity to refractive index changes. Thin films of gold are used as plasmonic material and as non toxic, fresh substrate for molecule adsorption. A multilayer film is formed at pH=4, from alternating BSA/CS layers based on the electrostatic interaction between the macromolecules. Chondroitin sulfate is a negatively charged polysaccharide while albumin has a net positive charge when the pH is lower than its isoelectric point (pH 5~5.5). BSA becomes negatively charged when the pH changes to neutral and so the attraction with CS turns into repulsion. The stability of the alternating multilayer is pH dependent, and at neutral pH the system is disassembled, as both the protein and the polysaccharide are negatively charged. The strength of the interactions within the multilayer can also be controlled by factors as ionic strength, temperature and the protein-polysaccharide charge ratios. The effect of these factors in our system will be investigated subsequently. As this system is based on natural macromolecules and is prepared by biocompatible processes, it has potential for applications in films for drug delivery and tissue engineering.

Cyclodextrin and surfactants: From inclusion complexes to pH and temperature responsive supramolecular aggregates

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Cyclodextrins (CD) are cyclic oligosaccharides playing an important role in the self-assembly of amphiphiles. The hollow shape structure of the molecules provides unique physicochemical properties, including the ability to form host-guest complexes. The high relevance in different fields, responsiveness to different stimuli, wide variety, versatility, and availability, make the surfactant molecules attractive host candidates [1]. Polyoxyethylene alkyl ether carboxyl acids ($C_iE_jCH_2COOH$) are an interesting class of surfactants to integrate the complex systems due to their pH and thermo-responsiveness [2]. The surfactant-CD inclusion complexes tend to form highly ordered supramolecular aggregates with desirable versatile characteristics for numerous applications, such as cosmetics, food, medicine, pharmaceutical, and nanotechnology industries [3].

Investigation of the inclusion complexes of $C_{12}E_5CH_2COOH$ and $C_{12}E_{10}CH_2COOH$ and α and β -CD in aqueous solutions was performed by ITC, DSC, and densitometry, and the structural characterization of their assemblies was conducted by small-angle neutrons scattering (SANS). The spontaneous formation of the host-guest complexes and their assembly as building blocks of large supramolecular aggregates with rich structural behavior was verified. The degree of ionization of the surfactant, temperature, and concentration of each component strongly affect the microstructure, mainly in terms of size and long-range ordering of the assemblies. The formation of well-layered structures exhibited long-range order in the most concentrated systems with ionized surfactant. The analysis also allowed an insight into the effect of the number of ethylene oxide units and CDs features in the formation and topology of the novel aggregates. Moreover, the low toxicity and biocompatibility of the assemblies open a wide scope for many applications.

Keywords: Surfactants, Cyclodextrin, Inclusion complexes, Self-assembly.

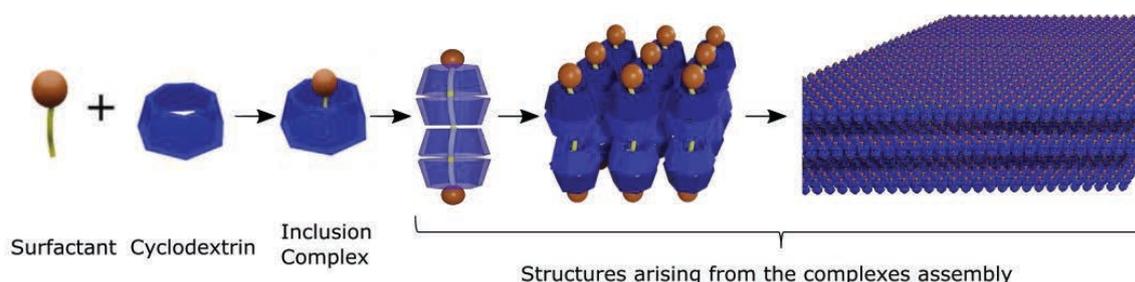


Figure 1. Representation of the inclusion complex formation and supramolecular structures arising from the self-assembly.

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Controlling Reservoir Formation at the Air/Water Interface

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Oppositely charged polyelectrolyte/surfactant (P/S) mixtures have been extensively studied because of their common use in everyday life products and their applications in materials science. In recent years, considerable efforts have been invested in understanding the relation between their interfacial properties and dominant non-equilibrium effects [1]. Recently, a novel methodology was developed to prepare P/S films at the air/water interface by spreading self-assembled aggregates through their dissociation by Marangoni flow [2]. In unprecedented control of film design, possibility to trigger the formation of extended structures (reservoirs) of material during compression/expansion of these films through tuning the charge of the aggregates used was later revealed [3].

We have extended the spread P/S films methodology to pharmaceutically relevant systems by aiming to control the formation of reservoirs and elucidate their structure in a system composed of poly(L-Lysine) (PLL) and sodium-dodecyl-sulfate (SDS). Neutron reflectometry was applied to determine the composition and structure of the films during compression/expansion cycles (Fig.1a). It was shown that there is no loss of material from the interface as reservoirs were formed during film compression and the material reincorporates to the surface monolayer upon expansion. The films adopt structures with an SDS monolayer, a PLL layer bound to the headgroups, and a surfactant bilayer (or hemimicelles) beneath the polyelectrolyte layer (Fig.1b).

This work shows the possibility to accurately design hierarchical 3D-structures at the air/water interface that have the potential to be transferred to solids for applications as antimicrobial coatings or used as biocompatible vehicles for encapsulation of poorly soluble molecules.

Keywords: polyelectrolyte/surfactant mixtures, air/water interface, spread films, reservoirs, neutron reflectometry, biocompatible.

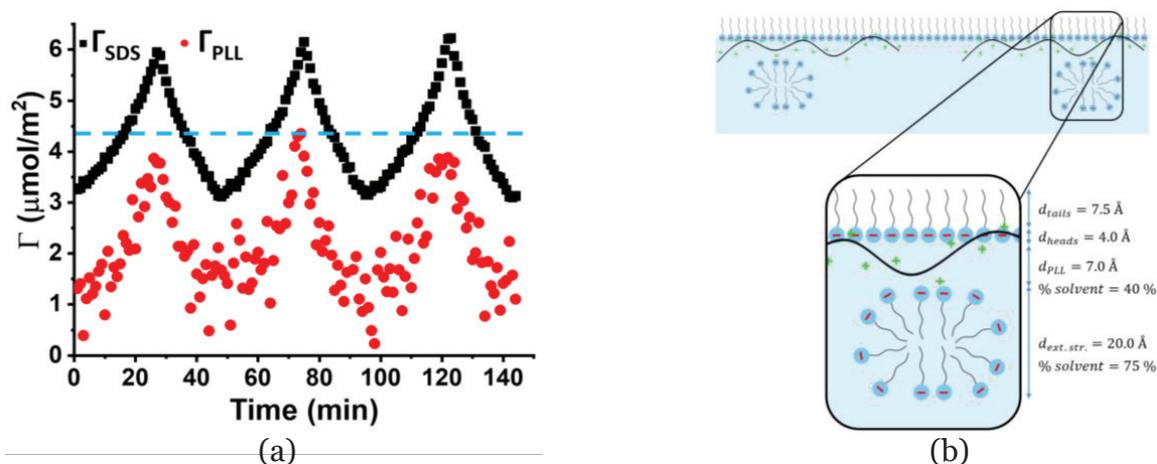


Figure 1. (a) Variation of the surface excesses of SDS (black squares) and PLL (red circles) vs. time during three compression/expansion cycles. The dashed blue line indicates the full monolayer coverage of SDS. (c) Interfacial structure of the film with reservoirs resolved from the neutron reflectivity profiles.

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Valorphins interaction with biomimetic lipid structures

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Alterations in opioid-like peptides are related to a variety of socially significant clinical conditions, comprising obesity, alcoholism, hypertension, diabetes. The morphinomimetic properties of these endogenous peptides are associated with their role in the response to pain, food intake, and many other physiological functions in the organism. Hemorphin-related valorphin, which is released from sequentially hydrolyzed hemoglobin, has been identified to exhibit affinity to opioid-receptors. The attention is focused on the detailed characterization of hemorphins' interaction mechanisms at cellular and biomembrane level regarding the increasing application of peptides in the prevention and treatment of various diseases and conditions.

The effect of valorphin (VV-hemorphin-5) and new VV-hemorphin-5 analogues on the membrane mechanical and electrical properties is probed. Valorphin is obtained to alter the bending elasticity of lipid bilayers in a concentration-dependent manner. The results from isothermal titration calorimetric measurements support the hypothesis about specific valorphin-membrane interaction related to the peptide bulk concentration. We measure membrane softening in the presence of H3-analogue with 2,4-diaminobutanoic acid at position 7, for which the nociceptive screening has shown dose-dependent and biphasic behavior. The analogue H2, where Gln is replaced by 2,3-diaminopropanoic acid, has previously shown the strongest antinociceptive effect compared to other studied peptides. For the same valorphin analogue we report the most pronounced alteration of the membrane capacitance without measurable effect on the membrane mechanics. The increase of the membrane specific capacitance for H2-containing systems accompanied by preservation of the bilayer mechanical properties suggests peptide interaction with the hydrophobic core of the bilayer.

Keywords: valorphin, lipid bilayer, bending rigidity, electrical capacitance

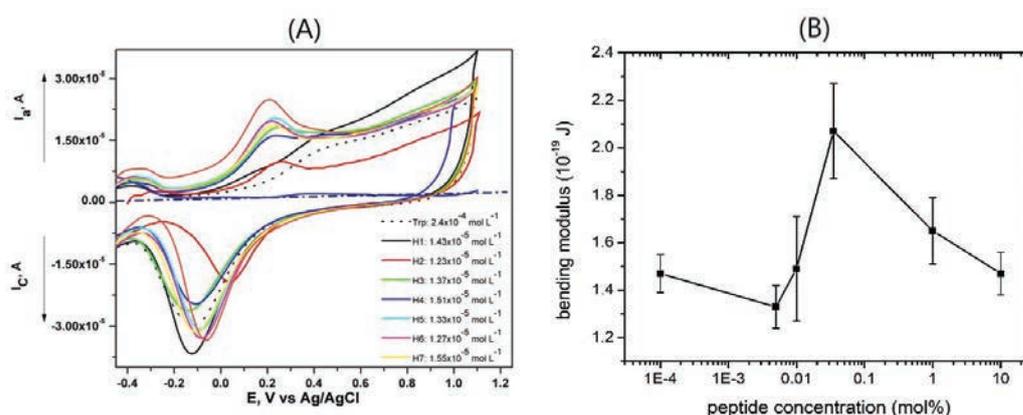


Figure 1. (A) Cyclic voltammograms of free tryptophan and new VV-hemorphin-5 analogues (H1-H7) in phosphates buffer at pH 6.86, Pt-working electrode, 100 mV s⁻¹ scan rate; (B) Bending elasticity of POPC/H1 bilayers.

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Supported bilayers of biological or synthetic lipids on silica nanoparticles for biomedical applications

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Interactions of lipids with nanoparticles (NPs) have been the focus of extensive research for developing efficient biomedical nanomaterials and understanding the impact of nanoparticles on biological fluids [1]. Coating of NPs surface with phospholipid bilayers (nano-supported lipid bilayers, nano-SLB) has been emerged as a central step for NP colloidal stability in biological fluids and biocompatibility. Here, we report on the formation of SLB on positive or negative silica nanoparticles (diameter 50 to 100 nm) using anionic Curosurf®, a biomimetic pulmonary surfactant of porcine origin [2,3]. Anionic synthetic lipids (POPG, DOPG) are also investigated and compared to Curosurf®. Dynamic light scattering, optical microscopy and cryo-TEM studies provide highlights about the structure of the mixtures. We demonstrate that mixing oppositely charged NPs and vesicles leads to a mixture of structures (fig.1a) including aggregation. Applying in situ mechanical energy causes reformation of the assembled structures yielding to well-defined nano-SLBs (fig.1b). On the contrary, sonication is not required when anionic silica is used. The stability of the obtained nano-SLB structures in biological fluids in presence of proteins was finally examined.

Keywords: supported lipid bilayers (SLB), silica nanoparticles, cryo-TEM, Curosurf, POPG

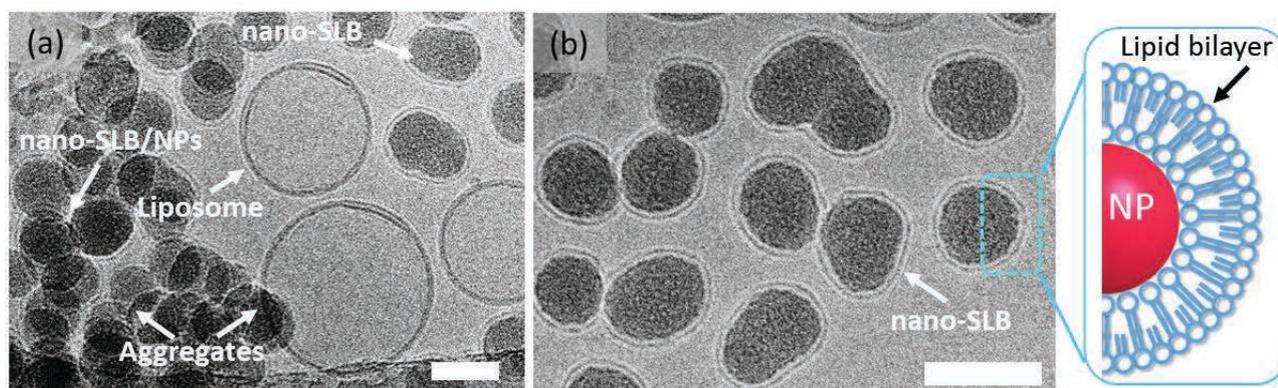


Figure 1. Cryo-TEM images of Curosurf® mixture with cationic silica NPs (a) before and (b) after sonication. Liposomes, liposome/NP aggregates, nano-SLB/NPs aggregates and nano-SLBs are observed. Scale bars are 50 nm. A schematic representation of nano-SLB structure is provided in (b).

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Phycocyanin and Phycocyanobilin Extraction and Purification from *Arthrospira maxima*

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Phycocyanin is a highly degradable light-harvesting protein produced in cyanobacteria. Its distinct blue color is produced by its chromophore, phycocyanobilin (PCB), bound to the protein via a thioether bond. So far, phycocyanin has found several applications in the fields of biotechnology, food science, cosmetics and pharmaceuticals, owing primarily to its ability to be used as a blue dye and its potential as an antioxidant.[1]

This work has aimed to produce cyanobacteria-derived extracts with high phycocyanin content, from commercially available *Arthrospira maxima*, whose production has not been specifically designed towards high phycocyanin yields. Phycocyanin extraction utilized simple, existing protocols that involve biomass lysis, protein precipitation and dialysis. The extracts were further subjected to a gel filtration step that removed the relatively high chlorophyll content of the utilized cyanobacterial extracts, yielding enriched phycocyanin isolates, that can be used for PCB isolation or in phycocyanin encapsulation applications. PCB isolation was performed on lyophilized phycocyanin isolates, via boiling in methanol under reflux. The afforded PCB was finally evaluated with HPLC.

Keywords: Cyanobacterial biologics, Phycocyanin, Phycocyanobilin, Dyes, Antioxidant activity

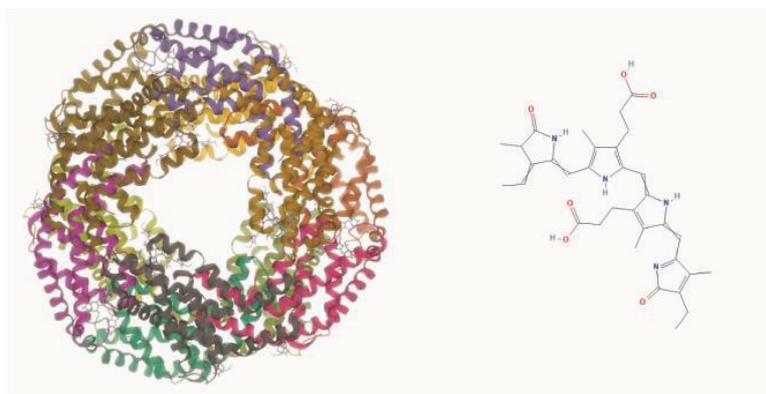


Figure 1. C-phycocyanin and Phycocyanobilin.

Acknowledgements: We acknowledge support of this work by the project “CO2-BioProducts” MIS 5031682), which is funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020) and co-financed by Greece and the EU (European Regional Development Fund).

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OP3.14

Designing and characterization of modern implant coatings

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Tissue engineering which deals with producing biocompatible materials used for replacing tissues and organs. Biocompatible material should not cause undesirable effects. For better material adaptation to the tissues researchers modify its surface, e.g. by deposition onto solid material a thin biological layer.

Cyclosporine A (CsA) is a member of cyclic polypeptides widely used to prevent implant/transplant from rejection. Moreover, the major clinical concern is CsA-induced nephrotoxicity, hepatotoxicity, neurotoxicity and cardiovascular diseases [1]. To minimize these effects lauryl gallate (LG) can be used. LG by capturing free radicals protects the lipids from peroxidation which is the main source of damage to the cell membrane integrity [2]. In addition, a cell-friendly component of natural membranes, i.e. 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC), was used.

The aim of our work was designing and characterization of new biocompatible coatings. To achieve the goal the Langmuir trough coupled with Brewster angle microscope and surface potential meter were used. Intermolecular interactions and arrangement of molecules within the monolayers were determined. Then, the best miscible films were deposited onto solid support by means of the Langmuir-Blodgett (LB) technique. The obtained LB films were characterized by quartz crystal microbalance, cyclic voltammetry and atomic force microscopy. The mass of deposited films, their homogeneity and the surface nanostructure were determined showing that all studied monolayers were homogeneous, with molecules inclined in respect to the surface normal, and the most packed film was obtained in the case of ternary DOPC-CsA-LG monolayer at 1:1:2 molar ratio.

Keywords: Langmuir monolayer technique, Langmuir-Blodgett technique, cyclosporine A, lauryl gallate

Acknowledgements: Małgorzata Jurak acknowledges the National Science Centre in Poland for partial funding the studies in the framework of the project 'Comprehensive physicochemical studies of multi-component films: phospholipid-immunosuppressant-antioxidant on liquid or solid support', no 2019/03/X/ST4/01470.

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Ionic Liquids $[M^{3+}][A^-]_3$ with three-valent cations and their possible use to easily separate rare earth metals

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Ionic Liquids (ILs) are generally defined as salts with a melting point below 100 °C, and have garnered large popularity due to their high customisability and beneficial properties. Most conventional ILs are composed of organic cations such as imidazolium, pyrrolidinium, pyridinium or phosphonium derivatives, and weakly coordinating anions [1,2]. However, these compounds are often toxic and poorly biodegradable, and their synthesis and the subsequent purification is laborious and costly.

Alkyl polyethylene oxide carboxylates provide a simple and clean way to liquefy rare earth metals (REM) by incorporating the corresponding cations, in particular Eu^{3+} , La^{3+} and Y^{3+} into polyvalent Ionic Liquids. In contrast to conventional methods, this is achieved not by transforming them into anionic complexes, but by keeping them as bare cations and combining them with convenient, cheap and commercially available anions (A) in the form $[REM^{3+}][A^-]_3$. To do so, we follow the COnccept of Melting Point Lowering due to EThoxylation (COMPLET) [3].

Despite the similarities of their cations, the provided ILs possess remarkably different properties, and their water-octanol partition coefficients P show that the studied rare earths can be separated via liquid/liquid extraction without the use of toxic extractants. Furthermore, the ILs possess interesting luminescent properties as non-conventional fluorophores.

Keywords: Ionic Liquids, Surfactants, Rare Earth Metals, Metal Separation, Luminescence, alkyl ethylene glycol carboxylates



Figure 1. Fluorescence of $[Y][C8E5c]_3$, $[La][C8E5c]_3$, and $[Eu][C8E5c]_3$ solutions under excitation with UV light at 365 nm.

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Photophysical investigation of cobalta-bis-dicarbollide

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Metalla-bis-dicarbollides, such as COSAN [Co(C₂B₉H₁₁)₂], are inorganic ionic complexes composed of a central metal cation, sandwiched between two dicarbollide cages, which confers a global negative charge delocalized across its entire structure (Fig. 1a). Despite lacking a classical amphiphilic structure, COSAN is distinguished for its surfactant properties,^[1] forming monolayer vesicles at low concentrations in water (<10 mM). As the concentration increases (>10mM), COSAN forms small aggregates (micelle-like).^[2]

The photophysics of COSAN in aqueous solutions have not been thoroughly investigated so far. It was shown that COSAN has interesting redox properties and can therefore be used as a photocatalyst.^[3] Moreover, the formation of supramolecular assemblies appears to significantly influence electron transfer processes, and thus photocatalytic efficiency. Therefore, it is crucial to comprehend the photophysics of COSAN derivatives.

In the present work, we studied the influence of the self-assembly of COSAN on its photophysical properties in water using steady state and time resolved fluorescence spectroscopy. 2D fluorescence spectra were measured at different COSAN concentrations (Fig. 1b). The steady state emission spectra of COSAN show quenching effect ($\lambda_{\max} \approx 390$ nm) and a break by increasing concentration, (Fig. 1c). Remarkably, we observed also variations in the emission signal of water (Raman scatter peak) with respect to the concentration of COSAN (Fig. 1d). The evolution of the signal, shows two breaks that most likely correspond to the appearance of vesicles and micelles. The time-dependent fluorescence of COSAN at different concentrations was also determined on exciting at 400 nm laser. The fluorescence decays give two discrete lifetimes in the range of ns and what appears to be a longer component in the range of microseconds. Pump-probe photoluminescence brings fundamental information on the electronic energy levels and intermolecular energy transfer. The femtosecond fluorescence decay of COSAN follows an exponential function with three ultrafast decay times, between 1 and 120ps.

Keywords: photophysics, COSAN, fluorescence spectroscopy.

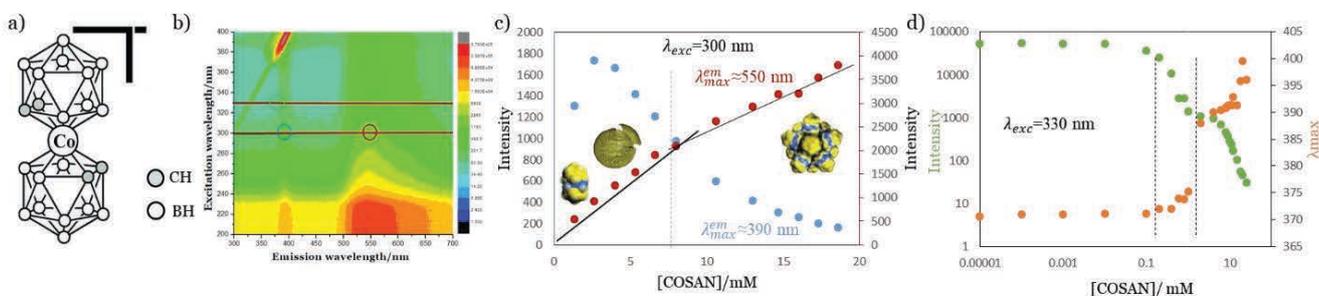


Figure 1: a) Chemical structure of COSAN, b) 2D fluorescence spectra of 13 mM COSAN, fluorescence intensity at c) $\lambda_{exc} = 300$ nm [$\lambda_{max}^{em} \approx 390$ nm (blue circle), $\lambda_{max}^{em} \approx 550$ nm (red circle)] and d) $\lambda_{exc} = 330$ nm [$\lambda_{max}^{em} \approx 370$ nm (green circle)].

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Surface-Active Protein-Tag Enabling Enzyme Enrichment in Surfactant-Free Flotation

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In the provisioning of enzyme preparations from fermentation processes downstream processing can account for up to 70 % of the total manufacturing costs [1]. A major part of these costs can be attributed to chromatographic steps for protein capture, purification and polishing.

In the last years, considerable effort has been put into the establishment of non-chromatographic purification methods, including adsorptive bubble separation (ABS) also known as preparative foaming or foam fractionation. ABS utilizes the adsorption of surface-active components at a gas-liquid interface for enrichment and purification. It offers mild conditions of operation, lack of organic solvents and a simple construction of devices [2]. However, the employment of surfactants is a major drawback, as these can effectively inhibit the enzyme function. Furthermore, the direct adsorption of enzymes at the gas-liquid interface, which can result in denaturation, as well as the untargeted nature of the method, prevents its general implementation in downstream processing. Consequently, ABS has only been employed for a rather low number of enzymes with a confinement to very stable candidates (mainly hydrolases and oxidoreductases) [2].

Here, we introduce a molecular tag derived from a natural surface-active protein for directed adsorption of a target enzyme at the bubble surface and thus, enrichment of the tagged protein in the foamate. Apart from successful enrichment, we demonstrate considerable preservation of the enzyme activity, presumably because the tag and not the enzyme adsorbs at the interface. Furthermore, the hydrophobicity of the tag leads to high surface coverage achieving foam stability without an additional foaming agent.

Thus, a surface-active enzyme tag provides promising features for the development of adsorptive bubble separation into an efficient alternative for the downstream processing of enzymes.

Keywords: protein, flotation, adsorption, enzyme activity, enrichment, surfactant-free

Acknowledgements: This work has been funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 407649267

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Solvation of Brij35 in Alcohol and Alcohol/Water Systems: Structure and Dynamics

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Surfactant molecules present in sufficient concentration in various solvents self-assemble and can form various structures such as micelles, bilayers, bicontinuous structures, reverse micelles, etc. If their concentration is low, the formation of such structures is not necessarily favorable and usually only single solvated surfactant molecules are present. Such conditions are ideal for the theoretical and experimental study of the structural and dynamic aspects of the solvation of surfactant molecules and various effects that influence it. We focus on the nonionic surfactant Brij 35 (dodecyl-poly(ethylene oxide-23) ether; C₁₂E₂₃) in various pure simple alcohols (ethanol, *n*-butanol and *n*-hexanol) and alcohol mixtures with low concentration of water [1]. By combining experimental small- and wide-angle X-ray scattering (SWAXS) and molecular dynamics simulations, we were able to obtain detailed information about the intra- and inter-molecular structure of the systems, which could not be obtained using previous approaches based on the inverse Fourier transform alone [2]. We were also interested in how the presence of water in the system affects its structural and dynamical properties. The structural validity of the simulation results was checked by calculating the scattering intensities using the ‘complemented system approach’ [3] and comparing them directly with the experimental SWAXS data. This is the first time that the complemented system approach has been applied to the surfactant system and the second time that it has been applied in the colloidal domain [4].

Keywords: SAXS, Molecular Dynamics, Complemented-system approach

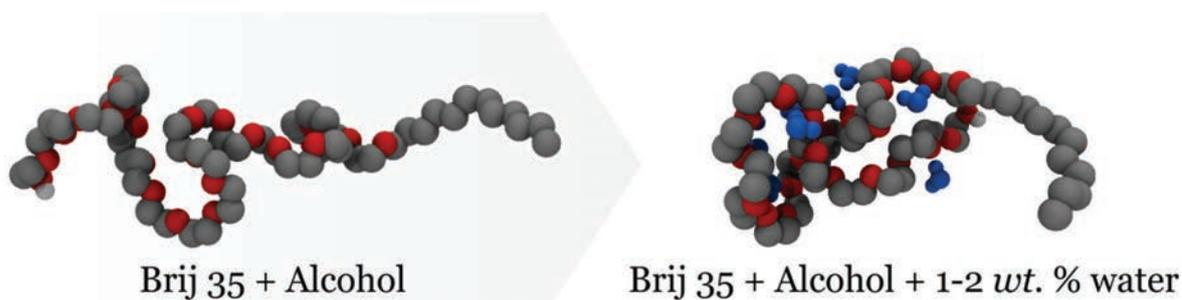


Figure 1. Schematic representation of the effective structural changes influenced by the presence of water.

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Aggregation of NaCOSAN and NaFESAN aqueous mixtures

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Self-assembly of amphiphilic ions and molecules is a well-known and extensively studied process with widespread application.[1] The process in aqueous solutions is usually entropy driven due to the release of water hydrating the non-polar parts into the bulk.

Metallacarboranes, such as the $[3,3'\text{-Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anion (COSAN anion) and the $[3,3'\text{-Fe}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ anion (FESAN anion), are boron cluster compounds containing metal sandwiched by two dicarbollide clusters. The COSAN and FESAN anions have a low charge density, which leads to specific interactions such as the hydrophobic/chaotropic effect. Therefore, alkali salts of metallacarboranes are also regarded as amphiphilic compounds.[2]

In our recent publication isothermal titration calorimetry (ITC) was used to study thermodynamics of COSAN aggregation with Li^+ , Na^+ , K^+ as the counterions and of the acid HCOSAN. The effects of added salt and acetonitrile were further examined.[3] With the improvement of the ITC data interpretation, the thermodynamic parameters as well as the average aggregation number and the degree of counterion binding can be reliably determined.[4]

In this contribution we will present the experimental results of NaCOSAN and NaFESAN mixtures. From ITC measurements, using an appropriate model, the thermodynamic parameters of aggregation were obtained for NaCOSAN and NaFESAN in water and mixtures of both in water. The observed differences in the values are minor with most notable dependence of the enthalpy of aggregation on the mixture composition. Using NMR spectroscopy, we follow changes of proton chemical shifts upon aggregation in pure NaCOSAN, pure NaFESAN and mixtures of the two. The paramagnetic effects of NaFESAN on NaCOSAN shifts allow for the estimation not only of aggregation number but also the structure of the aggregates.

Keywords: metallacarboranes, isothermal titration calorimetry, aggregation

Acknowledgements: The bilateral Grant No. N1-0186, 21-20008K funded by the Slovenian Research Agency and the Czech Science Foundation is acknowledged.

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Equilibrium and dynamic adsorption of volatile surface-active amphiphiles on vapor/solution interfaces

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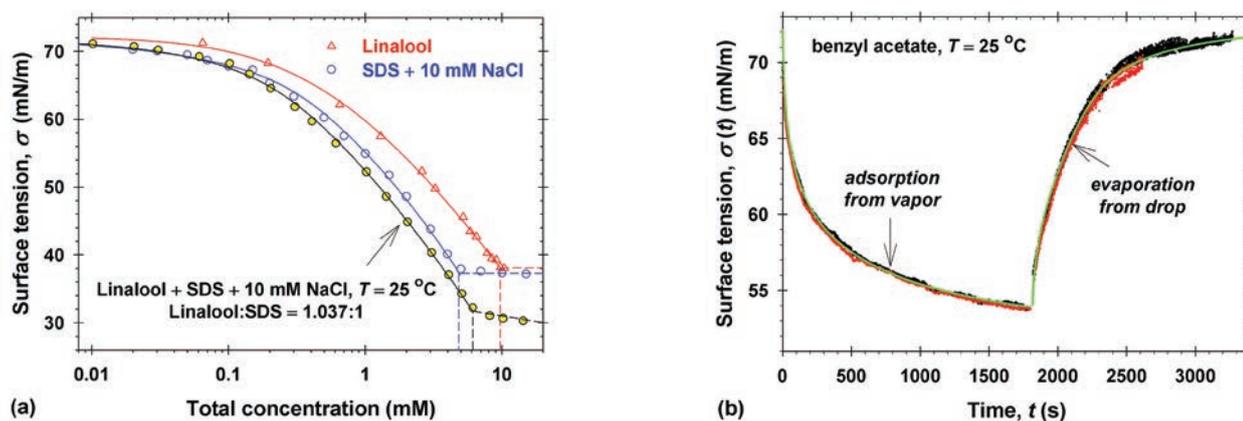
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Subject of this work is to investigate the equilibrium adsorption of volatile surface-active amphiphiles on vapor/solution interfaces. The used amphiphiles are benzyl acetate, linalool, and citronellol, all of which have low saturated vapor pressures, appreciable solubility in water, and well pronounced surface activity. The effect of added sodium dodecyl sulfate (SDS) on the formation of mixed adsorption layers is quantified. The adequate theoretical processing of the equilibrium surface tension, s , isotherms is applied to construct the two-dimensional equation of state, which relates s to the species adsorptions at the interface.

The obtained physicochemical parameters (excluded areas per molecule, adsorption energies, lateral interaction parameters, counterion binding energy) give possibility to explain the synergistic effect of volatile amphiphile and SDS mixing on the adsorption and surface tension (Fig. 1a). The adsorptions, occupancies of the Stern layers and surface electrostatic potentials in the case of added SDS are calculated and illustrated.

The dynamics of studied volatile surface-active amphiphiles adsorptions in the regimes of adsorption from vapor and desorption from solution drop is studied experimentally using the axisymmetric drop shape analysis (Fig. 1b). The obtained rates of adsorption and desorption of benzyl acetate, linalool, and citronellol are summarized in Ref. [1].

Keywords: volatile surface-active amphiphiles; sodium dodecyl sulfate; equilibrium surface tension; dynamics of adsorption



Figure

1. (a)

Synergistic effect of linalool + SDS mixed solutions on surface tension; (b) Kinetics of adsorption of benzyl acetate in the adsorption from vapor and evaporation from drop regimes.

Acknowledgements: The authors are grateful to the project # DO 02/4 – 12.06.2018 with the Bulgarian Science Fund (FNI-MON), for the financial support.

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OP3.21

Specific ion effects on Hemoglobin and Bovine Serum Albumin evidenced in denaturing conditions through ESI-MS investigation.

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In the last two decades ESI-MS techniques have received great attention for the potential in investigating proteins and their features in terms of stability and interactions [1]. Electrospray ionization is a soft ionization technique that allows to produce intact multiple charged species, without significant fragmentation. In this work the effect of different metal-chlorides, along with sodium and potassium bromides, iodides and thiocyanates, added to Hb or BSA [2-3] aqueous solutions at pH = 2.7, is investigated. Different salt concentrations were used to maximize the quality of the ESI-MS spectrum, in terms of peaks' intensity and bell-shaped profile. The charge state distribution, in terms of average charge Z_{av} , has been related to both molecular mass and solvent accessible surface area [4]. ESI-MS data, particularly peaks' intensity, allowed to recognize a specific effect of Li, K, and Mg chlorides towards Hb, and of NaCl towards BSA. A worsening of the ESI-MS spectra was found according to the increasing anion chaotropicity, namely $Cl^- < Br^- < I^- < SCN^-$. ESI-MS data indicated that in most cases proteins undergo liquid-gas phase transition upon solvent evaporation according to a chain ejection model where unfolded proteins come out of the droplet as a result of ion mediated charge rebalancing between the droplet and the protein. In the case of BSA it was also observed the formation of a fragment due to collision induced dissociation whose extent was strongly dependent on salt type. Fragment formation was particularly favored by chaotropic ions such as Rb^+ and Cs^+ cations or SCN^- anion.

Keywords: proteins, ESI-MS, specific ion effects

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Aqueous phase behavior and microstructuring of octyl octaethylene glycol ether carboxylic acid (C₈EO₈CH₂COOH)

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Octyl octaethylene glycol ether carboxylic acid (C₈EO₈CH₂COOH) with the commercial name Akypo™ LF2 is a cheap surfactant, commercialized by Kao Chemicals. In its acid form, it is essentially a nonionic surfactant with a short alkyl chain and a significantly larger hydrophilic part, which should cause a considerable steric constraint on micelle formation. In analogy to its C₈EO₈ counterpart, as mentioned by Mitchell et al. in 1983 [1], Akypo LF2 is expected to form only direct spherical micelles. To the best of our knowledge, no in-depth structural elucidation of a similar system was reported to date. Since the additional carboxylic acid function should also offer new opportunities for possible applications, especially in the field of organic catalysis, it is worth having a closer look at the system's microstructuring.

Phase diagrams of binary mixtures of Akypo LF2 and water are established over a large concentration and temperature range. Further, the system's microstructuring is elucidated through a combination of Small-Angle X-ray Scattering and Vapor Pressure Osmometry experiments.

Direct spherical micelles persist over the whole temperature and composition range. For surfactant concentrations up to about 60% by weight, spherical core-shell micelles of constant size (aggregation number ≈ 30) and shape are observed. Above 60% by weight of surfactant, the headgroups are no longer fully hydrated and start to interdigitate. The core-shell structure vanishes, and the system can be described as confined spherical hydrocarbon cores dispersed in a hydrophilic medium of interdigitated headgroups. With decreasing amount of water, the extent of interdigitation increases, while the aggregation number decreases. In absence of water, hydrocarbon cores consist of 8 octyl chains. Transformation of half of the carboxylic acid moieties into sodium carboxylate moieties does not change the general structuring, but does partially impede interdigitation, thus increasing the aggregation number.

Keywords: surfactants, surface active ionic liquids, spherical micelles, alkyl ethylene glycol ether carboxylates, colloids

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Where is a direct dye located in a micellar solution?

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Solutions of dye and surfactant are of major significance for industrial applications such as textile-dyeing, wastewater-treatment, and cosmetics. As the presence of surfactant in a dyeing solution significantly influences its properties, considerable attempts have been launched based on various dye-surfactant combinations to gain a systematic understanding of dye-surfactant-interactions. Since many organic dyes show environment-sensitive absorption, it is promising to study dye-surfactant interactions with UV/vis-spectroscopy. However, UV/vis-spectroscopy does not reveal aggregate shape and location of the dye within the aggregates. These properties are expected to influence diffusion and the interaction between the dye and a substrate and are therefore important to study. Surprisingly, only little has been done in this field. The few studies available on mixed cationic surfactant - dye systems mostly suggest the presence of worm-like or cylindrical aggregates.^[2-4] Kutz et al. located the position of the dye within the aggregates, based on geometrical considerations.^[4] However, this is not unambiguous.

Small-angle neutron scattering (SANS) is a powerful technique to elucidate the structure of aggregates in solution. In addition to that, it offers the possibility to hide certain parts of the aggregate by isotopic substitution. This is called contrast variation and aids to unambiguously reveal the position of a direct dye in a micellar solution.

We studied solutions of a commercial, anionic direct dye and the surfactant dodecyltrimethylammoniumbromide (DTAB). We will present SANS data that reveal the formation of flexible cylinders from dye and DTAB. Contrast variation shows, that the anionic dye constitutes the shell of the cylinder. Structure formation depends on the ratio between dye and surfactant. Reference experiments indicate that the dye without surfactant does not form large aggregates, even though this could have been anticipated from a concentration-dependency of its absorption spectra. The results underline the significance of scattering experiments.

Keywords: SANS • Contrast Variation • Aggregation • Dye • Surfactant

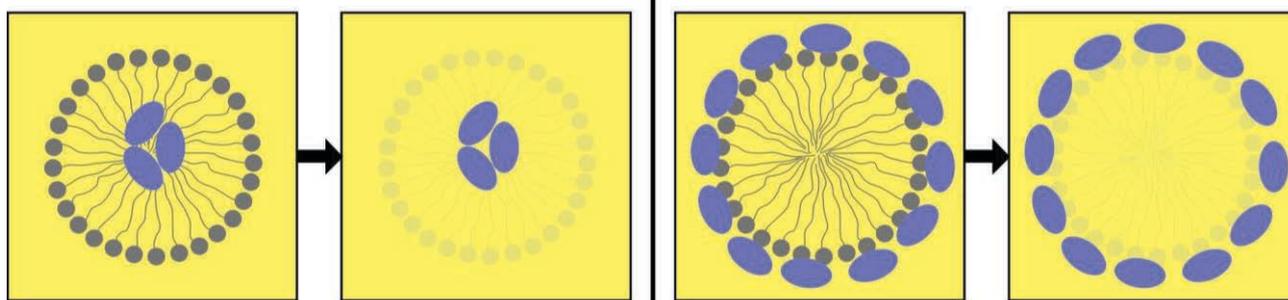


Figure 1. Principle of contrast variation in SANS by hiding the surfactant in a mixed micellar aggregate.

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OP3.24

Membrane behaviour of Cationic Ion Pair Amphiphile Vesicles with different amount of cholesterol

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This contribution is focused on the study of the effect of cholesterol on the properties of vesicular membranes of ion pair amphiphiles (IPAs) at different temperatures. IPAs are promising pseudodouble chained surfactants formed by electrostatic binding between oppositely charged surfactants with removed counterions. IPAs in an aqueous environment form liposomal-like vesicular systems with hydrophilic and hydrophobic domains. Because of versatile composition and lower price, IPAs vesicles can take part as delivery systems [1,2].

The hexadecyltrimethylammonium-dodecyl sulfate with 10 mol. % dioctadecyldimethylammonium chloride and with 0–73 mol. % cholesterol was chosen for study of vesicles properties in the temperature range 10–80 °C. Under these conditions, the size distribution by dynamic light scattering and the membrane behavior of inner and outer part by fluorescence spectroscopy were studied.

Vesicles with a cholesterol content of 23–53 mol. % have no changes in their size or polydispersity index (PDI) due to temperature change. Samples with 63 and 73 mol. % were polydisperse in a given temperature. For samples to 13 mol. % increasing temperature leads to a decrease in their size and PDI. Membrane core fluidity monitored by Diphenylhexatriene (DPH, steady-state anisotropy) shows small variations in the anisotropy value at low temperatures. Higher temperatures show a monotonous increase in anisotropy with increasing cholesterol. The outer part of vesicles solvation and fluidity was studied by Laurdan (generalized polarization and steady-state anisotropy) and Trimethylammoniumdiphenylhexatriene (TMA-DPH, steady-state anisotropy). All three variabilities show similar dependence on temperature as DPH anisotropy. If we focus on the stable region of vesicles, the thermal driving of the membrane leads to a radical change in fluidity and solvation, which, however, does not mean a change in size distribution. These findings and detailed description of the temperature-concentration dependency provide an overview for further study of the membrane.

Keywords: Ion pair amphiphile, Vesicles, Cholesterol, Fluorescence.

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Study of cholesterol's effect on the properties of cationic vesicular systems

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This work is focused on the study of properties and stability cationic vesicles at laboratory temperature. Cationic vesicles were based on the ion pair amphiphile (IPA), which was prepared by mixing equivalent volumes of aqueous solution HTMAB (hexadecyltrimethylammonium bromide) and SDS (sodium dodecylsulphate). Then the precipitate was obtained and after removal of the counterions of these surfactants, IPA was formed. The residue IPA was denoted as HTMA-DS. To improve stability positively charged double-chained dioctadecyldimethylammonium chloride (DODAC) and cholesterol were added [1,2]. The total amount of cholesterol was set to 0, 3, 13, 23, 33, 43, 53, 63 and 73 mol.%. In this system, the size distribution was studied using the dynamic light-scattering (DLS) and zeta potential was determined by electrophoretic light-scattering. These standard techniques were supplemented by fluorescence spectroscopy technique. Specifically, generalized polarization (GP) was measured using a Laurdan probe. This probe is sensitive to fluidity and membrane hydration at a particular temperature [3].

Due to low stability and high opalescence of samples, spectral techniques were used only for the samples with cholesterol content above 23 mol.%. The results from fluorescence spectroscopy point to a change in the amount of hydration water in the membrane, the largest amount of which is present in the samples with 43 and 53 mol.% cholesterol. Using the light-scattering technique, the short-term stability of prepared vesicular systems was also observed over the first 36 days. Obtained results confirmed that the most stable systems are those containing 43 or 53 mol.% of cholesterol.

Keywords: ion pair amphiphile, cationic vesicles, cholesterol, hydration water, generalized polarization

Acknowledgements: This work was supported by the Czech Science Foundation [project No. 19-14024J (GACR)], and Ministry of Science and Technology, Taiwan [project No. MOST108-2923-E-006-006-MY3].

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Reduction-Sensitive Cationic Bolaamphiphiles Derived from Cystine

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Bolaamphiphiles consist of two hydrophilic heads connected by one hydrophobic skeleton. This bipolar structure requires a higher temperature to induce its phase transition, which ensures structural stability even in harsh environments.[1]

Cationic lipids spontaneously self-assemble with anionic nucleic acids (NAs) through electrostatic interactions, forming nanoparticles, which provide NAs protection against nuclease degradation and drive the genetic cargo into cells.[2] Having a disulfide bond within the hydrophobic skeleton of the carrier, provides high circulation stability and fast intracellular drug release, due to its degradation in the presence of reducing agents such as glutathione.[3] Here we report on the synthesis of two derivatives of cystine which contain two terminal ammonium units and a preliminary study of their aggregation and response to reducing agents in aqueous media (Figure 1)

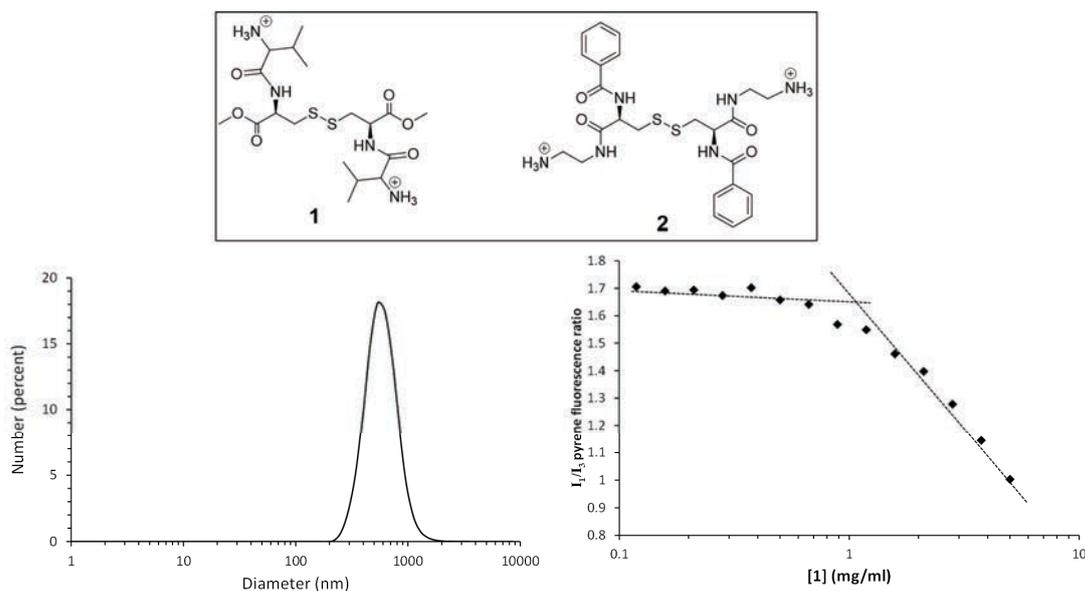


Figure 1. a) Structure of cationic bolaamphiphiles. Size distribution of the nanoparticles and critical aggregation study for compound 1.

Keywords: cationic bolaamphiphiles, stimuli-responsive, nanocarriers

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Stimuli-Responsive Molecular Gels and Nanoparticles from Amino Acid-Derived Anionic Surfactants

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Supramolecular or molecular gels are formed from low molecular weight organic molecules that self-organize into a fibrillar-shaped network through non-covalent interactions. Supramolecular gels have been studied and used in industry for a long time, obtaining low-cost bulk materials. In the last decades, applications have appeared in biomaterials, drug delivery, advanced materials (“smart materials”) and electronic devices. Molecular gels can present improved properties such as reversibility and biocompatibility when compared with polymer gels.[1]

Surfactant-like molecules can form gels by assembling micelles into fibers that grow and overlap or become entangled, building a three-dimensional network. Here we report new surfactant-like anionic molecules derived from L-Valine that form nanosized aggregates and gels. The materials are responsive to the nature and concentration of the alkaline cation present. Additionally, reduction-sensitive materials are obtained by the introduction of disulphide units in the structure of the molecules.

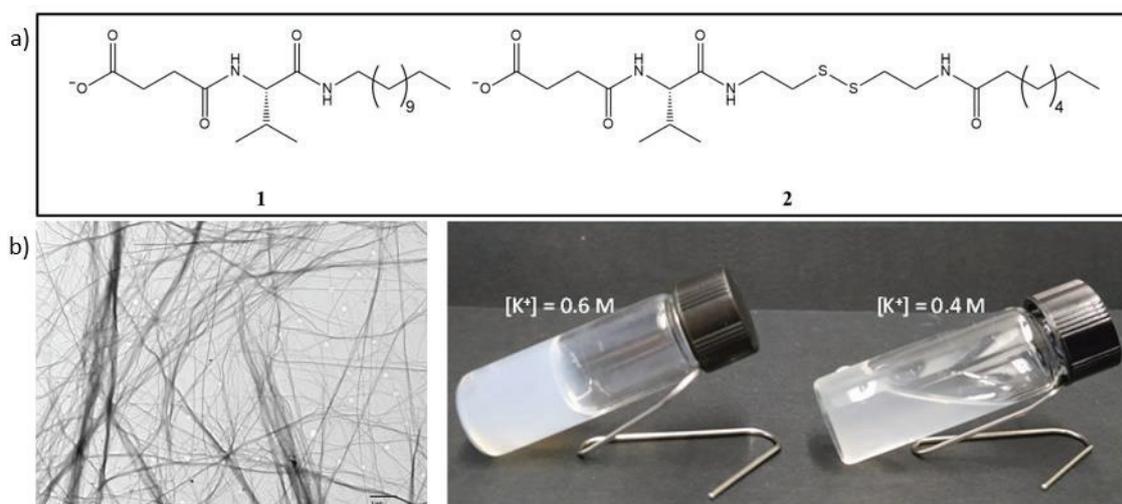


Figure 1. a) Structure of some of the studied anionic surfactants. b) TEM image of the fibres formed by compound **1** in presence of 0.6M Na⁺ (left) and influence of potassium cation concentration on gel formation by compound **1**. (right).

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Morphology of Fluid Domain and Line Tension in Lipid Vesicle Containing Sphingomyelin

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Biological membrane express many advanced functions by forming in-plane nanoscale heterogeneous structure called raft. To gain insight into rafts formation, lipid vesicles composed of phospholipids and cholesterol are often studied as its simplest model. In such model systems, it has been confirmed that liquid-ordered (Lo) phase and liquid-disordered (Ld) phase coexist depending on the composition and temperature. In this phase separation, an excess energy, called line tension, is generated at the boundary between Lo and Ld phases, and thus the investigation into the correlation between morphology of domain and line tension is important to clarify the principle of raft formation.

In this study, we employed a ternary *N*-palmitoylsphingomyelin (PSM) / 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) / cholesterol (Chol) vesicle and a quaternary PSM / DOPC / 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) / Chol one. We observed morphology of domain by fluorescence microscope at 25 °C and measured line tension by flicker spectroscopy method.

In ternary system, phase separation into Lo and Ld phases was observed respectively by the dark and bright regions in microscopic images in Figure 1. As the compositions of two phases become close in the vicinity of critical point, line tension decreased, and the fluctuation of boundary was large enough for domains to take mosaic pattern. The line tension was roughly 1.15 pN. Taking note of our previous results that the line tension was roughly 0.9 pN in 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) / DOPC / Chol system, it is expected the high affinity between PSM and Chol increases the line tension.

In quaternary system, furthermore, as the molar fraction of POPC was increased with fixed molar ratio of PSM / DOPC / Chol, the line tension decreased gradually, and eventually vesicles become homogeneous at 58 mol% of POPC fraction.

Keywords: lipid vesicle, sphingomyelin, domain, line tension, hybrid lipid

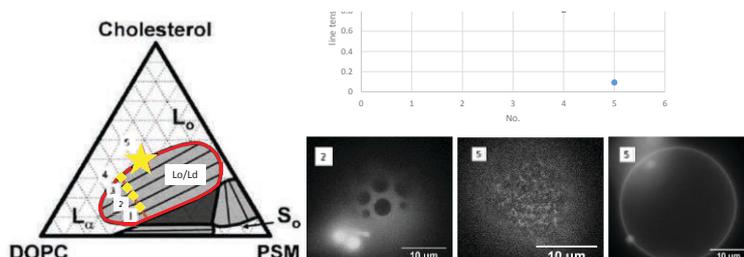


Figure 1. (left) The phase diagram of PSM / DOPC / Chol system at 25 °C.^[1] (upper right) The line tension value on composition (1)~(5). (lower right) GUVs observed at each composition.

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Bioinspired Sticky and Slippery Boundary Layers

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Reducing CO₂ emissions is a key challenge in 2021, with transport contributing a significant proportion of annual emissions. In passenger cars, 33% of fuel usage derives from friction [1], representing significant potential for emission reduction through improved lubrication. Additionally, developing better lubricants aids in wear reduction, increasing component lifetime-relevant to machinery in extreme environments.

Boundary lubricants address both problems, providing a low coefficient of friction and wear-protection by forming self-assembled layers on surfaces. For longevity, this layer must robustly anchor to surfaces and withstand harsh conditions such as the high temperatures and pressures occurring within car engines.

Nature provides inspiration for new developments. Mussels, a group of mollusks that live underwater, adhere very strongly to a range of organic and inorganic materials using specialized mussel-foot proteins (mfps). Mfps provide adhesion through the presence of catechol groups, which form anchoring hydrogen bonds and complexes with surfaces (**Fig. 1**) [2]. This project aims to investigate the self-assembly, adhesive and lubricating ability of novel mussel-inspired, catechol-containing surfactants and polymers using surface-force apparatus [3], SANS and SAXS, and X-ray reflectivity to identify candidates for the development of novel, improved friction modifier additives.

Keywords: Lubrication, bioinspired, self-assembly, surfactants, polymers

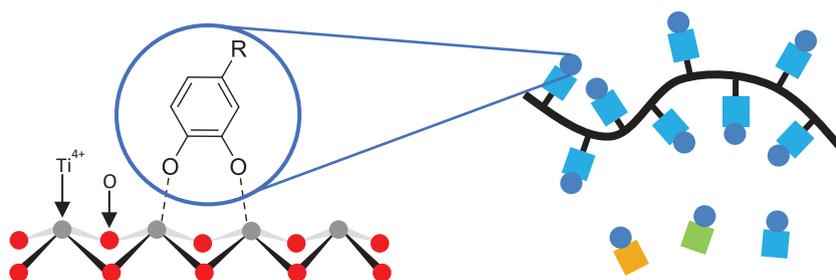


Figure 1. (Left) Proposed mechanism of catechol binding to TiO₂ (adapted from [2]). (Right) Representations of catechol-containing polymer and surfactants with catechol-containing headgroups.

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Thermally stabilized trypsin-chondroitin sulfate nanoparticles with tunable response in pH

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Trypsin is a protein secreted by the pancreas that acts as a proteolytic enzyme in the small intestine. It has been formulated in nanocapsules for oral administration to support digestion [1] and used in mucus penetrating drug delivery systems [2]. In this work, electrostatic complexation of trypsin with chondroitin sulfate is used to prepare nanoparticles of well-defined size that are stabilized against disintegration at neutral and acidic pH by thermal treatment (Figure 1). At pH 4 complexes of radius about 50-70 nm are formed due to the electrostatic attraction between the positively charged trypsin and the negatively charged chondroitin sulfate. At pH 7 the untreated complexes transform into clusters with a wide size distribution (Figure 1a) while their mass is diminished (Figure 1b). When the complexes are thermally treated, they keep their integrity at pH 7. This is due to the tendency of trypsin to denature and aggregate at elevated temperatures [3]. The secondary conformation of trypsin in the complexes has been measured by spectroscopy methods and the spatial arrangements at the 1-100 nm length scale by small angle X-ray scattering. This work proposes a simple and biocompatible methodology for trypsin nanoparticles preparation with potential in drug delivery applications.

Keywords: chondroitin sulfate; trypsin; complexation; thermal treatment; nanoparticles.

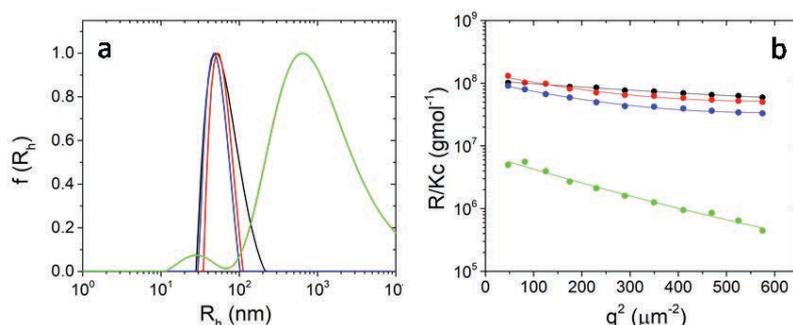


Figure 1. Dynamic light scattering (a) and static light scattering (b) results from trypsin-chondroitin sulfate complexes at pH 4 (black), at pH 4 after thermal treatment (red), at pH 7 after thermal treatment (blue) and at pH 7 without thermal treatment (green).

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Influence of CTAB on the surface properties of polylactic acid films

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Surfactants are amphiphilic compounds consisting of a polar and an apolar moiety, so doping biomaterials with them is an interesting way to change their surface properties, such as hydrophobicity, surface tension or roughness. Furthermore, it is important to study how their presence into the bulk material can affect the degradation of these materials in physiological environments.

The material under study is polylactic acid (PLA), a biodegradable, hydrophobic polymer characterized by our research group [1], in which variable amounts of cetyltrimethylammonium bromide (CTAB) have been included. In order to determine whether the surface on which the PLA is deposited influences both the way in which the polymer chains are oriented [2] and the distribution of the surfactant within the film, PLA films containing CTAB have been prepared on both hydrophobic (silicon wafer) and hydrophilic (glass) surfaces. Samples were also incubated at 37 °C in a physiological buffer PBS (phosphate buffered saline) for 0, 7 and 28 days to study the changes in surface properties induced by CTAB release.

Thus, differences in contact angle and surface tension are observed between PLA films prepared on silicon wafers and glass, the latter being more hydrophilic. Furthermore, as the CTAB content increases, the contact angles of the films decrease, although it seems that the surfactant particles are not distributed in the same way on both surfaces. Changes in contact angles, surface tension and roughness are also found before and after degradation.

Keywords: polylactic acid, CTAB, surface properties

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Improving antibacterial efficacy in laundry formulations

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Diclosan, also known as Tinosan HP100, is one of the technologies used to deliver antibacterial control in various laundry formulation. This work was focused on the mechanistic understanding of diclosan deposition on fabric during the wash process. This study explored the impact of various factors on diclosan deposition such as 1) active concentration; 2) surfactant type; 3) the surfactant charge; 4) surfactant concentration. In this work, we examined diclosan deposition for surfactants used in the laundry industry and adsorption isotherms were constructed for each system. Deposition on fabrics was tracked using an in-situ UV-Vis technique and the results are validated against antibacterial benefits. Due to its poor solubility in water ($\log P$ (4.53)), diclosan requires the presence of surfactants to enhance its water solubility and enable its delivery on fabric, so antibacterial deposition is minimal without the use of surfactants. Surfactant concentration considerably above the critical micelle concentration of the system has been correlated consistently to lower levels of on fabric deposition (Figure 1), due to the lower micellar loading levels and the finite number of micelles that will be deposited on a specific area. Presence of attractive electrostatic interactions with the use of positively charged surfactants or reduction of the repulsive electrostatic interactions in low pH conditions lead to a significant increase of Diclosan deposition levels. From this study we concluded that with regards to the delivery of Diclosan on fabric, the use of positively charged carriers or a concentration equal to 10% higher than the critical micelle concentration (CMC) are deemed beneficial.

Keywords: deposition, formulation, antibacterial

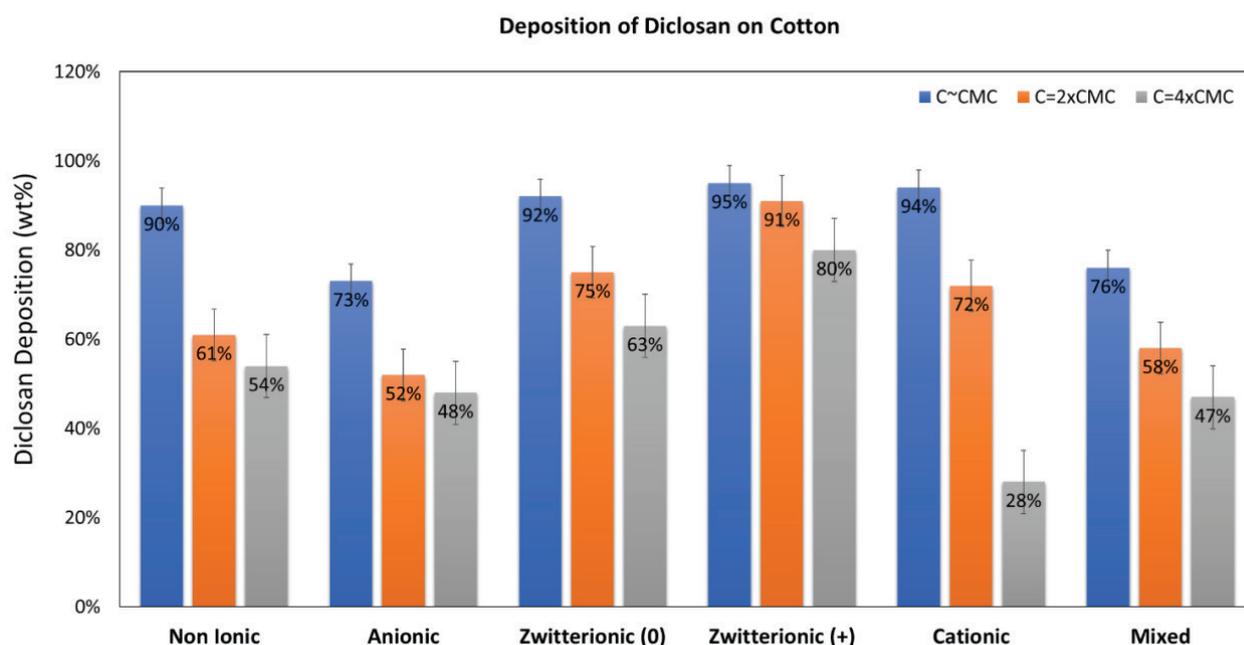


Figure 1. Tinosan deposition through the wash for various surfactant systems, in relation to critical micelle concentration (CMC) on cotton.

OP3.33

Designer Phosphocholinated Nanoparticles as Robust Superlubrication Vectors

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Phosphatidylcholine lipid bilayers or liposomes at interfaces in aqueous environments can provide physiological-level lubrication. This is attributed to the hydration lubrication mechanism acting at the highly hydrated phosphocholine-headgroup layers exposed at the outer surface of each bilayer as they slide past each other.[1, 2] However, instabilities of liposomes are a serious limiting factor for their applicability due to their fusion and aggregation with time, which often needs steric stabilization, and the extrusion for liposomes is always time consuming.[3] Micelles exposing such highly hydrated and biocompatible phosphocholine groups could be an attractive alternative to liposomes due to their much easier preparation and structure control, but all studies to date of surfactant micelles have revealed that at relatively low normal stresses the surface layers rupture and friction increases abruptly.[4, 5] Here, we examine surface interactions between three kinds of phosphocholine-exposing micelles with different designed structures: single-tail surfactant micelles, homo-oligomeric micelles, and block copolymer micelles.[6] Normal and shear forces between mica surfaces immersed in solutions of these micelles were measured using a surface force balance (SFB) (as shown in Figure 1). The structures of the adsorbed layers on the mica were obtained using atomic force microscope (AFM) imaging, revealing surface structures ranging from wormlike to spherical micelles. The block copolymer micelles showed relatively low coverage arising from their stabilizing corona and consequently poor lubrication ($\mu \sim 10^{-1}$). In contrast the surfactant and homo-oligomeric micelles fully covered the mica surface and demonstrated excellent lubrication ($\mu \sim 10^{-3}$). However, while the boundary layer of single-tailed surfactant micelles degraded under moderate pressure, the homo-oligomeric micellar boundary layer was robust at all applied contact pressures in our study (up to about 5 MPa). We attribute the difference to the much greater energy required to remove a homo-oligomeric molecule from its micelle, resulting in far greater stability under pressure and shear.

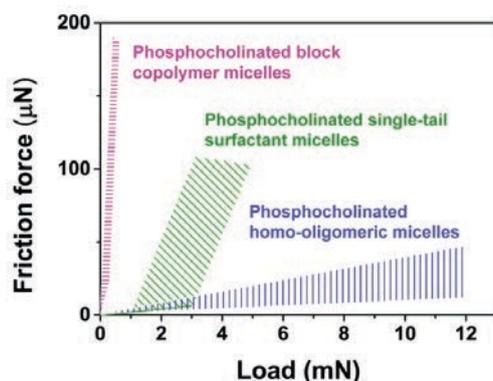


Figure 1. Summary of lubricating properties of phosphocholinated single-tail surfactant micelles, homo-oligomeric micelles, and block copolymers micelles between two mica surfaces.

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Polymer Threaded Wormlike Micelles

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Self-assembled wormlike surfactant aggregates have attracted considerable interest in both fundamental research and practical applications as drag reducing agents, hydraulic fracturing fluids in oilfields, templates for polymerization, etc. Therefore, the ability to modify or control wormlike micelle properties is highly desirable. Using atomistic and coarse grained molecular dynamics simulations we investigate polymer-threaded wormlike micelles (WLM) formed when a hydrophobic polymer such as polystyrene (PS) is encapsulated (“threaded”) within the center of wormlike micelles (WLM) of potassium oleate in 6% (by weight) of potassium chloride aqueous solutions (as shown in the Figure). We investigate the PS conformation and surfactant reorganization within the WLM and compare it to the case of a less hydrophobic polymer, polycaprolactone (PCL), which is found to wrap around the WLM at the interface between the headgroups and tails of the surfactants. [1] We demonstrate that different hydrophobicity of polymers leading to different localization within WLM results in a significant difference in polymer conformation and surfactant arrangement, which have important implications for the stress relaxation under shear flow, as has been previously demonstrated experimentally for polymer-wrapped WLMs. [2-3] This approach may also be extended for the encapsulation of polymers with conjugated hydrophobic drugs/fluorophores for drug delivery or imaging applications by bio-derived or biocompatible surfactant WLMs.

Keywords: surfactants, polymers, self-assembly, molecular dynamics simulations

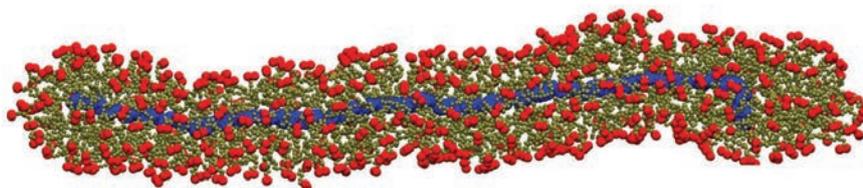


Figure 1. Computer simulation snapshots of polystyrene (shown in blue) in potassium oleate WLM (shown in olive with red head groups) in aqueous solution containing 6% of potassium chloride (not shown).

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From nanoaggregates to mesoscale ribbons: the multistep self-organization of amphiphilic peptides

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Atomic force microscopy results and molecular dynamics simulations of the striking differences of long-term self-organization of negatively charged (AcA4)2KD and AcA4D amphiphilic peptides are reported. The subsequent formation steps of the long-range nanoribbons, experimentally observed only for the “double tail” (AcA4)2KD peptide, are analyzed in detail, showing that the primary round-shaped aggregates progressively evolve into longer nanofilaments forming micrometer nanoribbon moieties. The diffusional degrees of freedom are stimulated by the formation of a dynamic ternary air/liquid/substrate interface, due to the water evaporation process from the ultra-thin films of the peptide solution cast onto a solid mica substrate. Overall, the initial aggregation of unstructured round-shaped moieties, for both the peptides, can be seen as an entropy-driven process, involving the intra- and intermolecular interactions of hydrophobic parts of the peptides. The further formation of long nanoribbons, only for “double tail” peptides, can be interpreted in terms of an enthalpy-driven process, mainly due to the predominant electrostatic interactions between the charged heads of the interacting peptides. The role of the solid–liquid interface, as the locus of the enthalpy-driven linear organization, is also highlighted.

Keywords: Adsorption, Molecular Dynamics, Nanoscale, Self-Aggregation

Self-Aggregation of Sugar Surfactants in Deep Eutectic Solvents and Their Solubilization of Terpenoids

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Amphiphilic self-assembly of surfactants in aqueous solutions is a well-studied phenomenon. Self-assembly of surfactants is also possible in deep eutectic solvents (DES), a novel class of polar solvents that has the potential to become a non-toxic and cheap alternative to conventional organic solvents, ionic liquids or even water[1]. Structure formation by surfactants in DES has been studied only to some extent, as their solubility in DES is often very limited[2]. The DES based on choline chloride and urea, known as “reline”, has been reported to dissolve only a few anionic surfactants, e.g. SDS[2].

As a result of our experiments, we were able to widen the limited scope of reline-soluble surfactants with sugar surfactants. They can be easily produced from biomass and are readily biodegradable[3]. More specifically, we examined alkyl glucopyranosides and maltosides using pyrene probe fluorescence spectroscopy, see Figure 1. This method allowed us to determine critical micellar concentrations (cmc) of APG surfactants. Structural characterization by light and neutron scattering is ongoing. Interestingly, APG solutions in “reline” could furthermore solubilize monoterpenoid compounds as limonene (25 wt%), menthol (5 wt%) and borneol (5 wt%), which are otherwise insoluble in neat “reline” or water.

All components were chosen thoroughly with an emphasis on biocompatibility, biodegradability and their potential use in medicine and cosmetics. In the case of menthol, the microemulsions exhibit remarkable viscoelastic properties. As seen from Figure 1, the shear-thinning behaviour indicates the presence of elongated structures, which disentangle upon shear stress. Such property could find application in creams and topical drug delivery.

Keywords: self-assembly, DES, sugar surfactant, microemulsion, terpenoid

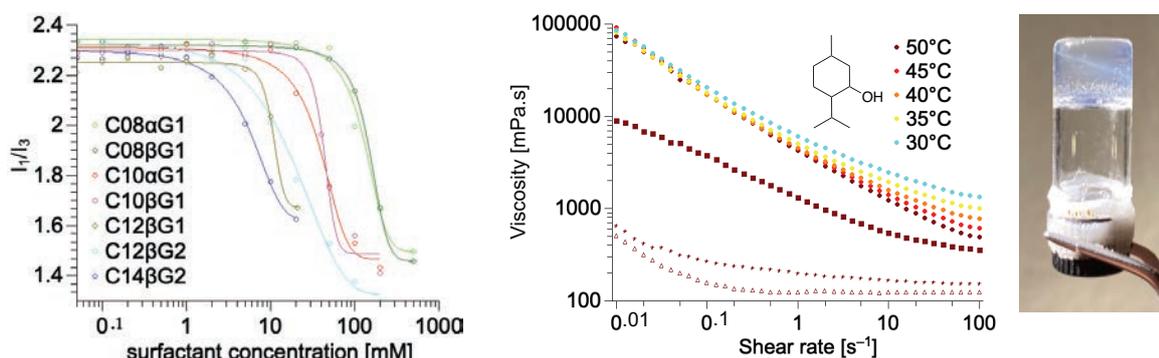


Figure 1. (Left) Band-I-to-band-III ratios of pyrene fluorescence spectra of sugar surfactants in “reline” at 30°C for cmc determination. (Centre) The viscosities of equimolar solutions of dodecyl-β-glucopyranoside and menthol in reline at 50°C and different shear rates: 400 mM (circles, different temperatures), 200 mM (squares), 100 mM (stars, photo right), neat solvent (triangles). (Inlet) Menthol structure.

Acknowledgements: We acknowledge financial support from DFG and TU Berlin

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EP3.38

Cleaning Ability of Mixed Solutions of Sulfonated Fatty Acid Methyl Esters

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Here, we present results from a systematic study on cleaning of oily deposits from solid surfaces (porcelain and stainless steel) by solutions of fatty acid sulfonated methyl esters (SME), sodium salts. The zwitterionic dodecyldimethylamine oxide (DDAO) has been used as cosurfactant. As representatives of the vegetable and mineral oils, sunflower seed oil and light mineral oil have been used. The process of oil drop detachment from the solid substrates (roll-up mechanism) has been monitored. In the case of porcelain, excellent cleaning of oil is achieved by mixed solutions of SME and DDAO. In the case of stainless steel, excellent cleaning (superior than that by linear alkylbenzene sulfonate and sodium lauryl ether sulfate) is provided by binary and ternary mixtures of SMEs, which may contain also DDAO. For the studied systems, the good cleaning correlates neither with the oil/water interfacial tension, nor with the surfactant chainlength and headgroup type. The data imply that governing factors might be the thickness and morphology of admicelle layers formed on the solid/water interface. The results indicate that the SME mixtures represent a promising system for formulations in house-hold detergency, having in mind also other useful properties of SME, such as biodegradability, skin compatibility and hard water tolerance.

Keywords: Sulfonated methyl esters; oily stain cleaning; stainless steel

Volatile aroma surfactants: characterization of the interfacial behaviour at dynamic and equilibrium conditions

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Presented work discloses characteristic interfacial behavior of amphiphilic aroma molecules and justifies the advantages of their usage as surfactants and co-surfactants in dynamic interfacial processes [1,2]. Time-dependent surface tension γ of solutions of volatile compounds - a mono terpene alcohol (linalool), an aromatic alcohol ester (benzyl acetate), and of conventional surfactant sodium dodecyl sulfate (SDS) is shown to depend strongly on the chosen method (Figure 1).

At non-equilibrium conditions, aroma compounds demonstrate a high interfacial dynamic activity, i.e. an ability to decrease the surface tension of aqueous solutions at a time scale of milliseconds. Tensiometric measurements with pendant drop reveal that in open systems the adsorption-desorption at the liquid / air boundary is accompanied by evaporation, and the dynamic interplay of these processes defines the surface tension. A phenomenological model is developed and applied to account for the increase of the surface tension of the drop with time, $\gamma(t)$, spanning the time range of ~ 10 min, which allowed to achieve a good agreement between theory and experiment. One adjustable parameter (material constant) is determined – the mass transfer coefficient of the volatile amphiphile across the water-air boundary.

Revealed synergetic behavior of volatile and conventional surfactants suggests revisiting numerous interfacial phenomena and processes which involve aroma molecules (perfumes), such as emulsion preparation, foam stability, spraying and cleaning.

Keywords: Volatile surfactants, dynamic surface tension, adsorption-desorption, evaporation

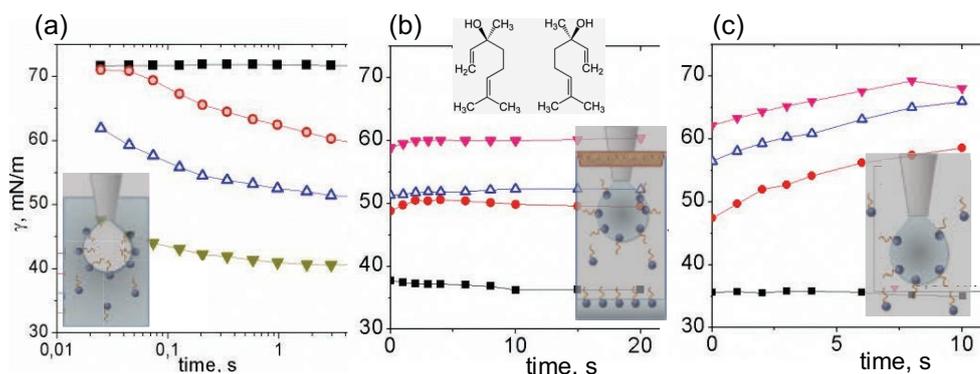


Figure 1. Kinetic curves of the surface tension of linalool solutions measured using indicated methods. Solution concentrations (mM) from top to bottom: (a) 0, 10, 2.5, 7.5; (b-c) 1, 2.5, 5, 10.

Acknowledgements: This work is supported by the Russian Foundation for Basic Research (RFBR), project N 18-53-76005 20-53-18008\20, and by Bulgarian Science Fund (FNI-MON), project #KP-06-Russia/3 – 09. 12. 2020.

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All-nanoparticle Layer-by-Layer Capsules – Mechanically Strong, Easily Breakable, and Good Sensors

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Nanoparticles as surfactants and stabilizers of particles have been widely used in interfacial sciences[1]. Using nanoparticles as a sole component of microcapsules, for example, applying Layer-by-Layer assembly can bring extensive benefits, but it has not been yet explored. We have investigated various approaches for building the so-called all-nanoparticle capsules, including Ludox (silica particles) particles, gold and silver nanoparticles. Details about using Ludox silica particles are discussed, while microcapsules templated on calcium carbonate microparticles are developed comprised of either silver or silver-gold nanoparticles instead of polyelectrolytes extending the LBL assembly.

The morphology of these capsules was investigated, and the minimum essential number of layers has been identified by scanning electron microscope (SEM). This novel approach reported here yields extra strong microcapsules than polymeric capsules, as measured by atomic force microscopy (AFM). Besides, they can be easily broken by low-intensity ultrasound stimuli, which would open a range of applications [2], including intracellular opening. In addition, such capsules have been used for surface-enhanced Raman scattering, producing a high amplification factor.

The new capsules presented here are envisioned to enable a variety of applications [3], including opening of capsules, intracellular delivery for therapeutics and cell biology, and molecular sensors for detection, selection and monitor of molecules.

Keywords: LbL, nanoparticles, capsules, SERS, ultrasound, release

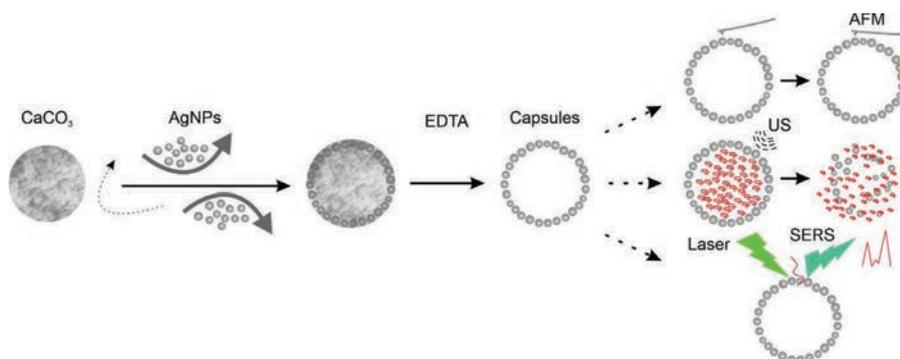


Figure 1. Schematics of the work showing major steps employed all-nanoparticle capsules.

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Effect of hybrid lipid on line tension and domain morphology of lipid vesicle

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In vesicles composed of saturated phospholipid, unsaturated phospholipid, and cholesterol, raft-like domain structure is formed by lateral phase separation into liquid-ordered (Lo) and liquid-disordered (Ld) phases depending on the composition. Because of heterogeneity, multi-component lipid vesicles are regarded as a simple model of biological membrane. Morphology of domain is controlled by line tension which is an excess energy at domain boundary [1,2].

In this study, we aim at investigating the effect of hybrid lipid on domain formation and adopted vesicle of quaternary lipid mixture: 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC)/1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC)/1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC)/cholesterol (Chol). The effect of POPC on domain morphology was examined by line tension as a function of POPC mole fraction quantified from Fourier Analysis of domain contour fluctuations observed by fluorescence microscope.

Phase separation into Lo phase enriched in DPPC and Chol, and Ld one in DOPC was observed in DPPC/DOPC/Chol system as shown respectively by the dark and the bright regions in Fig.2. For the composition relatively far from the critical point in Lo/Ld coexistence without POPC, line tension of around 1.0 pN (Fig.1) was obtained. As the molar fraction of POPC was increased with fixed DPPC/DOPC/Chol molar ratio, line tension decreases gradually and the corresponding domain shape changes from circular at high to mosaic at low line tension (roughly < 0.3 pN), and finally disappeared within a resolution of microscope. This result is attributed to the affinity of POPC for both DPPC and DOPC, that makes the physical properties of Lo and Ld phases similar.

Keywords: lipid vesicle, domain formation, line tension, hybrid lipid

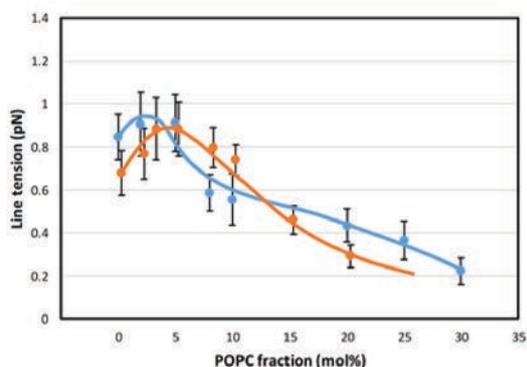


Figure 1. Line tension vs. POPC mole fraction curve at given DPPC/DOPC/Chol molar ratio; 49 : 25:26 (blue) and 45:25:30 (orange)

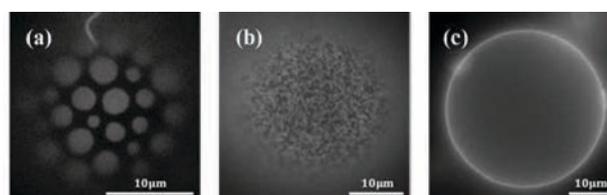


Figure 2. Microscopic images observed at given POPC fraction; (a) 5, (b) 30, (c) 35 mmol %.

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Mucoadhesive Properties of Amphiphilic Calix[4]resorcinols Bearing Viologen or Acetate Substituents at the Upper Rim

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The nanocontainers with mucoadhesive properties are capable of retaining the drugs on mucosal surfaces, which will facilitate their better absorption and will improve bioavailability. The properties of mucosal surfaces are governed by the presence of mucin glycoproteins, which are secreted by specific epithelial cells. The epithelial cells are held together with the help of tight junctions, which contain calcium ions [1]. Therefore, the development of drug nanocontainers capable of interacting with mucins and calcium ions is of special interest. Considering the possibilities of modifying the rims of the calixarene platform with various functional groups, these macrocycles offer an excellent class of materials to develop novel mucoadhesive drug delivery systems. It is surprising that so far that no one has studied the mucoadhesive properties of calixarene derivatives. In the present work, the amphiphilic calix[4]resorcinols bearing viologen groups and calix[4]resorcinol bearing acetate groups at the upper rims were investigated for their ability to bind caffeine (a water-soluble model drug), to interact with mucin, and to form complexes with calcium ions. The cationic moiety in viologen calix[4]resorcinol is mainly responsible for the interaction with mucin, and the anionic groups in acetate calix[4]resorcinol are responsible for the extraction of calcium ions, which will facilitate the permeability of a drug through the epithelial cells. The main feature of the studied amphiphilic calixarenes is their spontaneous self-assembly due to non-covalent association, which reduces synthetic efforts in the preparation of useful nanoobjects with several binding sites.

Keywords: calixarene, mucoadhesion, self-assembly, drug delivery

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Insights into the Supramolecular Self-Assembly of Porphyrin and Metallosurfactant

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The incorporation of porphyrins into supramolecular aggregates or attachment to various delivery vehicles is a strategy for improving and prolonging their functional activity and overcoming their limitations as therapeutic and diagnostic agents. An important role in such supramolecular self-organization is assigned to amphiphilic systems due to their high ability to form aggregates at sufficiently low concentrations. Since the aggregation of supramolecular porphyrin–amphiphile complexes in the solution is poorly studied, in this work we investigated the possibility of the formation of non-covalent complexes of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TSPP) with metalloamphiphile and their aggregation capacity in an aqueous medium. A dicationic surfactant was chosen as the metalloamphiphile, which is a complex of two fragments of diazobicyclooctane with hexadecyl tails and lanthanum nitrate (LaSurf). Lanthanum compounds show high antitumor activity [1-3] and are able to regulate the antitumor resistance of the organism [4]. The choice of a lanthanum-containing amphiphile is due to its ability to form joint aggregates with an oppositely charged 3D macrocycle, which can act as a medicinal nanocontainer of cisplatin with improved selectivity towards diseased cells [5]. Moreover, there has never been the study of the complexation of porphyrin with metallosurfactant in the solution. Since the supramolecular amphiphiles TSPP–LaSurf exhibited the expected mixed aggregation ability, the aggregates based on the obtained supra-amphiphiles were used to encapsulate cisplatin. The choice of this anticancer drug is due to the revealed synergistic antiproliferative effect of photodynamic therapy using hematoporphyrin and cisplatin when acting on bladder cancer cells [6].

Keywords: porphyrin, surfactant, self-assembly, cisplatin, drug delivery, nanostructures

Acknowledgements: This research was funded by Russian Science Foundation, grant number 19-73-30012.

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Thermodynamics of Malonamide Aggregation Deduced from Molecular Dynamics Simulations

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Some papers are dedicated to the typical extractant molecules used in rare earth separation processes and to the structure of the aggregates they form [1,2], but very few have been published on the thermodynamics calculation related to these aggregates' formation. Using molecular dynamics simulations and numerical analysis methods, we developed a model describing the aggregation of a malonamide extractant characteristic of rare earth separation processes.

Numerical methods developed which are based on distances criteria between molecules and graphs theory allow us: (i) to determine exact distribution of species in an organic phase from molecular dynamics simulations; and (ii) to compute macroscopic and thermodynamics data like standard enthalpies of formation, mass action law constants, critical micelle concentration, aggregation numbers, or vapor pressure osmometric data [3]. The calculated data are in good agreement with the experimental ones reported in previous scholarship.

Keywords: Aggregation, Molecular Dynamics, Thermodynamics

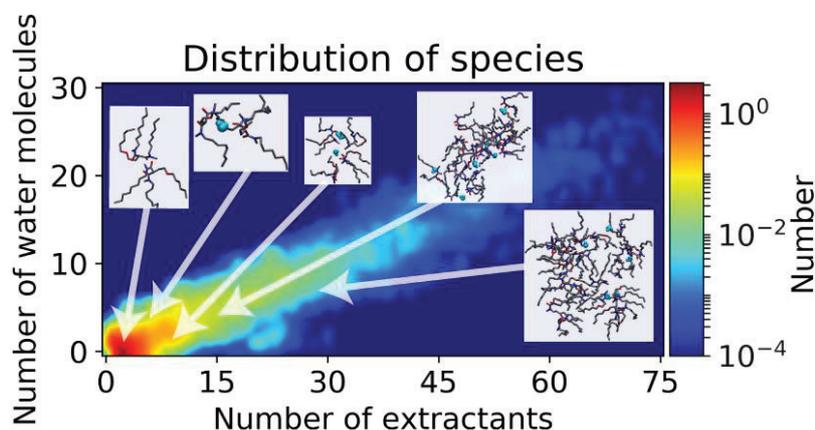


Figure 1. Distribution of species in n-heptane-extractant-water mixture as a function of the number of extractants and the number of water molecules. Captions represent examples of the molecular structures and were placed according to their composition.

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Interfacial Properties and Surface Aggregates of Redox-Active Surfactant

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An anionic surfactant molecule, AQua (AQ-NH-(CH₂)₁₀COOH; where AQ is anthraquinone), which has two stimuli responsive functional-groups, can form interfacial aggregates at the air-water interface and, their morphologies can be controlled by changing the subphase conditions such as the pH of the subphase or the type of the electrolyte. These changes at the subphase give rise to changes at the interfacial configuration of the molecule at the air/water interface which also presented to be affective at the morphology of the interfacial aggregates. These interfacial morphologies may be altered from planar structures to wormlike aggregates which is a very rare observation in the literature. Moreover, the unique functional groups of AQua give possibility to reduce metal cations (silver or gold) and allow the formation of organic/inorganic nanocomposite structures. In this context, formation of silver nanoparticles (AgNPs) via AQua-based self-assembled structures at the interface was studied using Langmuir techniques. In order to investigate this marvelous feature, the reduction ability for Ag ions systematically examined. AQua molecules were reduced at different reaction times with the different pH of the subphases and Ag₂SO₄ concentrations to provide AgNP synthesis at the air/water interface. Based on these results obtained within the intention of the study, it is thought that the new redox-active surfactant will attract great attention due to its remarkable properties. This study demonstrates that interfacial configuration of the AQua molecule at the interface as well as its orientation has a vital role in the morphology of either organic or inorganic self-assemblies formed.

Keywords: Langmuir monolayer, surfactants, silver nanoparticles, worm-like aggregates

EP3.49

Superparamagnetic colloids in rotating field: transition state from chains to disks.

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Colloids made of superparamagnetic microbeads offer the possibility to be controlled remotely with a magnetic field. This enables various applications such as mixing, transport of fluids through microscale channels or propulsion in a viscous fluid. In order to achieve such goals, understanding the interactions between the field, the microbeads and the liquid medium is fundamental.

When exposed to an external magnetic field, 2D layers of superparamagnetic colloids form specific structures which depend on the features of the field. If the magnetic field is constant along time, superparamagnetic colloids self-organize into chains oriented in the direction of the field. If the magnetic field is rotating in the plane of the suspension, the beads still aggregate into chains, but these chains rotate with the field. Due to the competition between the magnetic and the viscous effects, those chains length decreases with the increase of the magnetic field frequency of rotation. When the rotation reaches a certain speed, the dipole-dipole potential on the colloids can be averaged over one rotational period of the field. This leads to an isotropic interparticle attraction that causes the colloids to aggregate in rotating disk-like clusters.

In our work, we focused on the early stages of the disk-like clusters aggregation and the dynamics of this process. We performed experiments and observed that before clustering into disk-like structures, the colloids were aggregating into rotating chains, just as they did in suspensions submitted to a magnetic field rotating at a lower rate. Over time, the chains interact with one another and aggregate into disk-like clusters, resulting in a mixture of chains and disks in the sample, until only disks remain. The duration of this phenomenon depends on the frequency of the magnetic field, as it is shown in Fig.1.

Keywords: superparamagnetic, aggregation, experimental

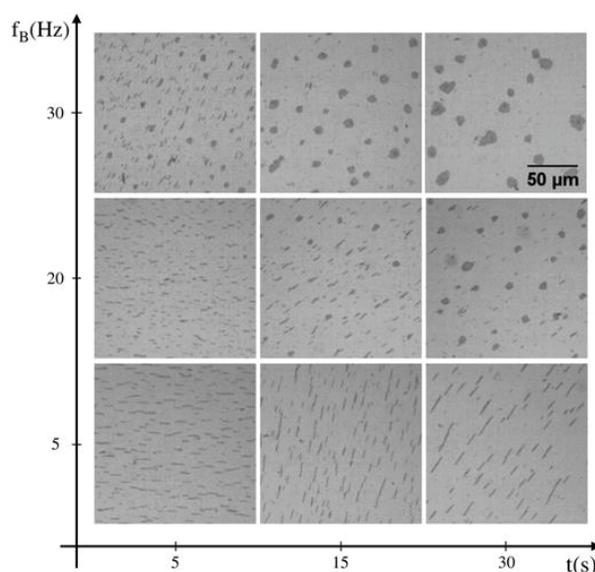


Figure 1. Snapshots over time of 3 samples under a magnetic field with a frequency of rotation $f_B = 5, 20, 30$ Hz. The activation of the magnetic field corresponds to $t = 0s$.

Protein on Steel

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Protein fouling and subsequent cleaning are important cost and sustainability factors of many processes in the food industry. Protein adsorption to surfaces is an extensively studied subject, and usually substrate materials are chemically pure and well defined [1,2]. However most of the fouling in food industry occurs on stainless steel surfaces. These surfaces typically vary in topography and chemical homogeneity. We aim to research the interaction of milk proteins with these surfaces including the effect of rinsing and cleaning agents.

We investigate protein adsorption to stainless steel surfaces at a fundamental level using: QCM, AFM and X-ray based surface analysis techniques. We compare the results to existing models and to findings from a dedicated fouling set up in which fouling under industrial conditions (high pressure, temperatures up to 140°C) can be induced and made experimentally accessible. In this study we focus on β -lactoglobulin (with folding) and caseinate (without specific folding) as representatives for proteins in pasteurized and heat-sterilized food. Experimental variables include: temperature, protein adsorption time, protein concentration and rinsing time. For the lab-scale experiments, we use QCM-d sensors coated with stainless steel to follow quantitatively the protein adsorption over time. Subsequently we image the build-up of fouling on that same sensor using AFM.

In this presentation, the focus is on concentration, time and rinsing. Preliminary results show different adsorption and desorption behaviours between the different proteins. β -lactoglobulin tends to form a stable adsorption weight quickly whereas caseinate adsorption layers show more development over time. Also the effect of rinsing (cleaning) with buffer was found to be different for the two proteins. For caseinate, we observed increased desorption by buffer rinsing after longer casein adsorption times. This suggests ageing of the adsorbed layer. For β -lactoglobulin no such effect was seen.

Keywords: Protein, fouling, steel, dairy

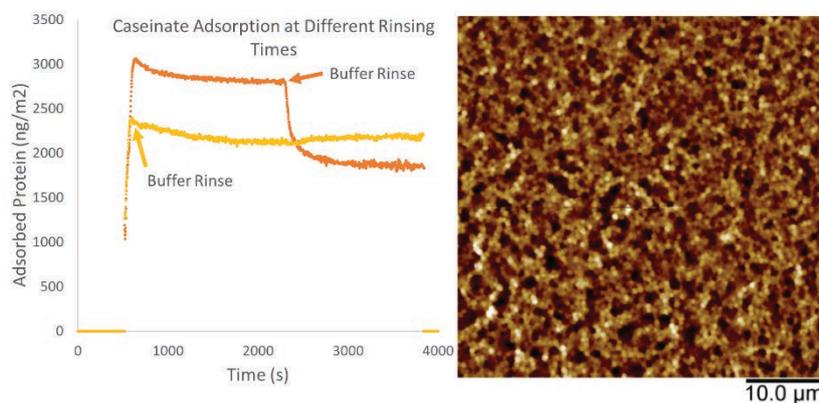


Figure 1: Calculated protein adsorption from QCM-d data plotted to adsorption time. The sensor is exposed to a 0.1% caseinate solution until the buffer wash is indicated with the arrows (left). A typical AFM image of fouled stainless steel at 90°C with 1% whey protein concentrate solution.

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Embedment of Quantum Dots in a Dipeptide Hydrogel Using Microfluidics

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Supramolecular assembly is a bottom-up method in which building blocks are spontaneously integrated into various nanostructures through non-covalent interactions.¹ Biomolecules such as peptides is an important assembly element in living system and biological engineering to achieve sophisticated functions, such as immune response and drug delivery.¹

As low-molecular-weight hydrogelators, dipeptide hydrogel materials are suited for embedding multiple organic molecules and inorganic nanoparticles. Herein, a simple but precisely controllable method is presented that enables the fabrication of dipeptide-based hydrogels by supramolecular assembly inside microfluidic channels.² Water-soluble quantum dots (QDs) as well as premixed porphyrins and a dipeptide in dimethyl sulfoxide (DMSO) were injected into a Y-shaped microfluidic junction. At the DMSO/water interface, the confined fabrication of a dipeptide-based hydrogel was initiated. Thereafter, the as-formed hydrogel flowed along a meandering microchannel in a continuous fashion, gradually completing gelation and QD entrapment. In contrast to hydrogelation in conventional test tubes, microfluidically controlled hydrogelation led to a tailored dipeptide hydrogel regarding material morphology and nanoparticle distribution.

Furthermore, energy transfer was confirmed in our supramolecular hybrid system, exhibiting energy transfer from inorganic QDs to the organic TCPP, further illustrating the extreme small distance between them and the superiority of low-molecular-weight dipeptide hydrogelator to efficiently entrap and integrate QDs. Accordingly, the formation of dipeptide-based multicomponent hydrogels opens up new possibilities for applications in biomedical devices, photodynamic therapy, or continuous bio-printing of these hybrid gels.

Keywords: dipeptide; hydrogel; supramolecular assembly; microfluidics

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Specific interactions of nano-ions with proteins

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Ion specific effects (ISE) have a high impact in many biological and physicochemical phenomena. According to the salts ability to influence aqueous proteins solubility, ions were classified as salting-in and salting-out.^[1] ISE were also investigated with nanometric size ions, such as boron clusters and polyoxometalates anions. Low charge density nano-ions were called “superchaotropes”, because their “salting-in” effects were found to be more pronounced than classical ions.^[2a-b] Recently, nano-ions have attracted much attention in biology due to their potential applications regarding their interactions with proteins which are involved in several diseases.^[3a-d]

In the present work, we focus on the cobalta-bis-(dicarbollide) anion, COSAN [$\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2$]⁻, (Fig. 1a). Although lacking the classical amphiphilic structure, COSAN has surfactant properties: surface activity, self-assembly^[4-a] and formation of lyotropic lamellar phases.^[4-b]

This work aims to better understand COSAN-protein interactions. The effect of COSAN on the isoelectric point (pI) of nine standard proteins was investigated using isoelectric focusing (IEF) coupled to mass spectrometry. We observed preferential interactions of COSAN with carbonic anhydrase (BCA) and myoglobin (Mb) but not with trypsin inhibitor (SKTI, Fig. 1b). COSAN interactions with the three proteins were further characterized using (i) UV, fluorescence and circular dichroism (CD, Fig. 1c) to obtain information on the local environment of COSAN and on the secondary structure of the proteins, (ii) small angle light (DLS) to obtain information on the hydrodynamic diameter, polydispersity and protein aggregation, (iii) zeta potential of the proteins/COSAN to determine the change in the protein pI in different conditions.

CD results indicate strong interaction between COSAN and the two proteins, BCA and Mb, which is causing reduction in the β -strand and in the α -helix content, respectively. CD, zeta potential and DLS results are in good agreement showing COSAN interacting with BCA and Mb and to a lesser extent with SKTI.

Keywords: Nano-ions, COSAN, proteins.

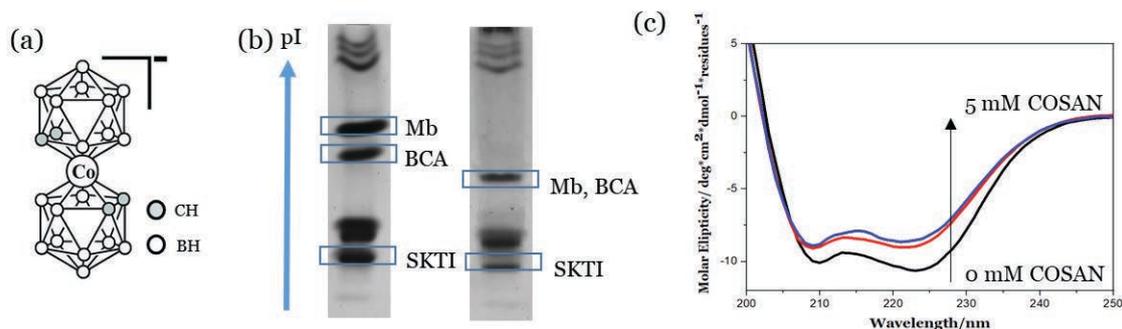


Figure 1. (a) Chemical structure of COSAN, (b) IEF gel of 9 standard proteins in absence (left) and in presence (right) of COSAN (10mM), (c) Far UV-CD spectra of 0.01 mM Mb in presence of different COSAN/Mb molar ratios: 0 (black), 1 (red) and 5 (blue).

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EP3.53

Impact of processing conditions on the aggregation behavior of demineralized arabinogalactan-proteins from Acacia seyal gums

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Acacia *seyal* gum (*Asey*) is an edible dried gummy exudate obtained from the trunk and branches of Acacia *seyal* trees, widely used in food and non-food applications for its emulsifying and stabilizing properties. *Asey* is defined as a continuum of arabinogalactan-proteins (AGPs) differing by their biochemical, physicochemical and structural properties¹. AGPs are known to self-assemble and aggregate during the maturation step of Acacia gum² and its post-harvesting treatments³. In this study, we investigated the aggregation behavior of AGPs from *Asey* powder depleted in minerals (Arabic acid) according to their temperature of storage.

Whatever the temperature studied, aggregates were formed with temperature-dependant aggregation kinetics. The soluble AGPs fraction after centrifugation reached a maximum constant plateau value around 20%. At 40°C, AGPs were totally soluble in water until 2 days of storage before the formation of pelleted (insoluble) aggregates after centrifugation for longer storage time. Microscopic observations and static light scattering experiments of these pelleted aggregates formed after 2 days of storage showed that these aggregates were characterized by a spherical shape and heterogeneous surface with sizes ranging from 1 to 100 µm. The structural properties of the soluble AGPs, determined using SEC and A4F MALS experiments, showed the increase of the molar mass from $1.3 \cdot 10^6$ to $7 \cdot 10^6$ g.mol⁻¹, the hydrodynamic radius from 14 to 40 nm and the gyration radius from 20 to 140 nm during the first 2 days of storage. The analyses of the conformation plots of soluble aggregates evidenced aggregation mechanism followed a self-similar assembly mechanism without changes of the AGPs building blocks conformation. The AGPs assembly involved sensitive covalent bonds as suggested by moderate activation energy and pH-induced aggregate dissolution. In conclusion, this study evidenced aggregation of Arabic acid upon powder storage, and gave a first physicochemical and structural characterization of AGPs aggregates.

Keywords: Acacia gum, arabinogalactan-proteins, aggregation kinetics

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Countering the nanoparticle protein corona via binding of HSA with an Albumin-binding Hydrophobin chimera.

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Nanoparticles that contact biological fluids will usually adsorb several of their proteins, resulting in a protein-based surface formation known as a “protein corona”. The protein corona poses a major obstacle to nanoparticle bioavailability and efficiency [1]. Most commonly, it will cause the opsonization and removal of the particle, while obstructing any potential tissue targeting properties. A simple way to restrict protein corona formation has been to engineer nanoparticle surfaces to contain or bind albumin, since this abundant serum protein limits the adsorption of other proteins. Lipid-based and solid nanoparticles have already been successfully modified with albumin, showing improved bioavailabilities.

Therefore, a chimeric protein was designed to i) assist in the surface modification of a nanoparticle and ii) allow capture of Human Serum Albumin (HSA) on its surface. The first task is achieved using a class II hydrophobin; an amphipathic fungal protein with the ability to attach on hydrophobic surfaces [2]. As such, the HFBI hydrophobin module in the described chimera can be used to modify hydrophobic surfaces, such as these of preformed nanoparticles or lipid droplets. The second task is achieved by an Albumin-Binding Domain (ABD) in the chimeric protein [3]. Being fully water soluble, the ABD will be displayed on the surface of the nanoparticle, allowing it to capture HSA in circulation and restrict the adsorption of other serum proteins. Thus far, the chimeric protein has been produced and purified from a bacterial expression system. Current experiments are focused on nanoparticle formation/modification and interactions of the chimeric protein with HSA.

Keywords: Hydrophobins, Nanoparticles, Protein Corona, Protein Engineering.

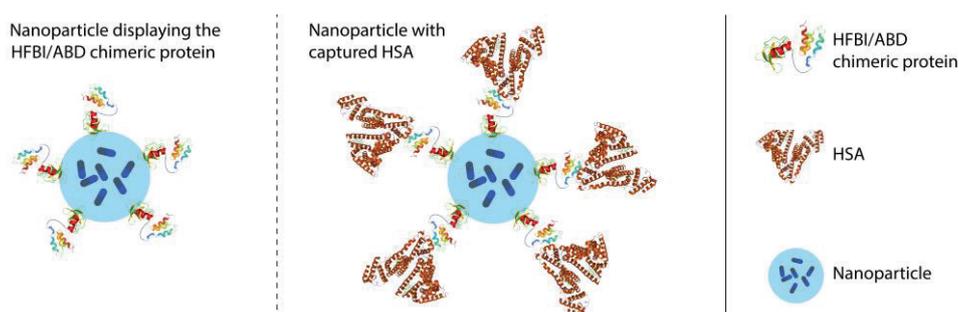


Figure 1. Nanoparticle utilizing the HFBI/ABD chimeric protein to capture Albumin.

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Unravelling the adsorption mechanisms of fatty acids on calcium minerals surfaces

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Froth flotation, which relies on the selective adsorption of surfactants at the mineral/water surface, is the most used mineral separation technique worldwide, processing several billion tons of ore per year. The adsorption mechanisms of fatty acids on calcium minerals are largely debated, and their understanding is required to improve flotation processing in the critical context of raw materials. Three wavenumbers have been observed in the literature for the asymmetric stretching vibration of COO⁻ after the adsorption of fatty acids on mineral surfaces. They have been interpreted as different adsorbed forms, such as a precipitate formation, an adsorption of sole or bridged carboxylates, an anion exchange, or as different adsorption configurations.

Here, we combined diffuse reflectance infrared spectroscopy with *ab initio* molecular dynamics simulations and simulation of infrared spectra to gain understanding in sodium octanoate adsorption on fluorite.

At low fatty acids concentration, the asymmetric stretching vibration of COO⁻ peaks at 1560 cm⁻¹ while, at higher concentration, this infrared band converts into a doublet peaking at 1535 and 1572 cm⁻¹. Using molecular simulations, we assign the band at 1560 cm⁻¹ to the adsorption of a carboxylate molecule bridged on a sodium counter-cation and the doublet at 1535 and 1572 cm⁻¹ to the adsorption of the sole carboxylate anion under a monodentate or a bidentate binuclear configuration, respectively. The formation of an adsorbed layer on the mineral surface is initiated by the adsorption of a sodium carboxylate and followed by the adsorption of mixed sole anionic forms. The role of the carboxylate counter-cation is highlighted for the first time, which particularly opens the path to the development of innovative strategies to enhance the separation contrast between minerals, which is of uttermost importance for the recovery of critical raw materials.

Keywords: Density Functional Theory, Ab Initio Molecular Dynamics Simulations, FTIR, fluorite, Density Functional Perturbation Theory

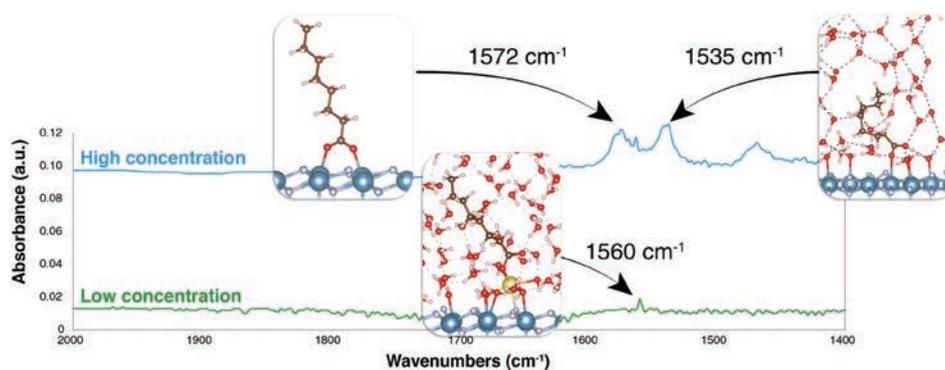


Figure 1. The three wavenumbers observed experimentally by FTIR spectroscopy for the adsorption of fatty acids on fluorite unraveled by *ab initio* molecular dynamics simulations and IR spectra simulation

Lipo-oligoureas as a new class of antimicrobial compounds

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The discovery of antibiotics became a turning point in the struggle against infectious diseases and contributed to a significant improvement in the quality and length of human life. However, the widespread abuse of antibiotics caused that numerous bacteria have developed a resistance to their action [1]. Therefore, it is necessary to look for new, natural or synthetic active substances with a broad spectrum of antimicrobial activity and at the same time with low cytotoxicity on the eukaryotic cells [2]. The typical antibiotics act on specific biochemical processes and bacteria can develop resistance mechanisms. A possible solution to this problem involves the use of compounds with less specific action, based, for example, on damaging the bacterial cell membrane [3].

Possible alternatives to traditional antibiotics are lipopeptides. These compounds consist of two parts: a lipophilic fatty acid chain attached to the peptide moiety. It is observed that this type of compound gives promising results against model bacterial cell membranes [3-4]. However, lipopeptides have certain drawbacks limiting their use as therapeutic agents. These include hemolytic activity and susceptibility to enzymatic degradation. As a possible pathway to overcome these limitations, we propose an entirely new class of fully artificial compounds based on oligourea foldamers coupled with lipophilic moiety of fatty acid, further referenced as lipo-oligoureas.

In this project, I have investigated the interactions of lipo-oligoureas with lipid films mimicking bacterial cell membranes. For these purposes, three techniques were employed: Langmuir monolayer technique, fluorescence microscopy with giant unilamellar vesicles (GUVs) and quartz crystal microbalance with dissipation monitoring. Three model bacterial membranes were used reflecting the lipid composition of Gram-negative bacteria: *Escherichia coli* and *Pseudomonas aeruginosa* and Gram-positive bacteria: *Staphylococcus aureus*. Physicochemical characterization demonstrates that lipo-oligoureas affect lipid membrane organization, which indicates their possible membranolytic activity.

Keywords: lipo-oligoureas, bacteria resistance, antimicrobial peptides, Langmuir monolayer, Fluorescence Microscopy

Acknowledgments: The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project cofinanced by European Union from the European Regional Development Fund under the Operational Program Innovative Economy, 2007–2013.

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Initial Stage of Adsorption of Monomer of SARS-CoV-2 Spike Protein on Graphene

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The infectivity of SARS-CoV-2 virus is dictated by the structure of the protruding spike glycoprotein [1,2]. This study reports on the initial stage of the adsorption of the non-glycosylated monomer of the spike glycoprotein (S-protein) onto graphene investigated by atomistic molecular dynamics simulations, in order to disclose the triggered structural changes of the S-protein through the comparison with the freely relaxed analogue. The adsorption is slowed down after 10 ns of simulations and after 20 ns, the number of contacts as well as the distance between the S-protein and graphene get saturated. The shape of the S-protein becomes more prolate. The receptor-binding domain (RBD) of the free and adsorbed S-protein manifests itself as the most rigid fragment. The adsorption even enhances the rigidity of the whole S-protein. Only one residue of RBD involved in the specific interactions with ACE2 receptor during the cell infection is involved in the direct contact of the S-protein with the graphene. The new intramolecular hydrogen bonds during the adsorption replace the S-protein-water hydrogen bonds. The adsorption of the S-protein is responsible for disappearance of one α -helix and stabilization of the two existing α -helices. Formation of one new α -helix during the adsorption is related to the relaxation of the S-protein in water rather than to its adsorption on the graphene. The secondary structure of the RBD fragment specifically interacting with ACE2 receptor is not affected during the adsorption. Similar structural behavior might be expected for the interactions between the S-protein and aggregates of cigarette smoke.

Keywords: molecular dynamics simulations, SARS-CoV-2, spike protein, graphene, adsorption, secondary structure

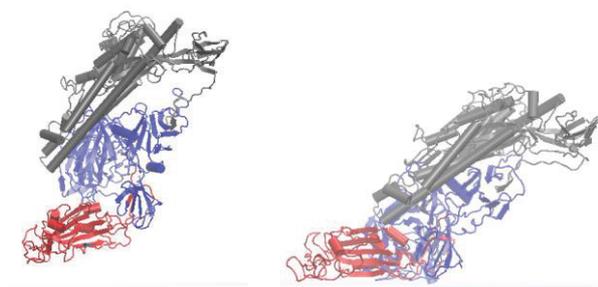


Figure 1. Initial (left) and final (right) conformation of the S-protein interacting with the graphene surface.

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Adsorption of Pluronic F-127 on Kappa-casein fibrils

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Kappa-casein (κ CN) is a milk protein that forms dynamic micelles as well as irreversible amyloid-like fibrils in aqueous solutions. The addition of beta-casein (β CN) lead to the formation of mixed κ CN/ β CN micelles [1]. In the early stages the mixed micelles inhibit κ CN fibrillization, and at later stages, β CN species absorb onto preexisting fibrils, and prevent their further growth [2].

Adsorption of amphiphiles on fibrils lead to the formation of new functional nanobiomaterials. Therefore, in this work we have expanded the study of the adsorption of amphiphiles onto κ CN fibrils, this time using a synthetic block copolymer, Pluronic F-127 (Lutrol). Data from Isothermal Titration Calorimetry (ITC) experiments are shown in Fig. 1 A & B, emphasizing the initial injections. Fig. 1 A shows the heat flow of the control - titration of 1% Lutrol into buffer, and Fig. 1 B - the titration into a κ -casein fibril dispersion. The typical exothermic peaks in Fig. 1A correspond to the heat of dissolution and demicellization of Lutrol. However, in Fig. 1 B where κ CN fibrils are present, splitting of every enthalpy peak into two is observed, which, reasonable to assume, reflects coexisting processes. The first part of the splitting peak reflects the dilution and demicellization of Lutrol, as in the control. The second is most likely associated with the adsorption of Lutrol on κ CN fibrils. By deconvolution of the splitting peaks we were able to obtain thermodynamic characteristics of each of these processes separately.

Keywords: ITC, adsorption, kappa-casein fibrils, Pluronic F-127

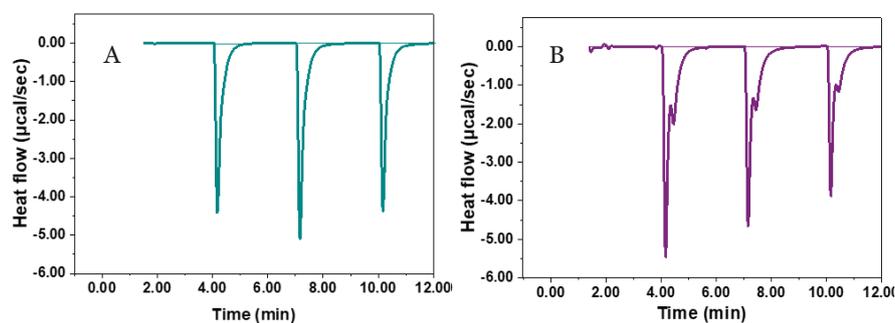


Figure 1. The initial peaks of the heat flow diagrams during titration of 1% Lutrol at 30°C: A - into buffer and B - into 1% κ CN dispersion incubated for a week. Note splitting of peaks in B due to coexisting processes.

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Using novel ionic liquids based on imidazolium derivatives to improve lubricating oil efficiency

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The global lubricant additives market size was USD 14.35 billion in 2015. The industry is characterized by increasing additive usage in base oil blending for longer service life and performance. These additives improve the viscosity of oil, act as detergents, defoamers, antioxidants, and antiwear agents. Since additives play a significant role in base oil blending and subsequent formulations as they are critical materials in improving specification and performance of oils. Herein, we report on the synthesis and characterization of three imidazolium derivatives and their application as antioxidants, detergents and antiwear agents. The molecular structure and characterizations of these ionic liquids were confirmed by elemental analysis, FTIR, X-Ray Diffraction (XRD) and ¹HNMR spectroscopy. Thermo gravimetric analysis (TGA), is used to study the degradation and thermal stability of the studied base stock samples. It was found that all the prepared ionic liquids additives have excellent power of dispersion and detergency. The ionic liquids as additives to engine oil reduced the friction (38%) and wear volume (76%) of steel balls. The obtained results show that the ionic liquids have an oxidation inhibitor up to 95%.

Keywords: ionic liquids; lubricating oil; imidazolium derivatives

EP3.61

Detection of ovalbumin amyloid-like fibrils at the oil-water interface in oil-in-water emulsions by spinning disk confocal microscopy

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Protein amyloid-like fibrils (ALFs) and amyloid fibrils (AFs) can display positive techno-functional properties in oil-in-water emulsions. AFs are widely studied in a medical context, but similar structures occur in certain processed food products. Whereas AFs are characterized by transmission electron microscopy, Congo Red birefringence, X-ray diffraction, and Thioflavin (ThT) fluorescence measurements, ALFs are not confirmed by all previous techniques. It has been suggested by Huyst et al. (2021) that upon intensive emulsification of both unheated and heated ovalbumin (OVA) dispersions as continuous phase, fibrillar structures are formed. However, the presence of OVA ALFs at the oil-water interface was not unambiguously proven. Here, the presence of ThT-positive fibrillar proteins at the oil-water interface was investigated. A clock scan image analysis approach was developed and optimized for this study. Whereas emulsions stabilized by either unheated or heated OVA did not clearly show an increased ThT fluorescence at the interface, ThT fluorescence was clearly detected when re-dispersing the cream phase obtained by ultracentrifugation. The increased ratio of ThT fluorescence at the oil-water interface to the background signal at the oil-water interface of the three times washed emulsions allowed concluding that ALFs accumulate at the interface. Furthermore, comparison with Fast Green For Coloring Food (FCF)-labelled emulsions suggested that ALFs more than other protein structures preferentially adsorbed at the interface. Confocal microscopy confirmed that ALFs accumulate at the oil-water interface and as such provided evidence for the hypothesis that hydrophobic interactions between proteins and oil droplets induced the formation of ALF structures during emulsification. The present observations contribute strongly to the interpretation of the interfacial properties of ALFs in O/W emulsions.

Keywords: amyloid-like fibril; ovalbumin; oil-in-water emulsion; oil-water interface; spinning disk confocal microscopy; clock scan

Huyst, A. M. R., Deleu, L. J., Luyckx, T., Lambrecht, M. A., Van Camp, J., Delcour, J. A., & Van der Meeren, P. (2021). Influence of hydrophobic interfaces and shear on ovalbumin amyloid-like fibril formation in oil-in-water emulsions. *Food Hydrocolloids*, 111, 106327. <https://doi.org/10.1016/j.foodhyd.2020.106327>

EP3.62

Characteristics of beta - lactoglobulin from whey protein isolate

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The aim of this study was to isolate β -lactoglobulin (β -LG) from the whey protein isolate (WPI) solution using the column chromatography with SP Sephadex. The physicochemical characterization (self-association, the pH stability in various buffers, the identification of oligomeric forms) of the protein obtained have been made. The WPI fractions were applied by the polyacrylamide gel electrophoresis (SDS-PAGE), thus determining the degree of purity. The electrophoretic pure β -LG fraction was obtained at pH 4.8. The fraction was characterized by the matrix-assisted laser desorption ionization-time of the flight mass spectrometry (MALDI-TOF/TOF MS) technique both in a "intact" and "bottom-up" approach using matrices such as: α -cyano-4-hydroxycinnamic acid (HCCA), 3,5-dimethoxy-4-hydroxycinnamic acid (sinapic acid – SA) and 2,5-dihydroxybenzoic acid (DHB). The use of the HCCA matrix indicated the presence of oligomeric β -LG forms, while the SA and DHB matrices differentiated A and B isoforms in the sample. The impact of the sodium chloride, the potassium chloride, the ammonium sulfate, and the sodium citrate dispersants on the β -LG electrophoretic stability in the solution was also studied. The dispersant type changes the isoelectric point of protein. The sodium citrate stabilizes protein in comparison to the ammonium sulfate. The asymmetric flow field flow fractionation coupled with the multi-angle light scattering detector (AF4-MALS) shows that the β -LG is a monomer in the pH 3.0, dimer in the pH 7.0. At the pH 5.0, near the isoelectric point, the oligomerizations from the dimeric to the octameric structure are formed, however the equilibrium between the isoforms is controlled by the content of protein. The higher quantity of protein leads to the formation of the octamer.

Keywords: β -lactoglobulin (β -LG), zeta potential, asymmetric flow field flow fractionation (AF4), matrix assisted laser desorption/ionization (MALDI), oligomeric forms, protein stability

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The effect of bubble approach velocity and surfactants on coalescence of bubbles

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The coalescence of bubbles and drops is a very important phenomenon in multiphase flow systems, which controls the bubble size distribution and the interfacial area available for heat and mass transfer in multiphase reactors. In the present communication, we will resume the results of our observations of the coalescence of bubbles in surfactant solutions, at controlled approaching velocity between bubbles. Experiments were performed using high speed visualization of the life span of pairs of bubbles [1]. Detailed study of the dependency of the coalescent efficiency, the contact time till coalesce and the transition concentration, on the dynamics of adsorption of the surfactant molecule present in the solution and the state of contamination of the bubbles at the moment of contact. Experiments were done with five nonionic surfactants covering wide range of adsorption dynamics characteristics.

Keywords: coalescence, bubble, surfactants, adsorption kinetics, multiphase systems.

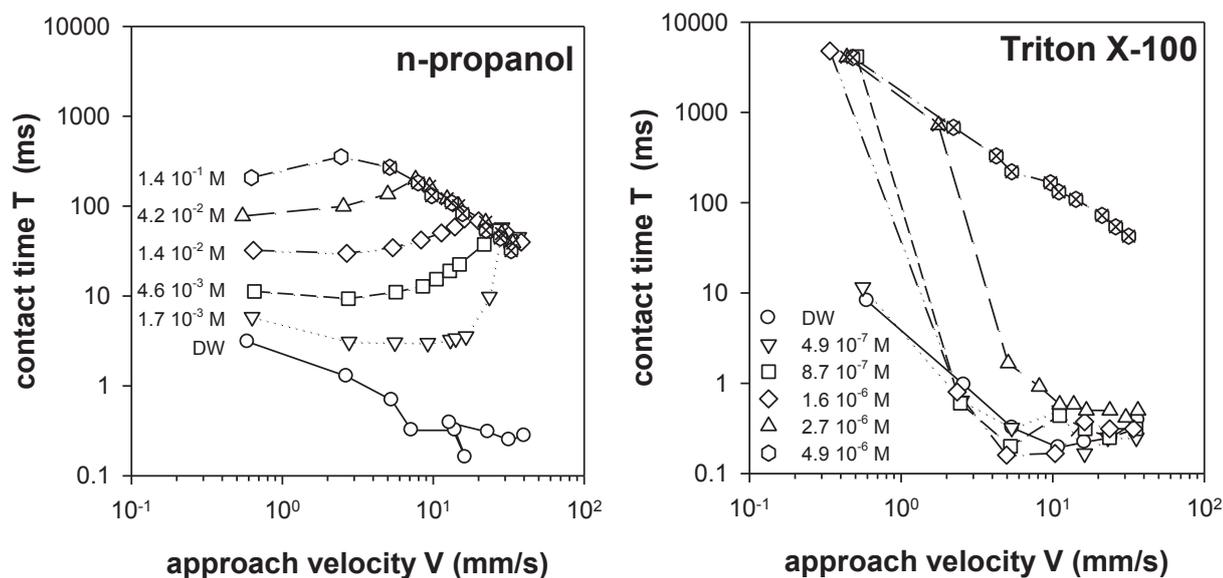


Figure 1. Characterization of the coalescence of bubbles in the presence of surfactants. Contact time till coalescence as function of approach velocity for “small” surfactant molecule (*n*-propanol) and “big” surfactant molecule (*triton X-100*)

Acknowledgements: The financial support by The Grant Agency of the Czech Republic (GACR Project No. 19-09518S) is gratefully acknowledged.

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Bubble–vortex-ring interactions: effect of surfactants on the bubble breakup

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The contribution is motivated by the understanding of fundamentals of bubble dynamics when interacting with vortex structures. The aim of the present contribution is to study the effect of specific surfactant, α -terpineol, on the bubble breakup arising from the interaction with a vortex-ring.

The study is based on the experimental visualization of a single bubble interaction with a single vortex-ring. A high-speed camera is used to record the interactions and to evaluate the breakup parameters. The breakup frequency, mean number of daughter bubbles and the final daughter size distribution are evaluated in dependence on Weber number characterizing the ratio of vortex inertia and bubble surface energy. The data for α -terpineol solution with concentrations 1 and 3×10^{-3} mol/L are compared with the data for distilled water [1].

The presence of α -terpineol affects the bubble dynamics, which influences also the bubble breakup process. Adsorption of surfactant molecules on the bubble interface suppresses the bubble deformation. As the interface in the presence of surfactant is more rigid, more time is needed to deform and break the bubble in comparison with a clean surface (distilled water). This results in the decrease of breakup frequency and mean number of daughter bubbles, which should be considered when modelling the multiphase systems including surface-active agents.

Keywords: bubble breakup, vortex-ring, surfactants, α -terpineol

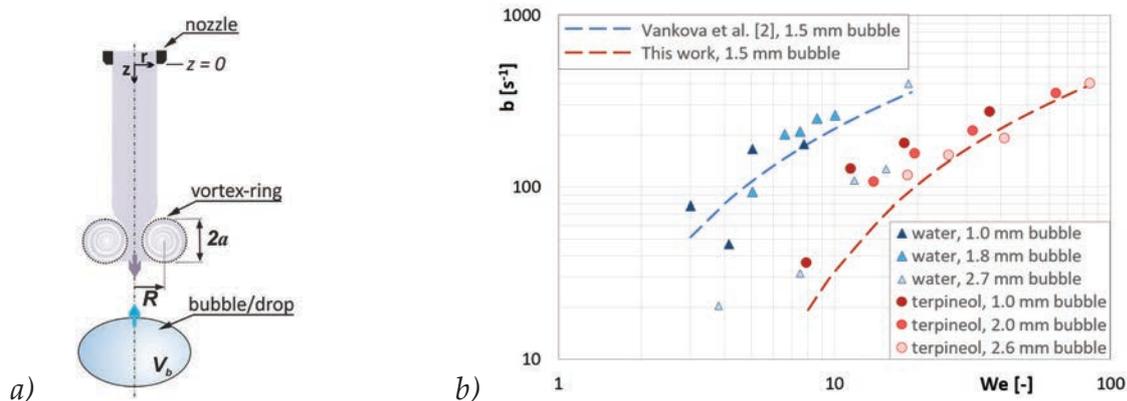


Figure 1. a) Illustration of bubble interaction with the vortex-ring; b) Dependency of breakup frequency on Weber number

Acknowledgements: The financial support by the Czech Science Foundation through project 19-09518S is gratefully acknowledged.

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Metal-biosurfactant ligand complex could promote the solubilization of copper oxychloride in water

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In a previous work [1] it was observed that the biosurfactant (BS) extract obtained from corn steep liquor (CSL) it is able to solubilize copper oxychloride (Cu-Oxy) in water up to 3,6 g/L. Therefore, in this work following the same procedure established by López-Prieto et al [1], formulations containing cuprous oxide (Cu-Ox) or copper oxychloride (2 g/L) were prepared in presence of biosurfactant extracted from CSL, in order to know if the biosurfactant under evaluation possess the same stabilizing effect in the two studied copper-based pesticides. Particle size (μm) distribution of formulations was evaluated in aqueous solutions prepared by mixing 2 g/L of Cu-Oxy (99.0 % m/m; provided by LGC Labor GmbH, Augsburg, Germany) or Cu-Ox (97.0 % m/m) with 2 g/L of the BS extracted with ethyl acetate from CSL. Analysis of particle size distribution was assessed by light scattering in the range from 40 nm up to 2000 μm , using a particle size analyzer model LS 13 320 (Beckman Coulter, Spain). For copper determinations, a double-beam flame Atomic Absorption Spectrophotometer (Thermo Scientific, iCE 3000 series) was employed.

The results showed a higher capability of the biosurfactant under evaluation to solubilize copper oxychloride than cuprous oxide. This fact could be explained because the biosurfactant extracted from corn steep liquor is amphoteric and probably it can form metal-ligand complexes with copper ions, so promoting the solubilization of copper oxychloride, whereas cuprous oxide cannot form these kinds of chemical bonds and probably the mechanism used to stabilize this compound in water is through the formation of micelles, where cuprous oxide is included. Those formulations containing copper oxychloride possess lower particle sizes than formulations based on cuprous oxide, what it is in consonance with the formation of metal-biosurfactant ligand complexes in the case of copper oxychloride and micelles in the case of cuprous oxide. **Figure 1** shows the behavior of the biosurfactant with the two copper derived pesticides under evaluation.

Keywords: corn, biosurfactants, cuprous oxide, copper oxychloride, ligands, micelles

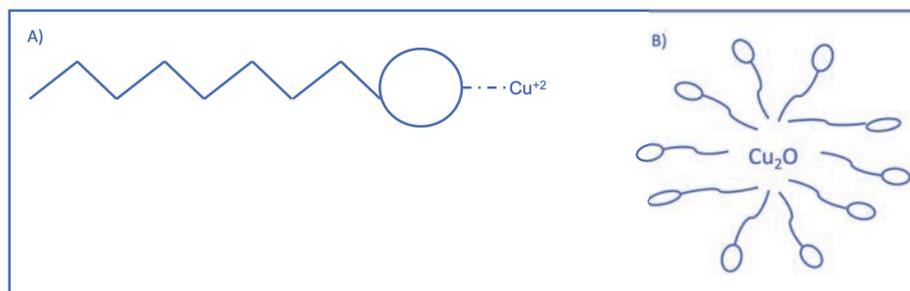


Figure 1. Solubilization of Copper oxychloride (A) and cuprous oxide (B) in water

Acknowledgements: this research was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under the project RTI2018-093610-B-100.

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Potential capability of biosurfactant extracts from corn steep liquor to be included in agrochemical and cosmetic formulations

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Biosurfactants can be considered a 3rd generation of surfactants as they are composed uniquely by natural polymers consisting of sugars, lipids and/or proteins; whereas chemical synthesized surfactants as well as bio-based surfactants present, in their composition, totally or partially nonrenewable substances, and they are less biocompatible and biodegradable than microbial surfactants. In this work, biosurfactants extracts were obtained from corn steep liquor (CSL) by liquid-liquid extraction with chloroform or ethyl acetate and diluted in aqueous solutions at different concentrations, depending on the industrial application, following the procedures described by Ricón-Fontán et al. [1] and López-Prieto et al. [2], respectively. Emulsions containing Zn pyrithione were prepared with a tea tree oil/water ratio (v/v) of 0.1 and biosurfactant extract, obtained with chloroform and named BS1 (2.5 %), being the concentration of Zn pyrithione of 0.5 % (w/w). On the other hand, emulsions containing copper oxychloride (0.4 %) were prepared in aqueous solutions using 2.0 % of biosurfactant extract, obtained with ethyl acetate (named BS2), or chemical surfactants including sodium dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB), or Tween 80. Zn pyrithione and copper oxychloride were quantified following the procedure established in previous works [1,2]. **Table 1** shows the results obtained regarding solubilization and/or stabilization of Zn pyrithione and copper oxychloride, in water and in presence of biosurfactant extracts, from corn steep liquor (BS1 or BS2), observing better results than those obtained with chemical synthesized surfactants. Therefore, it can be concluded that biosurfactants extracted from CSL not only are more biocompatible and biodegradable than chemical synthesized surfactants, but also are more effective as stabilizing agents for those formulations including Zn pyrithione or copper oxychloride.

Keywords: biosurfactants, copper oxychloride, Zn pyrithione, water, solubilization

Table 1. Comparative study of the stabilizing capacity of biosurfactants extracted from CSL.

Industrial application	Active principle (AP)	Biosurfactant	AP stabilized (%)
Cosmetic/pharmaceutical	Zn pyrithione	BS1 (2.5 %)	33.6
Cosmetic/pharmaceutical	Zn pyrithione	Tween 80 (2.5 %)	5.2
Agrochemical	Copper oxychloride	BS2 (2.0%)	90.0
Agrochemical	Copper oxychloride	SDS (2.0%)	0.3
Agrochemical	Copper oxychloride	CTAB (2.0%)	0.3
Agrochemical	Copper oxychloride	Tween 80 (2 %)	0.2

Acknowledgements: this research was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under the project RTI2018-093610-B-100.

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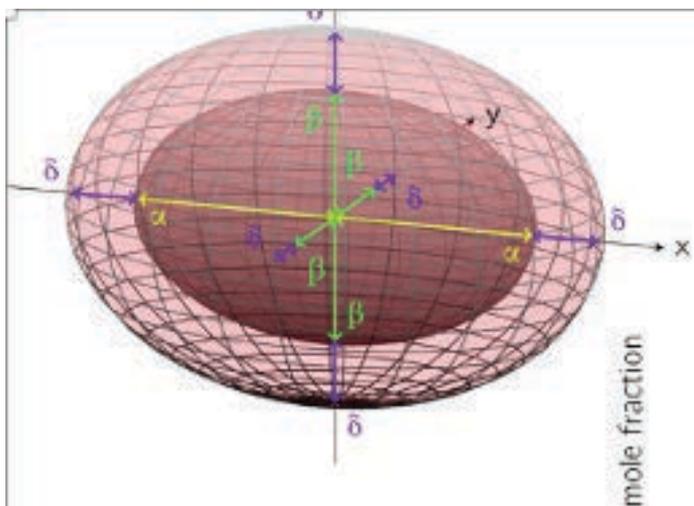
Non spherical micelles produced by molecular packing of chains combined to frustration of head-group packing:

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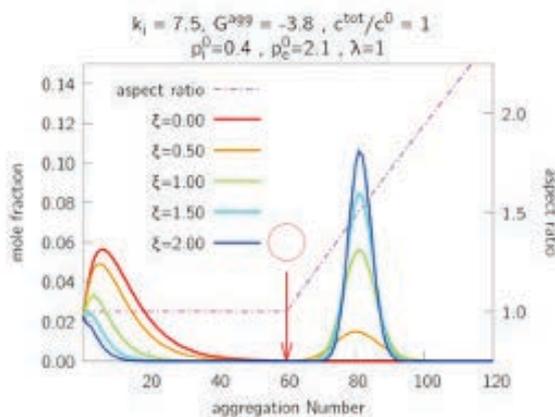
Surfactant film rigidity is a ubiquitous general concept that is quantified in two different units. We show here how to convert the bending rigidity from reduced units of a virtual infinitely thin film (not made of molecules) into the chemical unit (kJ.mol⁻¹) of a realistic film of monomolecular thickness.

The infinitely thin film considered by Helfrich for the case of liquid crystals leads to contradiction and inconsistencies as soon as the film thickness is of the same order of magnitude that radius of microemulsion droplets and strictly equal for micelles. The most general model of the free energy expressed in kJ/mole of bending postulates an harmonic expression of the difference between one spontaneous packing parameter and effective packing parameter (sometimes mixed up and both named “critical parameter”). This model is not compatible with the non-spherical micelles close to cmc. If not only hydrocarbons chains (brown) , but also bulky hydrated head-groups (pink) participate to the packing constraints, the free energy of formation of a micelle contains now two terms with spontaneous packing of chains as well as heads:



$$F = \frac{1}{2} k_c^* (p_c - p_{c0})^2 + \frac{1}{2} k_h^* (p_h - p_{h0})^2$$

The first consequence of the double frustration of chains by heads and chains is the mechanism of formation responsible for the observation of ellipsoidal micelles close to cmc. Maximal aggregation number possible for a spherical shape is 60. A typical distribution is shown on the figure to the right with molecular quantities typical for alkyl maltosides : small aggregates coexist with micelles formed with an ellipticity close to 1.5 as shown on the figure to the right, a common but previously unexplained observation



EP5.1

Formulation of Pickering emulsions for the development of surfactant-free sunscreen creams

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Surfactant-free Pickering emulsions can be stabilized by the UV-filter nanoparticles for the manufacture of sunscreen products. Pickering emulsions are increasingly used in the pharmaceutical and cosmetic fields, especially for topical applications, since these systems require solid particles as emulsifiers instead of surfactants which are known to cause skin irritation. The solid inorganic nanoparticles (TiO₂ and ZnO) used as UV filters in sunscreen formulations may also stabilize emulsion droplets, so that the utility of surfactants may be questioned. Surfactant-free sunscreen emulsions solely stabilized by such nanoparticles (NPs) have been studied.

The ability of these NPs to stabilize o/w emulsions containing a 'model' oil phase, the C₁₂-C₁₅ alkylbenzoate, has been assessed. ZnO and hydrophilic silica-coated TiO₂ NPs widely used in sunscreen products were used together with their mixtures. The emulsification efficiency, the control of droplet size and the stability of o/w Pickering emulsions solely stabilized by NPs were investigated. Stable Pickering emulsions containing 10 up to 60 wt% of C₁₂-C₁₅ alkyl benzoate were formulated with 2 wt% ZnO in the aqueous phase. The droplet size was controlled by the solid NPs content with respect to oil and the emulsification process. Hydrophilic TiO₂ NPs did not allow the stabilization of emulsions. The substitution of TiO₂ for ZnO up to 60–70 wt% in a 20/80 o/w emulsion was successful. Finally, a ZnO/TiO₂ NP mixture was tested as unique emulsifier system for the formulation of a sunscreen cream. Despite a lower viscosity, the obtained Pickering emulsion was stable and exhibited a photoprotective effect similar to the corresponding surfactant-based sunscreen cream with an *in vitro* SPF of 45.

Keywords: Pickering Emulsions; Inorganic nanoparticles; Sunscreen formulation; Formulation/stability; Skin photoprotection

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Study of the effect of peptides on the synthesis and properties of silver nanoparticles for topical application

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The aim of this work was the study of the effect of peptides on the synthesis and properties of AgNPs for topical application. The peptides used were commercially available cosmetic ingredients, namely Myristoyl Tetrapeptide-6 (MT-6) and the Cu containing Copper Tripeptide-1 (CuTP-1). AgNPs were prepared by adding the peptide: i. during AgNO₃ reduction (MT-6 AgNPs, CuTP-1 AgNPs) or ii. after AgNPs synthesis (AgNPs MT-6, AgNPs CuTP-1). AgNPs synthesized without peptide interaction were used as control.

The investigation of the presence of AgNPs and synthesis yield was performed using UV/Vis, while the study of their physicochemical characteristics was achieved with DLS, TEM, XRD, AAS, και FT-IR [1]. The stability of AgNPs was monitored for a period of three months. Because the addition of either peptide during the synthesis of AgNPs resulted in better yields by 38%, the wound healing capacity of MT-6 AgNPs and CuTP-1 AgNPs was assessed using scratch wound healing assay (SWA) on mouse fibroblasts (NIH3T3) for 48h [2].

The wound healing effect of both peptides (71.97% ± 4.35% and 62.37% ± 18.33% respectively) occurred at 24h and it was found 5.48 and 2.82 higher of that of the free peptides (MT-6 and CuTP-1 respectively) (Fig. 1). This result demonstrate the synergistic action of peptides with AgNPs on wound healing.

Keywords: silver nanoparticles, AgNPs, peptide, wound healing

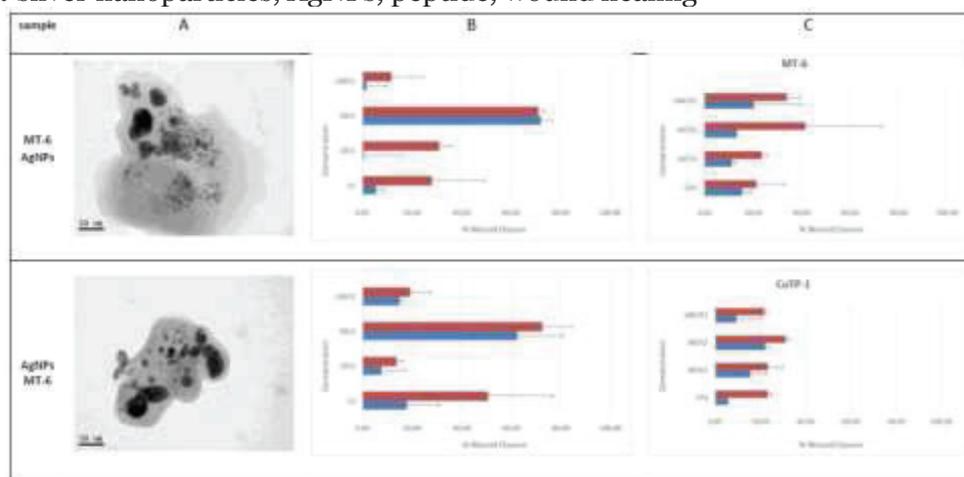


Figure 1. TEM photos (30000x) of peptide/AgNPs conjugates (A) and wound healing effect of MT-6 AgNPs and CuTP-1 AgNPs(B) and respective free peptides (C).

Acknowledgements: Authors would like to thank Dr. M. Kollia for TEM analysis in the Laboratory of Electron Microscopy and Microanalysis, University of Patras and COSMOCHEM CHEMICALS for the donation of peptides.

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EP5.3

**Liposomal Nanocarriers with Incorporated Dimethoxycurcumin.
In vitro Toxicity and Permeability**

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Drug delivery nanosystems, such as liposomes, are widely utilized for the incorporation and delivery of drug molecules, diagnostics and theragnostic agents [1,2]. In the present study, the curcumin analog dimethoxycurcumin (DMC) was incorporated inside different types of liposomes, while the toxicity and permeability of the nanocarriers was evaluated *in vitro*.

The development of liposomal nanocarriers with DMC was achieved through thin-film hydration. Their physicochemical properties were analyzed through light scattering techniques and the incorporation efficiency of DMC was also estimated. The MTT and Transwell methods were applied on CaCo-2/TC7 and HT29-MTX cells to assess the *in vitro* toxicity and permeability of the liposomes.

The physicochemical properties of the prepared nanocarriers were dependent on the lipid composition, with respect to the presence of cholesterol and charged molecules. After incorporation of DMC, the liposomes presented alteration in their properties, while the incorporation efficiency was found around 70-80% for all tested formulations. The toxicity of the nanocarriers was found to be low but also dependent on the liposomal composition. Transepithelial electrical resistance (TEER) measurements on the cells after addition of the liposomes indicated a temporal opening of the tight junctions, while the epithelium was not destroyed by the particle addition and permeation. Notably, the latter was enhanced 2 to 2.5-fold for the liposome-attached chromophore, compared to the free molecule, especially when utilizing cationic liposomes, probably due to the mechanism of adsorptive transcytosis [3].

The *in vitro* behavior of liposomes depends on their composition and properties. Biocompatibility and membrane permeability are crucial properties for such systems, in order to utilize them in biological applications. The present work lays the groundwork for further investigation of the herein developed liposomal nanosystems, which may be utilized for the delivery of drug molecules.

Keywords: liposomes; nanocarriers; dimethoxycurcumin; physicochemical properties; toxicity; permeability

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EP5.4

The Interactions of Liposomes with Serum Proteins as an Approach to Personalized Medicine

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Liposomes are investigated as drug delivery systems for a variety of diseases. An important factor that affects the effectiveness of a medicine is the genetic and pathophysiological background of each patient, hence the importance of Precision Medicine [1]. The aim of this study was to develop different types of liposomal nanoparticles, their physicochemical characterization and stability study, and the evaluation of their interactions with serum proteins from diabetic (type II) and healthy individuals.

Five different types of liposomal systems were prepared, conventional, with cholesterol, anionic, cationic and PEGylated, through the thin-film hydration method. Physicochemical characterization and stability studies were conducted by utilizing light scattering. Following a static incubation protocol, the interactions between the developed liposomes and serum proteins, originating from diabetic or healthy subjects were also assessed.

The initial physicochemical studies suggest that the use of different components leads to different effect and properties of liposomes. Regarding proteins, positively charged liposomes were more susceptible to interactions and protein corona formation, as confirmed by the alterations in their size, polydispersity and surface charge in both cases of diabetic and healthy individuals. In addition, cationic liposome-protein complexes were measured to have a by 35nm smaller size after incubation with serum proteins from diabetic patients. These results suggest that the polymorphic changes in the morphology of proteins (*e.g.* albumin) originating from diabetes affect their functionality and are reflected on their binding affinity for highly interactive nanoparticles [2].

In conclusion, the composition of liposomes is crucial for their properties, stability and biological interactions. This means that a liposomal medicine may have dissimilar behavior among individuals and a treatment outcome that is depended on underlying health conditions, such as diabetes. Further studies are needed to substantiate this claim and support this promising domain of Nanomedicine and Personalized Medicine [3].

Keywords: liposomes; physicochemical characterization; diabetes mellitus; protein interactions; precision medicine

Acknowledgements: We would like to thank Dr. George Koukoulis from the Henry Dunant Hospital Center for the provision of human serum samples.

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Structured nanoemulsions co-loaded by hybrid fluorophores for application in melanoma cancer theranostics

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We investigated new development in therapeutic and diagnostic (theranostic) applications of “soft” colloidal nanocarriers (NCs), aiming at enhanced tumour selectivity and biocompatibility, which included application of a third-generation photosensitizing agent, i.e. xanthene-origin Rose Bengal (RB) co-encapsulated with up-converting NaYF₄ nanoparticles (UPNPs) co-doped with lanthanide ions: Er³⁺ (2%) and Yb³⁺ (20%). The hybrid fluorophores were applied as components of double core NCs obtained by nanoemulsion structural design approach using biocompatible polymers and surfactants, intended for photodynamic therapy (PDT) [1,2]. After the engineering process, controlled by dynamic light scattering, ζ-potential, transmission electron and atomic force microscopy, as well as optical analysis provided by measurements of the up-conversion emission spectra and luminescence kinetics for co-encapsulated RB+UPNPs with average size <200 nm, were tested on human melanoma (Me45 and MeWo) and control human keratinocyte (HaCaT) cells using photocytotoxicity, immunofluorescence and internalization studies. Our results indicated the effective nanosystem delivery into the cancer cells and significant photodynamic efficiency enhanced by the near infrared (NIR)-activation of the encapsulated hybrid cargo in the skin melanoma cells.

Keywords: theranostics, nanoemulsion structural design, photodynamic therapy

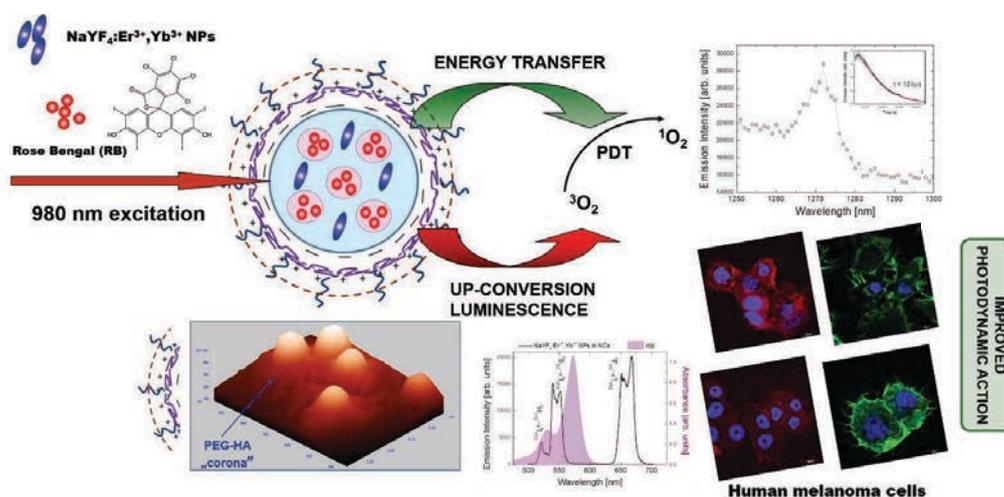


Figure 1. General idea of the proposed studies involving the NaYF₄ UPNPs and Rose Bengal photosensitizer co-encapsulation the nanoplatform application in NIR-induced photodynamic therapy upon human melanoma cells.

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EP5.6

Development of Stimuli-Responsive Lyotropic Liquid Crystalline Nanosystems with Incorporated PDMAEMA-b-PLMA Block Copolymer for drug delivery

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Non-lamellar lyotropic lipidic liquid crystalline nanoparticles are novel drug delivery nanosystems that are stabilized by suitable stabilizers, such as polymers [1]. The aim of this study was to incorporate the stimuli-responsive amphiphilic block copolymer poly(2-(dimethylamino)ethyl methacrylate)-b-poly(lauryl methacrylate) (PDMAEMA-b-PLMA) as a stabilizer in lipidic liquid crystalline nanoparticles, prepared by glyceryl monooleate or phytantriol, in order to provide steric stabilization and simultaneous stimuli-responsiveness, as well as upgraded functionality. For the first time, liquid crystalline nanoparticles with polycationic content were developed.

The physicochemical characteristics of the prepared nanosystems were investigated by dynamic, electrophoretic and static light scattering techniques, their morphology by cryogenic-transmission electron microscopy (cryo-TEM) and their microenvironmental parameters by fluorescence spectroscopy. The effect of the environmental parameters on their physicochemical behavior was also investigated.

Due to the protonation ability of PDMAEMA blocks in acidic pH, the nanoparticles exhibited high positive charge, as well as pH-responsive charge conversion. The ionic strength, temperature and serum proteins influenced the physicochemical behavior of the nanoparticles, while the polymer concentration differentiated their morphology [2].

In conclusion, the proposed liquid crystalline nanosystems can be considered as novel and attractive pH-responsive drug and gene delivery nanocarriers for pharmaceutical applications, due to their polycationic content.

Keywords: lyotropic liquid crystals, cubosomes, poly(2-(dimethylamino)ethyl methacrylate), cryo-TEM, stimuli-responsive

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Partially hydrophobically-modified random diblock copolymer colloids for insulin delivery

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Diabetes is a high-risk metabolic disorder that is induced due to the pancreas impairment to produce the proper rates of insulin or the cells are not responding to the insulin. Therefore, patients suffering from diabetes mellitus are subjected to insulin injections of several doses every day, in order to maintain their blood glucose levels at regular rates. Subsequently, the delivery of insulin should focus on the advancement of novel nanocarriers with specific features that will entitle the complexation with insulin, its release and other pathways of administration. Block copolymer nanostructures are used successfully as possible nanocarriers for insulin due to their small size, solubility in many solvents, colloidal stability, significant cellular uptake and high cell viability and in vivo biocompatibility [1].

We report studies on the complexation of partially hydrophobically-modified poly(2-(dimethylamino) ethyl methacrylate)-*b*-poly(oligoethylene glycol methacrylate) (P(DMAEMA-co-Q_{6/12}DMAEMA)-*b*-POEGMA) with insulin[2]. Complexation was accomplished via electrostatic interactions between the positive charges of the cationic QPDMAEMA segments and the negative charges of insulin. The presence of long alkyl chains (six carbons long in the case the quaternization agent was iodoethane and twelve in the case of iodododecane) contributed on the formation of complexes of high mass, small size and colloidal stability for more than twenty days. Four different charge ratios (ins/polymer=0.25, 0.5, 0.75, 1) were tested. In almost every case the size of the resulted complexes were below 100 nm (as determined by DLS), no precipitation occurred and no significant dimensional changes were detected over the period of twenty days. Furthermore, UV and FS studies confirmed that no structural of insulin take place throughout the complexation process. Finally, utilization of ATR-FTIR spectroscopy confirmed the development of physical interactions between insulin and the polymer nanostructures upon complexation. In conclusion, P(DMAEMA-co-Q_{6,12}DMAEMA)-*b*-POEGMA nanoscale colloids are propitious insulin nanocarriers and can be applied in insulin delivery applications.

Keywords: partially hydrophobically-modified copolymers, insulin vectors, complexes

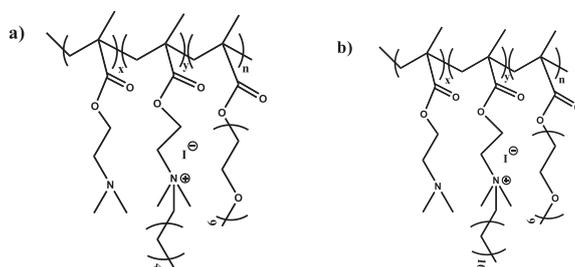


Figure 1. Chemical structures of a) P(DMAEMA-co-Q₆DMAEMA)-*b*-POEGMA, b) P(DMAEMA-co-Q₁₂DMAEMA)-*b*-POEGMA random diblock copolymers

Acknowledgements: The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant (Fellowship Number: 799)



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Antioxidant-loaded nanoemulsions for sun protection enhancement

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Sunscreens are cosmetic products that protect the skin from sunlight and its effects. They are typically emulsions that contain natural or synthetic components (filters) found to either reflect or absorb sunlight [1]. The major problem of synthetic filters is that they are producing harmful free radicals. To reduce free radicals, the industry uses synthetic antioxidants to the sunscreen products. On the other hand, climate change and the greenhouse effect have created the need for products with higher protection from the UV radiation [2].

The aim of this project was to formulate stable nanoemulsions to encapsulate antioxidants extracted from Olive mill wastewater (OMW) and phycocyanin extracted from *Spirulina maxima* taking advantage of the Greek biodiversity. For this purpose, water-in-oil nanoemulsions were prepared using a combination of the low energy method and high shear homogenization. Systems were based on isopropyl myristate (IPM) as the continuous phase while water or glycerol were used as the dispersed phase. Moreover, antioxidants extracted from OMW and phycocyanin from *Spirulina maxima* were encapsulated. The empty and antioxidant-loaded systems were then studied structurally using Dynamic Light Scattering (DLS) for the detection of their droplet size and stability over time. Electron Paramagnetic Resonance (EPR) Spectroscopy was also applied for the characterization of the surfactants' monolayer in the presence and absence of antioxidants. Finally, the encapsulated antioxidants were assessed for their scavenging activity by applying EPR spectroscopy.

It was found that the mean droplet diameter of the nanoemulsions was around 200 nm. The nanoemulsions remained stable for over 20 days. The systems retained their stability in the presence of antioxidants. The loaded nanoemulsions showed a relatively high scavenging effect towards specific free radicals. The proposed systems could act as good candidates for the protection and delivery of antioxidants for the cosmetic industry.

Keywords: Nanoemulsions, Antioxidants, Encapsulation, Olive Mill Wastewaters, *Spirulina maxima*

Acknowledgements: This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE, T2EAK_03640

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Glutathione-responsive molecular nanoparticles from a dianionic bolaamphiphile and their use for targeted delivery

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The development of nanocarriers for biomedical purposes is a very active area in the intersection of chemistry and biomedicine. In general, the purpose of nanocarriers is to overcome problems such as poor water solubility, reduced chemical stability or rapid excretion, among others, found in the administration of drugs or contrast agents [1].

Here we report the formation of molecular nanoparticles from a bolaamphiphile (SucIleCsa) incorporating a disulfide moiety in aqueous media. The particles can be loaded efficiently with the lipophilic mitochondrial marker DiOC₆(3), quenching its fluorescence, which is recovered upon reductive particle disassembly. DiOC₆(3) transport into human colorectal adenocarcinoma cells (HT-29) is demonstrated using flow cytometry and confocal scanning fluorescence microscopy. A significant increase in intracellular fluorescence is observed when the cells are stimulated to produce glutathione (GSH). These new molecular nanoparticles can be considered a theranostic tool that simultaneously achieves targeted delivery of lipophilic substances and signals high levels of GSH.

Keywords: nanocarrier, self-assembly, amphiphile, targeted delivery, glutathione-responsive

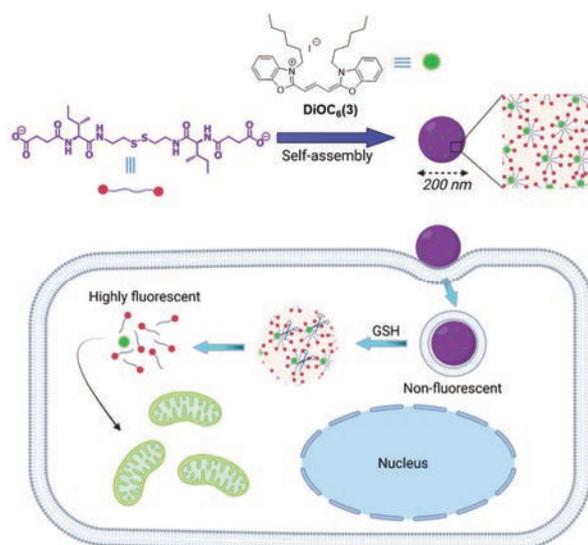


Figure 1. Schematic illustration of the chemical structure of the bolaamphiphile SucIleCsa and nanoparticle formation; GSH-promoted release of the dye DiOC₆(3) in cells.

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Flow Cytometry and Confocal Laser Scanning Microscopy Studies of Molecular Nanoparticles as Carriers of Photoactive Species

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The use of nanocarriers for the transport of bioactives into cells has been extensively studied in recent years and represents a central area of nanomedicine. Here we report on the use of flow cytometry and confocal microscopy to evaluate the activity of molecular nanoparticles as nanocarriers of two photodynamic therapy (PDT) agents, Rose Bengal (RB) and hypericin (HYP) or photoactive probes like the mitochondrial dye DiOC6 [1]. Despite the different nature of these PSs, nanogels from gelator **1** provide an efficient intracellular transport into human colon adenocarcinoma cells (HT-29) and a notably improved PDT efficiency, as assessed by confocal laser scanning microscopy and flow cytometry.

Keywords: nanocarrier, flow cytometry, confocal microscopy, photodynamic therapy, mitochondrial dye.

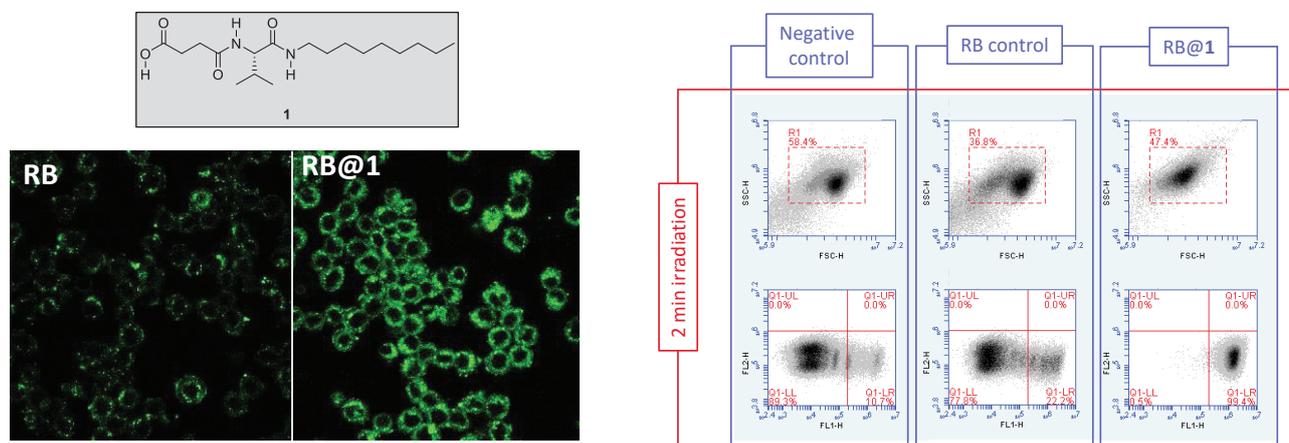


Figure 1. Left: Structure of compound **1**, a surfactant that forms nanoparticles, and confocal laser scanning microscopy images of HT-29 cells incubated for 24 h with free Rose Bengal (RB) and RB@**1** nanogels. Right: Dot plot obtained by flow cytometry in the analysis of PDT-induced apoptosis in HT-29 cells incubated with RB@**1**.

Acknowledgements: Ministerio de Economía y Competitividad of Spain (grant RTI2018-101675-B-I00) and Universitat Jaume I (grant UJI-B2018-54) are thanked for financial support.

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Electrostatic colloidal complexes between amphiphilic cationic block copolymer micelles and DNA

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The delivery of nucleic acids to target cells for the treatment of several diseases, including inherited disorders, viral infections and cancer, at a genetic level is defined as gene therapy and it is being considered as a revolution in molecular medicine [1]. A successful gene delivery strategy requires the design of effective gene transfer vectors that are able to target a specific tissue, protect nucleic acids from serum degradation, present high transfection efficiency, facilitate cellular uptake/endosomal escape, and regulate gene expression without any side effects or immunogenic response. Gene delivery carriers can be divided into viral and non-viral vectors. Viral vectors present high transduction efficiency and specificity, but they are associated with several dangerous immunogenicity issues. Hence, research has been focused on the development and improvement of non-viral vectors.

In this regard, amphiphilic block copolymers comprised of a cationic polyelectrolyte block have gained stupendous interest for their potential as non-viral vectors. They can electrostatically interact with nucleic acids, forming nanosized micelleplexes [2-3]. In our previous work, we reported the synthesis and self-assembly behavior of the quaternized poly(2-(dimethyl amino ethyl methacrylate)-*b*-poly(lauryl methacrylate) (QPDMAEMA-*b*-PLMA) amphiphilic polyelectrolyte copolymers [4]. Herein, we aim to investigate the ability of these copolymers to interact with linear DNA of different molar masses by forming stable micelleplexes, for their potent application as non-viral vectors for nucleic acids delivery. Micelleplexes were formed at various N/P ratios, through the electrostatic interaction of the positive charged nitrogen (N) of QPDMAEMA quaternary amino group with the negatively phosphate (P) groups of DNA. The successful complexation of QPDMAEMA-*b*-PLMA with DNAs and the formation of stable micelleplexes at various N/P ratios were confirmed by implementing several techniques for physicochemical and morphological characterization, including Light Scattering (DLS, SLS, ELS), UV/Vis Spectroscopy, Fluorescence Spectroscopy (using ethidium bromide quenching assay) and Cryogenic Transmission Electron Microscopy (Cryo-TEM).

Keywords: gene delivery, non-viral vectors, nucleic acids, micelleplexes, polyelectrolytes, block copolymers

Acknowledgements: The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the HFRI PhD Fellowship grant (Fellowship Number: 907).



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Design and evaluation of solid lipid nanoparticles obtained by ultrasonic-emulsification method

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Over last few decades, lipid-based formulations have emerged as a promising class of nanocarriers for encapsulating many active agents. Solid lipid nanoparticles (SLNs) combine the advantages and avoid the disadvantages of other colloidal systems. This type of carrier provides good stability (colloidal as well as physical) and high biocompatibility (biodegradable ingredients in combination with avoidance of organic solvents during production). Appropriate design of the carrier through a selection of components and preparation methods allows to obtain nanoparticles with desired physicochemical parameters and biological properties [1-3].

The present contribution has been carried out to investigate SLNs containing biocompatible phosphatidylcholine with non-ionic surfactant Tween 60 as stabilizing agents. The internal lipid phase consisted of glyceryl monostearate confirmed as safe for drug delivery by the Food and Drug Administration (FDA). Those formulations were fabricated by emulsification with the use of ultrasonic homogenizer. The preparation process was optimized in regard to variable parameters as ultrasonication time, used amplitude and number of cycles. The size along with size distribution of lipid nanoparticles was determined by the dynamic light scattering (DLS) technique, while the shape and morphology were studied by transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements. The colloidal stability of the studied nanoparticles was characterized by turbidimetric method. The obtained results indicate that the lipid nanoparticles may provide great potential for design and preparation of new effective delivery nanosystems encapsulating with both hydrophobic and hydrophilic agents. Those systems may be used in many pharmaceutical as well as cosmetic applications.

Keywords: lipid nanocarriers; process optimization; high-energy method; stability studies

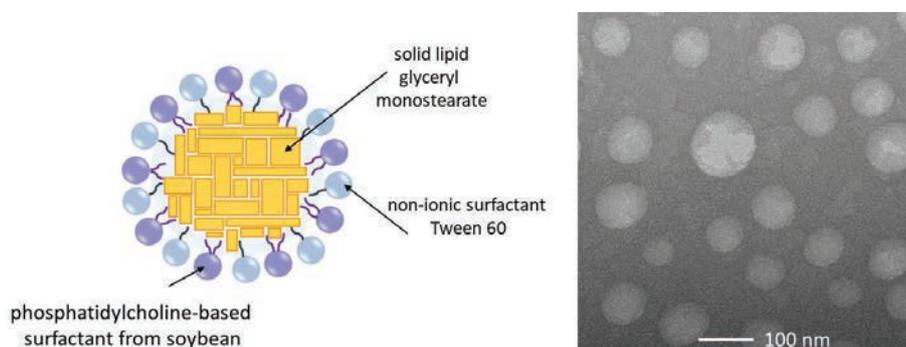


Figure 1. Schematic representation of solid lipid nanoparticles with imaging by transmission electron microscopy.

Acknowledgements: The support of Wrocław University of Science and Technology is gratefully acknowledged.

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Biocompatible control release bilosomes of hybrid agents

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The development of innovative and biocompatible nanoplateforms for the targeted delivery and the controlled drug release at target tissues can contribute to minimize the risk of side effects and increase the therapeutic efficacy of many active compounds [1]. Self-assembling bilosomes containing bile salts in their composition represent a new generation of “soft” lipid vesicle nanocarriers. These nanostructures are highly biocompatible, biodegradable, and non-toxic. The use of bile salts increases the colloidal stability of the system and enhances the bioavailability of poorly soluble pharmaceutical agents. And as a result, the bilosomal systems are a promising bioinspired platform, especially for anticancer treatment and diagnostics [2-3].

The present contribution deals with the encapsulation of the water-soluble photosensitizer (methylene blue) and the hydrophobic polyphenol (curcumin) in a novel class of colloidal vesicular nanosystem modified using bile salt – sodium cholate and functionalized with a biocompatible triblock copolymer – Pluronic P123. Surface-modified bilosomes prepared by thin-film hydration followed by the sonication method. Dynamic light scattering (DLS) measurements confirmed the particle diameter below 100 nm, transmission electron microscopy (TEM) their shape and morphology, while electrophoretic light scattering (ELS) exhibited a negative surface charge. Backscattering profiles (BS) confirmed the long-term stability of the nanostructures. UV-Vis spectroscopy was applied to determine the encapsulation efficiency (above 85% for both active compounds) and evaluation the hybrid agents' release characteristics under various environmental conditions. Overall, the data obtained indicate that functional bilosomes as a promising nanoplateform for the delivery and controlled release of hybrid cargo in further biomedical and pharmaceutical applications.

Keywords: bile salts, biosurfactants, nanocarriers, controlled release, anticancer pharmaceuticals

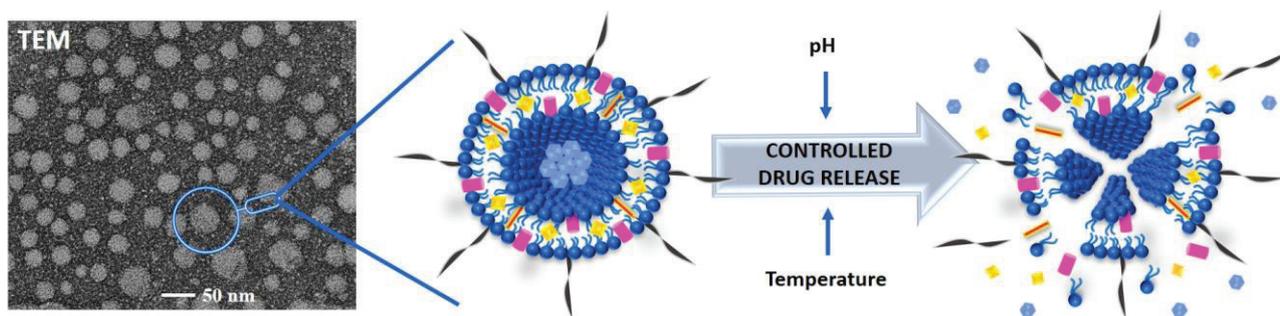


Figure 1. Schematic representation of controlled release of encapsulated hybrid agents and TEM image of bilosomes.

Acknowledgements: The support of Wrocław University of Science and Technology is gratefully acknowledged.

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Development, Characterization and Lyophilization of Liposomes. *In vitro* Toxicity Study on GL261 Glioma Cells

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Liposomes are considered one of the most advanced and widely established classes of drug delivery systems. Their structure includes a phospholipid bilayer that encloses an aqueous compartment and their building blocks range among a wide variety of molecules [1,2]. The aim of this study was the development of different types of liposomal nanoparticles, their physicochemical characterization before and after lyophilization, assessment of their interactions with serum proteins and the evaluation of their cytotoxic effect on GL261 glioma cells.

Four different types of liposomes were prepared, conventional, anionic, cationic and PEGylated, by using different phospholipids. Physicochemical characterization was conducted after preparation and over a period of 10 days. Evaluation of the interactions between the liposomes and serum proteins was also held. The formulations were subsequently lyophilized for stability during transfer and their concentration-dependent toxicity on GL261 cells was evaluated by MTT assay.

The physicochemical measurement of these nanoparticles revealed that different lipid composition leads to the appearance of different properties and has a significant effect on the stability of each system. Concerning the incubation with proteins, only positively charged liposomes were susceptible to interactions, while reconstitution studies confirmed the stability of the formulations after lyophilization. Finally, cell viability was dependent on the type and concentration of liposomes utilized, but also the incubation time.

In conclusion, herein were developed four different types of liposomal formulations. Lyophilization contributes to the development of stable pharmaceuticals that can be eventually used for other applications. The liposomal type defines the degree of interactions with serum proteins and as a result, their biological stability. Toxicity studies on GL261 lines allowed for the assessment of the effect of the developed liposomal systems on glioma cells. Such studies lead to conclusions about the biocompatibility and interactions of liposomal systems with cells *in vitro*.

Keywords: liposomes; lyophilization and reconstitution; MTT assay; GL261; cytotoxicity

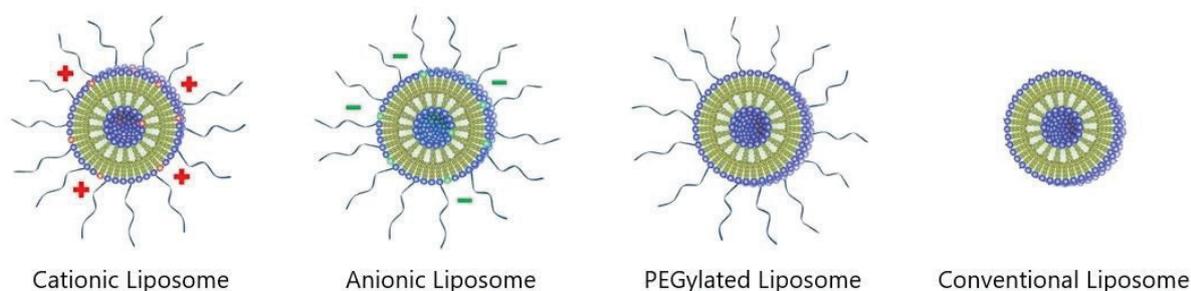


Figure 1. Different types of liposomes formulated during this study.

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Quantitative determination of the adsorption of nanoplatelets onto internally structured liquid crystalline cubic phase drops

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Aqueous dispersions of lipid-based lyotropic liquid crystalline phases are viewed as potential nanocarriers for cosmetics or medical applications. Their stabilization in water by nanoparticles (NPs) has been reported during the last decade, as a function of the types of lipid and nanoparticles [1-5]. Whereas the phase diagram of the internally structured drops has been perfectly understood, the spatial distribution of the stabilizers has not been determined and important questions are pending around the quantity of NPs necessary for stabilization. Answering these questions is fundamental for the optimal design of systems with targeted applications, such as physical hydrogels for external delivery drug systems.

The purpose of the present work is to determine, both qualitatively and quantitatively, such a localization in the case of Phytantriol (PT)-based cubic phases stabilized by Laponite nanoplatelets in water. Herein, we vary the PT concentration from 1%vol to 5%vol and the Laponite concentration from 0.05 wt% to 1 wt%.

Macroscopic observation as a function of both concentrations allows for an estimation of the threshold concentration of platelets necessary to stabilize a given amount of PT. It is found that this Laponite threshold is low, varying from 0.1 wt% to 0.3 wt%, for PT concentrations from 1%vol to 5%vol. Conductivity measurements reveal that once the stabilization threshold is reached, the number of nanoparticles adsorbed onto the drops remains constant. All platelets added above this concentration are not used for the stabilization of cubic drops, but stay in excess in the free water volume. SAXS experiments confirm the threshold values by a fine structural modelling of the scattering curves. The analysis also highlighted the dependency of the drop size on the total amount of PT.

This set of results leads to a fine understanding of the structural features of these systems as a function of all component parameters used.

Keywords: Microemulsions, Lipids, Self-Assembly, Nanoparticles

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Curcumin-loaded nanoemulsions in the view of dermal application: interfacial phenomena in the colloidal system and biological performances

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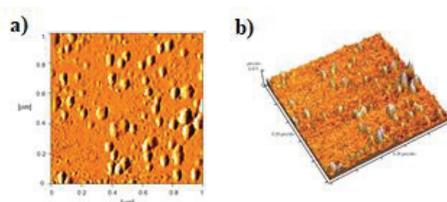
In the biomedical context, much has been expected from nanotechnology-based solutions. Among them, as drug carriers, nanoemulsions have been recognized as innovative colloidal systems matching various administration routes, providing solubilization, enhanced stability and improved delivery of active pharmaceutical ingredients (APIs) to the anticipated site of action [1]. However, drug interactions with the carrier and the phenomena at the bio-nano interfaces should be considered in order to understand the real potential of the designed nanotherapeutic. The aim of this work was to carefully investigate nanoemulsions (prepared through spontaneous emulsification) intended for dermal delivery of curcumin, linking microstructural properties, *in vitro*, and *in vivo* performances.

Composition of the selected blank and curcumin-loaded nanoemulsion is given in the Table 1. The average droplet size (dynamic light scattering) was 110 ± 1.77 nm for the blank, and 135.5 ± 2.3 nm for the curcumin-loaded nanoemulsion. Atomic force microscopy (AFM) provided direct insight into the dispersed droplets (Picture 1). Same measurements were performed in the serum-rich cell culture medium to mimic interactions that may occur during biological experiments, and no size change/protein corona formation was detected. Electron paramagnetic resonance spectroscopy revealed that curcumin took place at the water/oil interface, but in a very rigid microenvironment. Such localization provides stability of API against chemical degradation and readiness for interactions with biomolecules. Cell sensitivity assay (MTT) demonstrated high cytotoxic activity towards human melanoma cells ($IC_{50} = 42,88$ $\mu\text{g/ml}$), while no significant effect towards normal human keratinocytes ($IC_{50} > 200$ $\mu\text{g/ml}$). Excellent safety profile of these formulations was confirmed in the *in vivo* study with human volunteers, where transepidermal water loss and erythema index were followed as parameters related to skin barrier integrity and irritation. Obtained results demonstrated suitability of designed formulations for topical delivery.

Keywords: nanoemulsions, spontaneous emulsification, curcumin, dermal application

Table 1. Qualitative and quantitative (%) composition of the samples

Sample	MCT	Polysorbate 80	Soybean lecithin	Water	Curcumin
Blank	10	9	1	80	/
Curcumin-loaded				79.7	0.3



Picture 1. 2D (a) and corresponding 3D (b) AFM images of the blank nanoemulsion

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Development of superparamagnetic magnetite nanocarriers for targeted drug delivery

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Magnetic drug targeting is one of the most promising approaches for the treatment of various diseases in which magnetic drug nanocarriers are manipulated by external magnetic fields to reach the target area. [1] In recent decades, magnetite nanoparticles (MNPs) have attracted much attention due to properties such as superparamagnetism, high surface area and easy separation under external magnetic fields. [2] Therefore, MNPs were synthesized by solvothermal method. To enhance the surface functionality, the synthesized nanoparticles were stabilized by coating with poly(ethylene glycol) PEG-4000 Da, a hydrophilic and biocompatible polymer. Both bare and PEG-4000 coated MNPs were characterized by various techniques to appraise their suitability for drug delivery. The structure and morphology of bare and coated MNPs were characterized using X-ray powder diffraction (XRPD), field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Furthermore, the thermal property and colloidal stability of synthesized MNPs were studied. The magnetic measurements were carried out using a commercial Quantum Design superconducting magnetometer (SQUID). The interactions between iron, PEG and quercetin were studied by Fourier Transform-Infrared spectroscopy (FTIR). Within this research, quercetin as a model drug was investigated. The problems related to low solubility and instability in the physiological environment of quercetin are currently a challenge for medical application. [3] The UV/VIS spectroscopy was used to study quercetin loading and release from the prepared MNPs. *In vitro* kinetics of quercetin release has been controlled by using combined stationary and alternating magnetic fields. In addition, the superparamagnetic MNPs exhibited excellent chemical and physical properties, which makes them promising nanocarriers for targeted therapeutic applications.

Keywords: superparamagnetic nanocarriers, quercetin, drug delivery

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Liquid Marbles: a Tool for Tumor Spheroids Formation

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Liquid marbles, droplets of liquid coated with hydrophobic particles, have been increasingly studied for their wide range of possible applications from highly sensitive detection of heavy metal ions, water surface pollution detection to blood typing analysis. Herein we present liquid marbles as micro-bioreactors for multicellular tumor spheroids formation. Elastic hydrophobic shell with pores enables gas exchange, which is essential for long-term cultivation of cells. Humidity in liquid marbles is also regulated. Furthermore, the internal environment and fluid flow facilitate cell-cell interactions for three-dimensional cell culture growth [1-2].

In this study, growth kinetics of multicellular tumor spheroids created in liquid marbles was measured during 14 days long incubation and the suitability of this method for further drug screening tests was evaluated. Spheroids were formed within 3 days of incubation and formation of numerous spheroids per one liquid marble was observed. The highest number of spheroids created has a diameter in the range of 50 to 100 μm . A detailed size distribution of spheroids grown in liquid marble is shown in Figure 1.

Keywords: liquid marbles, micro-bioreactors, tumor spheroids

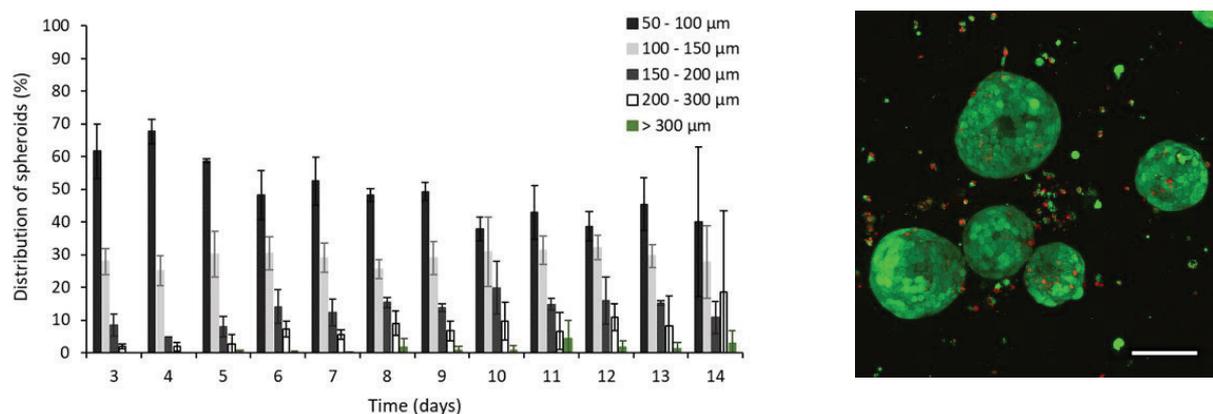


Figure 1. Size distribution of spheroids formed in liquid marble during cultivation. Image of spheroids formed in liquid marble (live cells are green and dead cells are red). Scale bar: 100 μm .

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Impact of Lipid Composition and Cholesterol Content on Size of Liposomes and their Penetration into Tumor Spheroids

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Chemotherapy is one of the most frequently used methods to treat cancer. However, cancer chemotherapeutics affect not only tumor sites but also healthy cells. To help solve this problem, new drug delivery systems are being developed [1]. Liposomes could be an option. Liposomes consisting of an aqueous core surrounded by a lipid bilayer can entrap hydrophilic and lipophilic compounds in their structure. Important properties of liposomes also include low toxicity, biocompatibility, and biodegradability, which predetermine them to be a system suitable for targeted drug delivery [2-3]. In this study, the effect of lipid composition and cholesterol content on the penetration depth of liposomes into multicellular tumor spheroids was investigated. Liposomes were prepared by a lipid film technique followed by extrusion through polycarbonate filters with 400 nm, 200 nm and 100 nm pore sizes. Liposomes were added to spheroids (HT-29) grown in liquid marbles and incubated for 48 hours. The penetration of fluorescently labelled liposomes was investigated by a laser scanning confocal microscope, which allows the observation of optical sections at different depths of the objects studied. It has been found that smaller liposomes penetrate deeper into spheroids than larger liposomes. It has also been found that the penetration depth depends on lipid composition and cholesterol content. Liposomes with a positive surface charge penetrate into spheroids deeper than liposomes with a negative surface charge.

Keywords: Liposomes, Spheroids, Penetration Depth, Laser Confocal Microscope

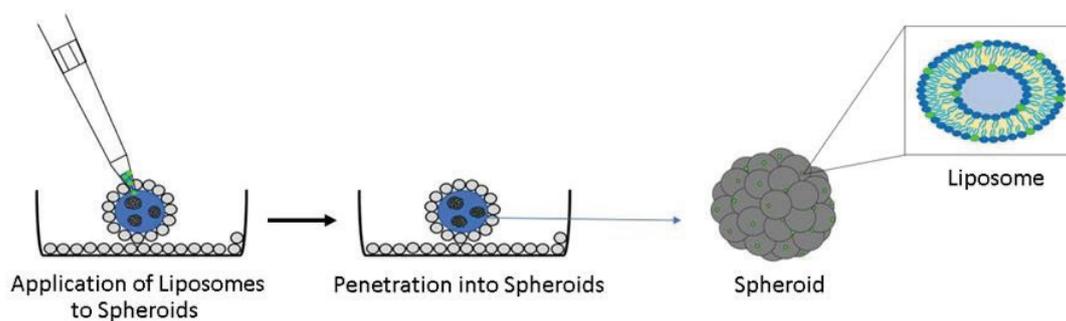


Figure 1. Application of liposomes to spheroids

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Comparison of Chitosan and Albumin influence on Calcium Phosphate formation on TiO₂ nanomaterials

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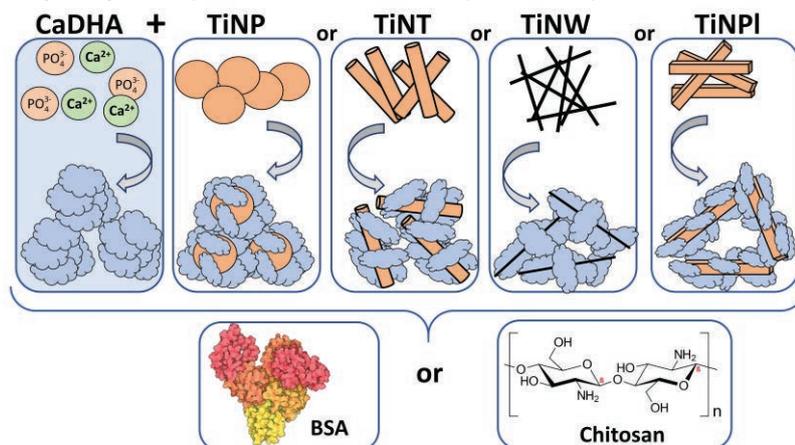
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The constantly growing need for advanced bone regeneration materials motivates the development of calcium phosphates (CaPs) composites with a different metal or metal-oxide nanomaterials, among which the TiO₂ nanomaterials (TiNMs) stands out [1]. The most important properties of bioimplant materials are mechanical properties and biocompatibility, which could be improved by incorporation of different organic additives. Albumin is one of the first proteins that adsorbs on the implant surface after implantation and affects their behaviour *in vivo*, i.e. their biocompatibility [2]. On the other hand, mechanical properties can be improved by preparing nanocomposites with chitosan, a polysaccharide with antimicrobial properties [3]. With the aim to develop the biomimetic route for preparation of multifunctional bone regeneration materials, the influence of bovine serum albumin (BSA) and chitosan on precipitation of CaP in the presence of TiNMs of different morphology (nanoparticles (TiNP), nanotubes (TiNT), nanowires (TiNW) and plates (TiNPI)) was investigated. The advancement of the precipitation was followed by monitoring pH changes in time. The obtained materials were characterized by powder X-ray diffraction, Fourier transforms infrared spectroscopy, scanning electron microscopy, and dynamic and electrophoretic light scattering. The results showed that BSA and chitosan inhibit the CaPs formation in precipitation systems, added alone or in combination with TiNM. The only exception is BSA in the presence of TiNTs. Neither BSA or chitosan influence the structure and composition of precipitated CaPs' phase. In all systems, calcium deficient hydroxyapatite (CaDHA) was formed within one hour [4]. On the other hand, BSA and chitosan influenced the morphology of the precipitated phase which seems to be more crystalline in the presence of these two additives.

Obtained results show that BSA and chitosan can be used as additives in CaP/TiNM nanocomposites preparations, and point to the fast and simple biomimetic route for multifunctional nanocomposite preparation.

Keywords: calcium phosphates, TiO₂ nanomaterials, chitosan, bovine serum albumin



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Development of nanoemulsion systems for the encapsulation and delivery of hypoglycemic drugs against Diabetes mellitus

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Nanoemulsion (NE) systems have attracted intense interest in recent years, as they comprise a flexible technology that improves transdermal drug delivery [1]. NE is defined as the dispersion consisting of an oil, a surfactant, a co-surfactant and an aqueous phase, which is an optically-only isotropic and thermodynamically stable liquid solution with droplet diameters usually ranging from 10–200 nm [1]. The superiority of the use of NE for transdermal application stems from the increased solubility of drugs in these systems, good thermodynamic stability and enhanced effect on transdermal capacity [2]. The ability of the NE to increase the concentration gradually, as well as the thermodynamic activity towards the skin simultaneously with the enhanced permeability of its components, make it a suitable system for transdermal transport.

The main objective of the current study is to develop NE systems for the encapsulation and transdermal delivery of hypoglycemic drugs (e.g., SGLT-2 inhibitor), that are commonly used as treatment against Diabetes mellitus (MD), increasing their effectiveness. Factors influencing the NE formation (e.g., temperature, molar ratios of the components) were determined and optimized; caprylic acid was used as the oil phase, while Tween-20 and propylene glycol (PG) were added as surfactant and co-surfactant, respectively, to produce stable nanoemulsions. Solutions containing SGLT-2 were prepared by dissolving the drug in water containing Tween-20 and PG. The synthesized NE were characterized regarding their size, stability and encapsulation yield.

Keywords: nanoemulsions, nanoencapsulation, diabetes mellitus, drug delivery

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Lipid liquid crystalline nanocarriers for chemotherapeutic and short-lived radionuclide for combination cancer therapy

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In this study we propose tailored lipid liquid crystalline carriers which incorporate an anticancer drug (doxorubicin) and complexed short-lived radionuclide (bismuth-213) in order to obtain more effective action towards the cancer cells.

Lipid liquid crystalline formulations, such as cubic phases and cubosomes, are promising nanomaterials as drugs carriers due to their biocompatibility and large internal interfacial area allowing to accommodate large amounts of therapeutic agents. Cubic nanostructures have been most extensively studied because of their sustained drug release properties and ability to maintain a three-dimensional structure under a range of physiologically relevant conditions and they have been already proven to be excellent drug delivery systems [1-4].

We prepared cubic phases and cubosomes formulated with doxorubicin (DOX) and an amphiphilic ligand which forms stable complexes with bismuth-213 radionuclide. We characterized the structure of lipid cubic-based formulations by small-angle X-ray scattering (SAXS) and we determined the stability of cubosomes by dynamic light scattering (DLS). To investigate the behaviour of the DOX incorporated in the carrier together with chelating agent, and to determine drug liberation profile we used electrochemical methods. We considered Korsmeyer-Peppas and other mathematical models in the determination of the DOX release kinetics.

We used MTS assay to evaluate cytotoxic effect of the cubosomes with doxorubicin and complexed ²¹³Bi upon selected cancer cell lines.

Keywords: drug carriers, cubosomes, doxorubicin, chemotherapy, radiotherapy

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Direct measurement of the efficiency of generation of singlet oxygen by nanostructures for PDT by a portable NIR spectrometer

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Nanostructures capable of generating reactive oxygen species (ROS) when activated by penetrating radiation (X-rays, NIR light) are widely investigated to apply Photodynamic Therapy (PDT) to tumours in deep tissue, where visible light cannot penetrate [1-3]. These nanostructures typically combine a scintillating nanostructure and a PDT photosensitizer molecule/nanomaterial; the therapy they promise to enable is known as Self-Lighted PDT.

A bottleneck in their characterization is the lack of a fast and reliable technique to quantitatively assess their performances in generating ROS, and in particular oxygen in its spin singlet state (¹O₂). This is mainly due to intrinsic limitations of standard chemofluorescent probes for ROS and ¹O₂, which are affected by self-activation and/or degradation under X-ray irradiation.

An attractive alternative is the direct detection of ¹O₂ via the measurement of its fluorescence emission, which is peaked in the near infrared (NIR) at . We explore the applicability of this technique to SLPDT nanostructures by means of a custom portable NIR spectrometer, specifically designed specifically to work under irradiation by Radiotherapy Linear Accelerators of clinical use. It couples a recently developed thermoelectrically cooled InGaAs single photon avalanche photodiodes (SPAD) to a custom-made integrating sphere. By calibrations in realistic experimental conditions on standard photosensitizers (see Fig. 1), we determined the detection threshold for our apparatus ¹O₂ molecules [4].

The same apparatus can be used to assess ¹O₂ generation from photoactivated nanostructures [5] for application in filters for photocatalysis and antibacterial treatments; the portable spectrometer is suited for the characterization of filters within prototype reactors.

Keywords: Singlet Oxygen, Self Lighted Photodynamic Therapy, photoactivated nanostructures, photocatalysis, NIR spectrometry

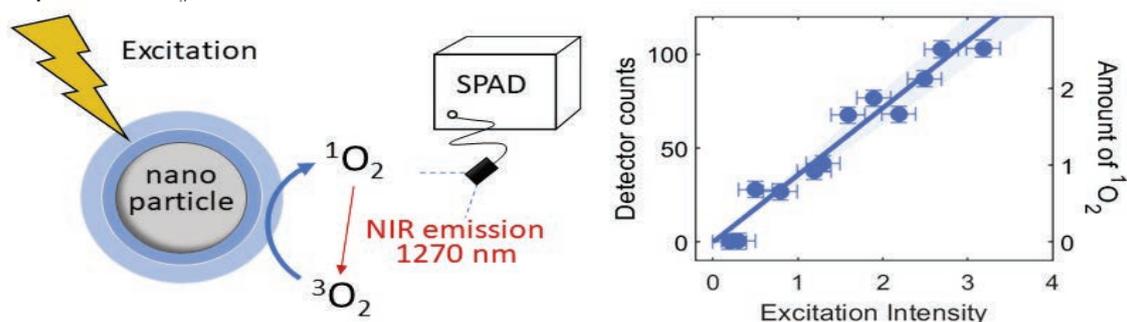


Figure 1. A photoactivated nanostructure generates ¹O₂, which is detected by measuring its NIR emission using a specifically developed portable spectrometer.

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New antimicrobial hydrophobized poly(acrylic acids) as functional coatings for curcumin-loaded hydrogel microparticles

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Hydrogel microcarriers functionalized with polyelectrolyte (PE) multilayer coatings of various chemical compositions and functions constitute one of the most interesting drug delivery systems (DDS). The application of layer-by-layer (LbL) films is a widely proven strategy that provides controllable drug release profiles and can form functional coatings exhibiting desired antimicrobial action. The hydrophobically modified PEs with quaternary ammonium groups are good candidates for antimicrobial coatings in DDSs and functional films.

The aim of the present work was to fabricate multilayered hydrogel microparticles functionalized with antimicrobial PEs and loaded with curcumin as a chemotherapeutic agent. Thus, we decorated poly(acrylic acid) (PAA) with different hydrophobic chains (i.e., *n*-hexane and *n*-dodecane side entities) and various percent degrees of substitution (*m*) of quaternary ammonium groups (abbreviated as PAA-X-(CH₂)_{*n*}-N⁺(CH₃)₃(*m*); X=-C(O)O- linker, *n*=6, 12; *m*=8, 10, 14%). The synthesis of hydrophobically functionalized PAAs were carried out under mild conditions using Steglich esterification followed by quaternization. We fabricated the curcumin-loaded microcapsules with alginate core and coated with LbL films consisting of three layers: chitosan, alginate, and the prepared PAA derivatives as an outer layer with antimicrobial function. The adsorption kinetics and viscoelastic properties of the functional layers were studied using Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D). The particle size and morphology of the microparticles were characterized by SEM. The curcumin release from the microcarriers was driven by diffusion or anomalous transport and the external copolymer layer did not change the release mechanism. The antimicrobial properties of PAA-X-(CH₂)_{*n*}-N⁺(CH₃)₃(*m*) and coated microparticles were assessed against *Escherichia coli* and *Staphylococcus aureus* by the inhibition zone method. The performed experiments have clearly shown that the antimicrobial PEs may constitute the added-value external layers to microcarrier systems. They are characterized by negligible interactions with the core microenvironment and reveal no impact on the release rates.

Keywords: antimicrobial polyelectrolyte, functionalized microparticles, LbL, hydrogel, curcumin

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Microgel particles for oral delivery of curcumin: compositional studies and anticancer effect in adenocarcinoma cell line (LoVo)

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Hydrogel microparticles are claimed to be interesting as an oral dosage form due to the multiple possibilities of their adjustment to the desired drug release behavior within the gastrointestinal tract. Therefore, recent studies on drug delivery systems (DDS) are focused on developing carriers for targeted administration of therapeutics with stimulus-controlled approaches to locally treat various bowel disorders, cancer specifically. Microgel particles aspire to enhance the treatment of intestinal diseases due to targeted delivery and reduced systemic exposure of therapeutic agents.

We studied biocompatible hydrogel carriers composed only of biopolymers. As a payload, curcumin was selected because it seems effective in the treatment of bowel cancer, although its beneficial activity is limited due to moderate solubility in physiological conditions [1]. Thus, we fabricated curcumin-loaded alginate-based beads and microspheres by means of ionic gelation and coated them with chitosan or gelatin layer via electrostatic complexation [2]. The prepared particles were characterized for entrapment efficiency with UV-Vis and FTIR measurements. Shape, size, and surface morphology were investigated with SEM, while moisture content and swelling kinetics with gravimetric techniques. Moreover, curcumin release was studied under three-phased conditions simulating gastric ones. The influence of the particles' composition on *in vitro* release were correlated with the help of mathematical models (i.e., hybrid, Korsmeyer-Peppas, Peppas-Sahlin) [2]. Finally, *in vitro* cytotoxic effect of the curcumin-loaded particles towards the LoVo human colon adenocarcinoma cell line was evaluated.

Our study demonstrated a clear correlation between the composition of curcumin-loaded microcapsules and the cytotoxic effect in LoVo cell line. Moreover, the investigated biopolymeric particles may be considered as a perspective approach for sustained release targeted drug delivery in the therapy of colon-associated diseases.

Keywords: encapsulation, biopolymer-based microparticles, *in vitro* release, LoVo cell line, colon cancer

Acknowledgements: This work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of the Wrocław University of Science and the Faculty of Pharmacy of the Wrocław Medical University.

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Poly[(vinyl benzyl trimethylammonium chloride)]-based hybrid colloids encapsulating insulin

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Double hydrophilic block and random copolymers, consisting of two water-soluble segments of different chemical nature in the macromolecular chain, have opened up new horizons in the research of polymer science, material science, pharmacy and biotechnology.[1]

Polyelectrolyte blocks or segments incorporated into double hydrophilic block and random copolymers are able to interact with oppositely charged biomolecules, such as insulin, whereas the neutral hydrophilic domains promote solubilization in water and provide stabilization of the formed hybrid colloidal nanostructures in aqueous media.[2] A polyelectrolyte poly[(vinyl benzyl trimethylammonium chloride)] (PVBTMAC) homopolymer, a double hydrophilic poly[oligo(ethylene glycol) methacrylate]-b-poly[(vinyl benzyl trimethylammonium chloride)] (POEGMA-b-PVBTMAC) block copolymer and a double hydrophilic poly[oligo(ethylene glycol) methacrylate-co-vinyl benzyl trimethylammonium chloride] (P(OEGMA-co-VBTMAC)) random copolymer were successfully synthesized by reversible-addition fragmentation chain transfer (RAFT) polymerization and further utilized for the complexation of insulin. The electrostatic interactions between the polyelectrolyte blocks and the oppositely charged insulin molecules, govern the complex formation and structure. The synthesized homopolymer, copolymers and polymer-protein hybrids were studied by means of light scattering techniques (DLS, SLS, ELS) in terms of their size, mass, R_g/R_{ho} ratio, surface charge and ionic strength dependence. The determined characteristics of the polymer-protein hybrids corroborated the efficient complexation of insulin with homo, block and random copolymers respectively. Moreover, attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy revealed relatively strong physical interactions between insulin and the respective polyelectrolytes. Ultraviolet-visible (UV-Vis) and fluorescence (FS) measurements provided information on the conformation of insulin after its complexation with VBTMAC based polyelectrolytes. In particular, insulin structural changes or denaturation did not occur during the complexation process. Lastly, FS results manifested no significant changes on the conformation of insulin after the formation of polymer-protein hybrids, revealing that the increase of insulin concentration did not result in fluorescence quenching or precipitation of the resulting polyelectrolyte-protein complexes.

Keywords: Double hydrophilic block copolymers, double hydrophilic random copolymers, polyelectrolyte blocks, insulin complexation, protein-polymer hybrids

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Glutathione–Responsive Cationic Bolaamphiphiles for Gene Delivery

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Polynucleotides can form lipoplexes with cationic nanoparticles and protect them against enzymatic degradation and enhance their cellular entry.¹ Here, we report the synthesis and aggregation of several cationic bolaamphiphiles containing a disulfide moiety and ammonium terminal groups. Cationic nanosized aggregates are formed at neutral pH values as detected by DLS and TEM. The nanoparticles can encapsulate several photoactive probes and the presence of glutathione or related reducing agents provokes their disassembly. Preliminary studies of their interaction with polynucleotides will be presented.

Keywords: cationic bolaamphiphiles, stimuli-responsive, nanocarriers, gene transfection

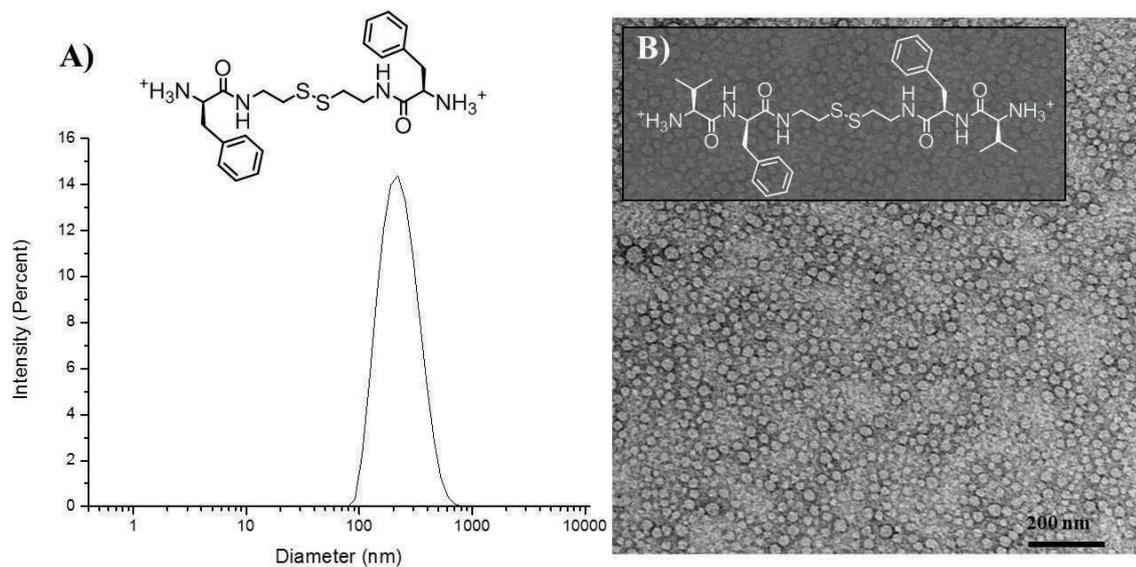


Figure 1. a) Structure of one of the studied cationic bolaamphiphiles and DLS size distribution. b) Structure of another cationic bolaamphiphile and TEM image of the nanoparticles.

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Fluorescent pH-sensitive nanosystems for anthocyanins delivery and tracking inside melanoma cells

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Discovering new targeted therapies for one of the deadliest types of skin cancer, melanoma, is still a pressing issue, given the lack of treatment options, frequent relapses and limited responders, even with the recent exciting approved drugs. This current work presents a fluorescent pH-sensitive nanocarrier of anthocyanins, that needs to be able to travel through cellular environment and resist at a continuous decrement of pH. The well-known biological properties of anthocyanins, and their wide distribution in human diet are the framework criteria that recommend them for biological applications, by designing and developing a proper intracellular carrier system. The fluorescent pH-sensitive nano-sized system, as a carrier for anthocyanins, was monitored for its delivery, subcellular localization and pH-controlled release of anthocyanins directly into melanoma cells.

The anthocyanins were extracted and purified from *Aronia melanocarpa var. viking* fruits, and each compound was identified and quantified using chromatographic techniques. Then, the anthocyanins were entrapped between the walls of the nanocarrier. The nanocarrier was constructed on a CaCO₃ template, on which alternative layers of selected polyelectrolytes poly(acrylic acid) (PAA) - the negative one and polyethyleneimine (PEI) – the positive one, both pH-sensitive, were added. In order to have a precise characterization of the nanosystem, the size and the nature of the electrostatic potential near the surface were assessed by Dynamic Light Scattering (DLS), Zeta-Potential, and Scanning Electron Microscopy (SEM). B16-F10 melanoma cells were treated with different concentrations of nanocarriers and the proliferation rate of metabolically active cells was evaluated by WST-1 assay. The cellular uptake events of anthocyanins-nanocarriers were captured by fluorescence microscopy, by labeling the acidic lysosomes, the nuclei and the cytoskeleton of the melanoma cells with different dyes that colocalize with the fluorophores labeled on nanosystems, on a pH-dependent manner.

Keywords: anthocyanin, fluorescent, nanosystems, pH, melanom

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Simultaneous fabrication and self-assembly of calcium carbonate particles for substrate functionalization to improve cell activities

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The colloidal assembly of micro/nanostructures to create arranged superstructures is of major importance in both fundamental studies and applications. Such applications are including the fabrication of optical devices, sensors, electronics, catalysts, and drug delivery systems.[1] However, it is still a challenge to achieve the desired particle distribution (self-assembly). One technique is spin-casting for making thin non-volatile surface coatings on solid substrates.[2] Porous CaCO_3 particles have advantageous properties such as biocompatibility and strong potential to load drugs. We design new material via simultaneous fabrication and deposition of the CaCO_3 particles on the spin-caster. The deposition of CaCl_2 and Na_2CO_3 solutions for CaCO_3 particle production and their deposition has been done during spin casting and dipping in water afterward in the ultrasonic bath. The size of the particles increased with increasing the salt's concentration. During the synthesis, self-assembly of nanoparticles on wafer surfaces takes place following the pure salts crystallization pattern but the arrangement of the heaviest microparticles is different due to the influence of gravity. To study the benefit of such coatings for tissue engineering, MC3T3-E1 cells were seeded on the coated substrates. Results could show that functionalizing the surface with CaCO_3 particles can enhance cell proliferation and adhesion on the surface. In cell communication and regulation, cell adhesion is a crucial value for tissue growth and maintenance. [3] Such an industrial-friendly coating design could be used in various fields of nanomedicine and beyond.

Keywords: Calcium carbonate micro and nanoparticles, self-assembly, MC3T3-E1 cells, cell adhesion, and proliferation

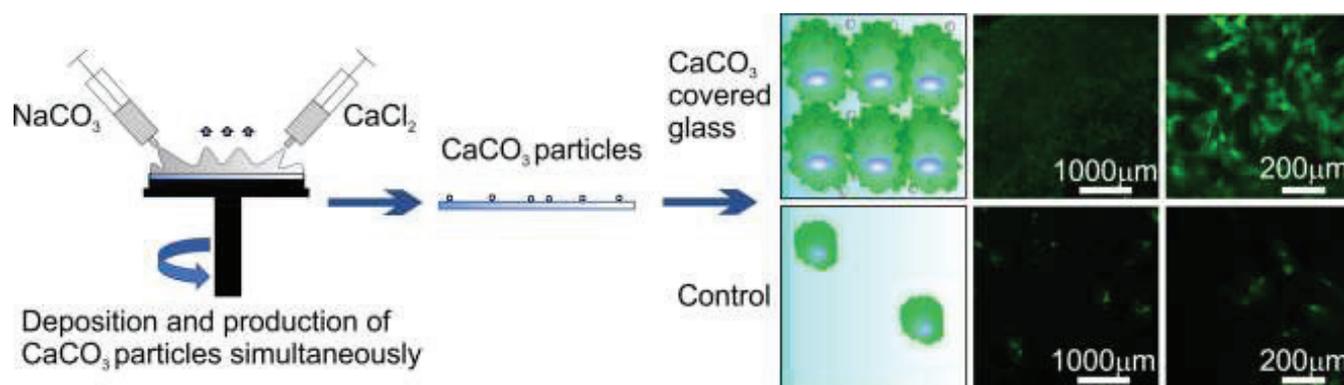


Figure 1: Deposited CaCO_3 particles can enhance cell proliferation and adhesion on the surface.

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Temperature stability of enzyme activity at the polyelectrolyte-hydrogel interface on colloids and at flat interfaces surfaces

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Alkaline phosphatase (ALP) is an important biomarker in tracking diseases, and it is also considered as a therapeutic enzyme for the treatment of cancer. Usually, it is applied as part of composite materials like hydrogels or polymer coatings and colloids, where temperature variations can affect enzymatic activity. The most interesting application of such therapeutic enzymes is the precise tuning of their catalytic function, which is often limited by proteolytic degradation and poor bio-distribution [1]. Thus, human ALP can be denatured and inactivated upon heating at or above 56°C [2]. However, there is a gap in the systematic study of the enzyme activity in the presence of various polymers. The influence of temperature on the enzymatic activity is relevant in neurology [1], drug delivery and tissue engineering [3]. Detailed evaluation of ALP activity in films and capsules was made containing various polymers like positively and negatively charged polyelectrolyte - polydimethyldiallylammonium chloride (PDADMAC), polystyrene sulfonate (PSS), alginate hydrogel, as well as studying their thermal stability.

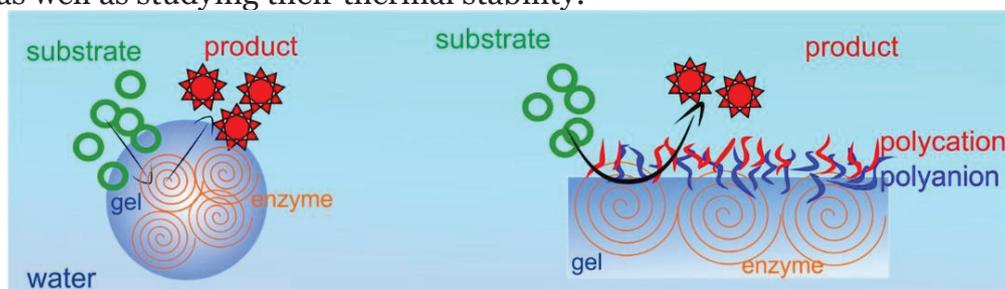


Figure 1. Schematic of designed hydrogel capsules (left) and film (right) loaded with enzyme.

We demonstrate that enzyme activity was increased in the presence of polymers [3]. Negatively charged polymers cause higher enzyme activity and better protection against high temperature. For example, PSS and PDADMAC increase the enzyme activity (three and two times, respectively) in comparison to free enzyme at room temperature.

Based on these results the optimal polymer/hydrogel composition is identified at the films and capsules upon ALP immobilization. In alginate capsules and polymer films, immobilized ALP demonstrates enhanced activity.

The presented results yield parameters that are critical for storage and stability preservation of ALP to be used for coating of bone implants. As an example of biological application, we show the potential use of such a system for osteoblast cell growth with enhanced ossification.

Keywords: ALP, hydrogel, polyelectrolyte, encapsulation, enzyme, stability

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Formulation of microemulsions as carriers of compounds of pharmaceutical interest –Biological applications

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Effective delivery of insoluble or slightly soluble chemotherapeutics remains a major issue. In this context, oil-in-water (O/W) microemulsions were developed to encapsulate and deliver lipophilic compounds with potential anticancer activity, namely PLX 4720 and DPS-2. PLX 4720 is a commercially available analogue of Vemurafenib, an anticancer drug against melanoma targeting BRAFV600E oncogenic kinase. DPS-2 is a benzothiophene analogue, designed to inhibit BRAFV600E, which exhibited potent cytotoxicity in a broad range of human cell lines.

Structural characterization of microemulsions was performed by various techniques including Dynamic Light Scattering (DLS), Electron Paramagnetic Resonance Spectrometry (EPR) and Cryogenic Transmission Electron Microscopy (cryo-TEM) [1]. The microemulsions were evaluated biologically, both in vitro and ex vivo. The effective release of a lipophilic encapsulated compound was evaluated via confocal microscopy. The cytotoxic effect of both empty and loaded microemulsions, was examined through cell viability assays and the mechanism of the cell death induced by fluorescence-activated cell sorting (FACS) analysis, comet assay and western Blotting of specific cell death markers. Overall, it was found that the proposed microemulsions are efficient carriers of bioactive compounds in all cell lines tested [2].

The ex vivo approach focused on dermal applications and DPS-2. Porcine ear skin was used as a skin model to evaluate the degree of permeation of DPS-2 through skin and assess its retention. It was found that the encapsulated compound was promptly distributed within full-thickness of stratum corneum (SC) and performed with a relatively high affinity to hair follicles. Thus, the developed O/W microemulsions could contribute to overcoming major problems related to administration through the skin barrier and the low water solubility of lipophilic compounds, in view of the development of anticancer drugs against skin cancers.

Keywords: nanodispersions, chemotherapy, encapsulation, ex vivo permeation, cell viability

Acknowledgements: We acknowledge support of this work by the projects STHENOS and STHENOS-b.

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Soluplus®: Understanding the behaviour of a polymeric solubilizer for drug delivery

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Soluplus® is an amphiphilic poly (N-vinyl caprolactam)-poly (vinyl acetate)-poly (ethylene glycol) from BASF used as a matrix polymer for solid solutions of poorly soluble drugs in oral drug delivery. A good solubilization is required for the optimal adsorption of drugs by the human gastrointestinal tract and, therefore, for a good therapeutic efficacy. [1,2] Nevertheless, poor drug solubility is nowadays one of the main challenges of pharmaceutical industry. A series of in vitro investigations have shown soluplus produces, indeed, a strong enhancement of the adsorption of model drugs. [3,4] However, very little information is known about the properties of this polymer along the oral route of administration which involves important changes in concentration, pH, salinity, and temperature.

The aim of this study is to delve into the behaviour and properties of soluplus aqueous solutions, mainly by static and dynamic light scattering, PGSE-NMR, and SAXS at varying soluplus concentration in the range 0.5 wt% - 20 wt%.

SAXS curves of the samples are accounted for by a core-shell structure of constant size regardless of concentration. According to the analysis of SLS the interactions between aggregates follow a hard spheres prediction plus a further repulsive contribution at high concentrations. However, SAXS and NMR indicate that only a fraction of the total polymer is involved in the formation of the aggregates (40%) (Figure 1). The size of the objects in the other 60% of the sample is around 3-5 nm, which could be compatible with free coils, although this interpretation is hardly compatible with the low CMC of soluplus. The possible coexistence of two classes of aggregates will be discussed.

Keywords: polymeric micelles, drug delivery, interactions, SAXS

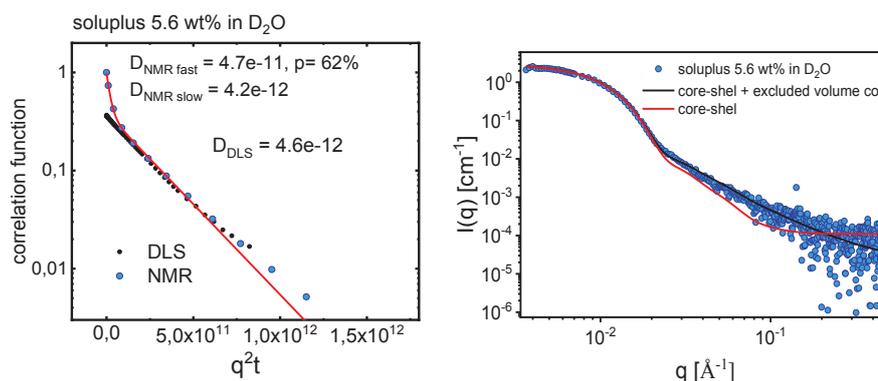


Figure 1. Soluplus solution of 5.6 wt%. Left echo decay from PGSE-NMR. The echo decay is fitted with a two-exponential equation that accounts for two populations of diffusing objects. Right SAXS curve and fits according to core-shell model with and without free coils.

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Characterization of particle sizes during precipitation of API and its impact on the membrane transport

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The oral bioavailability of active pharmaceutical ingredients is dependent on the solubility of the molecules in gastrointestinal tract (GIT). In case of poorly aqueous soluble drugs, it is necessary to find a suitable formulation to increase solubility, which is commonly done by using surfactants or polymers. In this way, there is a potential to reach a drug concentration above its supersaturation limit, resulting in a higher driving force for mass transfer through the intestinal wall. However, when precipitation cannot be avoided it is essential to control the size of formed particles. In this situation, it is important to properly characterize the size of formed particles to predict their dissolution rate and consequently the drug absorption rate.

In this contribution, we present a procedure, how to quantitatively determine the size of precipitated submicron or micron particles of the drug in highly turbid solutions without any dilution using modulated 3D cross correlation dynamic light scattering coupled with the sample goniometer and by optical videomicroscopy [1]. Particle size analysis is combined with the measurement of drug flux through the membrane. It was found, that there is opposite trend of surfactant concentration on the particle size and drug transport with larger particles resulting in higher transport of the drug through the membrane. It was found that this opposite trend is due to higher affinity of the drug with used surfactant. To extend this analysis same experiment was realized also for media containing bile salts, typically present in GIT.

Keywords: Light scattering, Optical microscopy, Particle characterization, Membrane transport, Nonionic surfactant

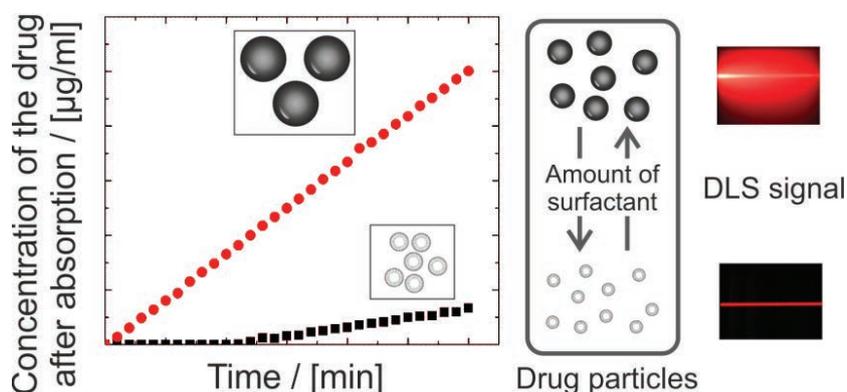


Figure 1. Correlation between size of the particles and its membrane transport.

Acknowledgements: this work was supported by the specific university research – grant No A1_FCHI_2020_005 and Pharmaceutical Applied Research Center (PARC).

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Hydroxyethylated and carbamate-bearing gemini surfactants: an insight into aggregation for the development of biomedical nanocontainers

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The liposomal drug delivery systems are being intensively researched worldwide. Among the methods of liposome modification, application of amphiphilic functions for non-covalent modification is one of the most promising approaches for the development of novel nanomedicines.

In our work, gemini surfactants with hydroxyethyl (1) and carbamate (2) fragments and different spacer lengths were thoroughly investigated from the aggregation standpoint. Methods included spectrofluorimetric analysis (with diphenylhexatriene, prodan and pyrene as probes), NMR self-diffusion technique, dynamic light scattering, dye solubilization, tensiometry. Altogether these techniques allowed us to describe the special properties of surfactants, such as aggregate morphology, sizes, micropolarity.

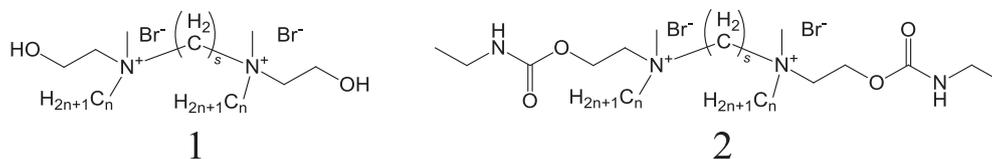


Figure 1. General structures of gemini surfactants

The studied cationic gemini surfactants possess a high solubilizing capacity which makes them good candidates for drug delivery applications. Additionally, complexation of some surfactant species with an oligonucleotide was evaluated for potential nucleic acid transfection applications [1]. Finally, various aspects of surfactant application for liposome modification are discussed, such as morphological influence on vesicles and applicability *in vivo*. Gemini-modified liposomes loaded with pralidoxime chloride made it possible to achieve 27% reactivation of brain acetylcholinesterase, inhibited by organophosphorous poison, suggesting possible use of the formulation for over-the-BBB therapy [2].

Keywords: liposomes, gemini surfactants, non-covalent modification, acetylcholinesterase reactivation.

Acknowledgements: The work was supported by Russian Science Foundation (project 19-73-30012)

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Liquid crystalline nanoparticles: the effect of polymeric stabilizer on internal organization and drug release profile

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Non-lamellar lyotropic liquid crystalline nanoparticles, such as cubosomes, are novel drug delivery nanosystems, formed via the self-assembly process of lipids into water and stabilized by amphiphilic stabilizers, such as polymers [1]. In the present study, poly(ethylene oxide)-block-poly(ϵ -caprolactone) (PEO-b-PCL) block copolymers and poly(2-methyl-2-oxazoline)-grad-poly(2-phenyl-2-oxazoline) (MPOx) gradient copolymers were utilized as stabilizers in liquid crystalline nanoparticles prepared from glyceryl monooleate. For the first time, gradient copolymers are utilised as polymeric stabilizers in liquid crystalline nanoparticles [2].

The physicochemical characteristics of the nanosystems were obtained from light scattering techniques, while their micropolarity and microfluidity from fluorescence spectroscopy. The effect of environmental parameters on the physicochemical behavior was monitored. Their morphology was assessed by cryo-TEM, while their thermal behavior by microcalorimetry. Subsequently, resveratrol was loaded into the nanosystems and *in vitro* release studies were carried out.

Their physicochemical and morphological properties were dependent on the stabilizer chemistry and topology (block/gradient copolymer), and its concentration. Polymeric architecture affected both the morphology and internal organization of the nanostructures, and differentiated also their drug release profile [2].

In conclusion, the proposed copolymers broaden the toolbox of polymeric stabilizers, with polymers of different topologies and chemistries, for the development of liquid crystalline nanoparticles intended for drug delivery applications.

Keywords: lyotropic liquid crystals, cubosomes, poly(2-oxazoline)s, poly(ϵ -caprolactone), cryo-TEM, resveratrol

Acknowledgements: This research is co-financed by Greece and the European Union (European Social Fund - ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Strengthening Human Resources Research Potential via Doctorate Research - 2nd Cycle” (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

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Poloxamer P407 as a promising alternative to PEGylation in lipid nanoparticle formulations

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The aim of this study is the design, development and evaluation of chimeric hydrogenated soya phosphatidylcholine (HSPC) and egg phosphatidylcholine (EggPC) liposomes with incorporated triblock copolymer Poloxamer P407 (P407). The two phospholipids differ on the saturation level and therefore, on their interaction with P407. P407 was the polymer of choice due to its interesting bio- and thermo-behavior [1,2].

Dynamic and electrophoretic light scattering (DLS/ELS) techniques were used for the measurement of the colloidal stability (hydrodynamic diameter, polydispersity index, and ζ -potential) of the prepared nanosystems. Thermo-responsiveness experiments were conducted at 4°C and 25°C, while Fetal Bovine Serum (FBS) protocol was chosen for evaluating the interaction of the chimeric lipid nanoparticles with the serum proteins.

As P407 is a triblock copolymer, we propose two different types of P407 interaction with the lipids, depending on the polymer concentration. The saturated lipid (HSPC) formulations seem to be more resistant to higher polymer concentration in comparison with the unsaturated lipid (EggPC) systems.

The addition of P407 provided promising results concerning systems' storage temperature. Although the majority of non-lyophilized lipid nanoparticles (LNPs), including the novel COVID-19 vaccine platforms, are currently stored at low temperature [3], we observed that the addition of the thermo-responsive P407 provided systems' physicochemical stability at higher temperatures (25°C).

Finally, FBS experiments showed that some of our systems, especially those with higher P407 concentration, appear to have stealth properties.

Concluding, we propose that P407 could be a great alternative to polyethylene glycol (PEGylation) in LNPs, as it not only provides the necessary stealth properties, but also optimizes the storage conditions of non-lyophilized LNPs.

Keywords: Poloxamer P407, liposomes, lipid nanoparticles (LNP), stealth, storage temperature

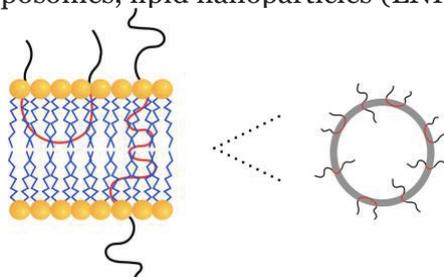


Figure 1. Conformation of the triblock co-polymer Poloxamer P407 in the phospholipid bilayer. P407 can either span the membrane or anchor into the bilayer, projecting the hydrophilic PEO chains in the same side of the membrane.

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Elucidation of the skin care mechanisms of liposomes, focusing on the lamellar structures they form

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Liposomes consist of vesicular phospholipid membranes and are reported to efficiently permeate and moisturize the skin. Because of their utility in skin care, liposomes are formulated as microcapsule preparations for use in cosmetics. However, there have been no detailed analyses of the effects of liposomes for skin care, and especially their mode of action on and inside the stratum corneum. In this study, we further elucidated the mechanism of action of liposomes on the skin by investigating the microstructures formed by liposomes on and inside the stratum corneum using X-ray diffraction measurements and transmission electron microscopy observations.

We first focused on the occlusive function of liposomes by analyzing the structure formed on the skin following the application of liposomes. We found that liposomes formed a lamellar structure on the surface of the stratum corneum. Furthermore, cholesterol, which together with phospholipids is a major component of liposomes, aids the occlusive effect. In addition, lamellar structures derived from the applied liposomes were observed in the intercellular lipid layer in the stratum corneum.

Our findings revealed that the conformation of the lamellar structures derived from liposomes on and inside the stratum corneum is key to the mechanism of action of liposomes and will provide hints for the development of further effective skin care applications for liposomes.

Keywords: liposome, skin, lamellar structure, X-ray diffraction analysis

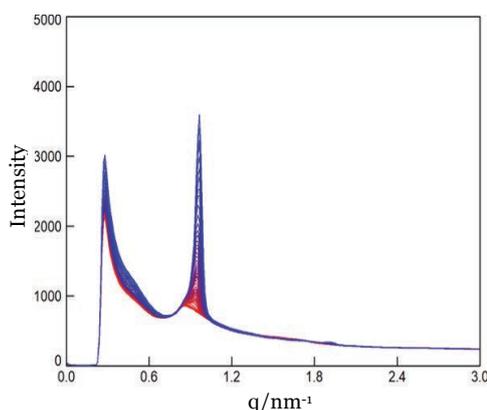


Figure 1. Results of X-ray dynamic measurement of a liposome preparation applied on the stratum corneum. The first measurements are indicated by red lines and the final measurements by blue lines. Measurements were made once a minute up to 50 times.

Acknowledgements: We would like to thank Dr. Hatta (Nagoya Industrial Science Research Institute) for helpful guidance and discussion. The X-ray diffraction experiments were performed using the BL19B2 and BL40B2 beamlines (proposal No. 2016A1754 and 2018A1388) at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI), and at the second hutch of SPring-8 BLO3XU (proposal No. 2018B7252 and 2018B7281) constructed by the Consortium of Advanced Softmaterial Beamline (FSBL). X-ray diffraction experiments were also conducted using the BL8S3 beamline at the Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation. This work was performed under the approval of the Photon Factory Program Advisory Committee (proposal No. 2017G599 and 2019G059).

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The enzyme-like catalytic activity of cerium oxide nanoparticles: Dependency on Ce^{3+} surface area concentration and coating effects

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Cerium oxide nanoparticles have been shown to mimic oxidoreductases by catalyzing the decomposition of organic substrates and reactive oxygen species such as superoxide radical and hydrogen peroxide, harmful molecules produced in oxidative stress associated diseases. In a first part, we examine the superoxide dismutase (SOD) and catalase (CAT) mimetic catalytic activities of nanoceria and demonstrate the existence of generic behaviors. For particles of size 4.5, 7.8, 23 and 28 nm, the SOD and CAT catalytic activities exhibit the characteristic shape of a Langmuir isotherm as a function of cerium concentration [1]. Results show that the catalytic effects are enhanced for smaller particles and for the particles with the largest Ce^{3+} fraction. The SOD-like activity obtained from the different samples is found to superimpose on a single master curve using *the Ce^{3+} surface area concentration* as a new variable. For the CAT assays the adsorption of H_2O_2 molecules at the particle surface modulates the efficacy of the decomposition process and must be taken into account [1]. In a second part, we study the influence of polymer coatings [2] on the enzyme-like catalytic activity [3,4]. PEGylated nanoceria were prepared by assembly of 7.8 nm cerium oxide cores with phosphonic acid PEG copolymers, which were shown to provide outstanding colloidal stability in biological media (Figure 1). The superoxide dismutase-, catalase-, peroxidase- and oxidase-like catalytic activities of the PEGylated nanoceria were systematically studied. It is shown that the polymer coatings do not affect the superoxide dismutase-like, impair the catalase-like and oxidase-like by 25% and surprisingly improves peroxidase-like catalytic activities of nanoceria [3]. The proposed scalings are predictive and allow determining oxydo-reductase catalytic properties of cerium oxide with or without coating, solely from physico-chemical features.

Keywords: Cerium oxide; Polymer coating; Phosphonic acid; Nanozyme

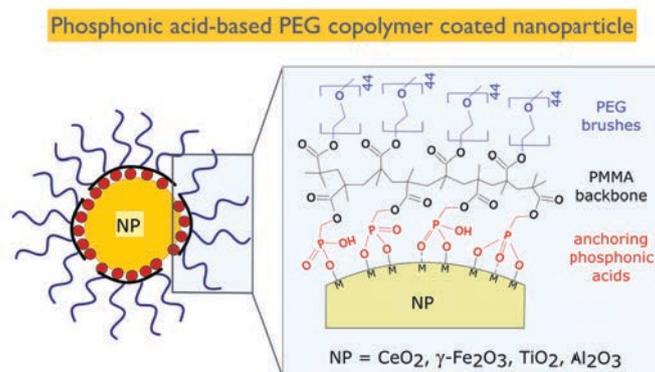


Figure 1. Schematic representation of a nanoparticle coated with phosphonic acid based poly(ethylene glycol) polymers. Inset: Possible mono-, bi- or tridentate anchoring modes for phosphonic acid at metal oxide surfaces.

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Functionalization, targeting and magnetic hyperthermia of poly(ethylene imine)-functionalized magnetite nanoparticles

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The many routes through which cancer progresses and affects different organs makes it necessary to tackle different approaches towards the treatment of this disease. In many cases, a combination of surgical resection of the tumor with radiation therapy, chemotherapy and/or immunotherapy are applied. But even in such cases there is no guarantee of success, and additional therapies are demanded. In particular, the long-time known positive effect of thermal therapy (hyperthermia) on cancer has gained attention. The efficiency of the thermal treatment is dependent on both the magnitude and the extent of the temperature increment [1, 2]. The range 41-48 °C is the so-called relevant temperature range suitable for hyperthermia treatments.

In this work, we report the synthesis and characterisation of Fe₃O₄ nanoparticles (MNPs) coated with the cationic polyelectrolyte PEI (poly(ethylene imine)) of different molecular weights, their covalent functionalisation with folic acid (FA), and the analysis of their viability and cytotoxicity, when exposed to an alternating magnetic field (AMF).

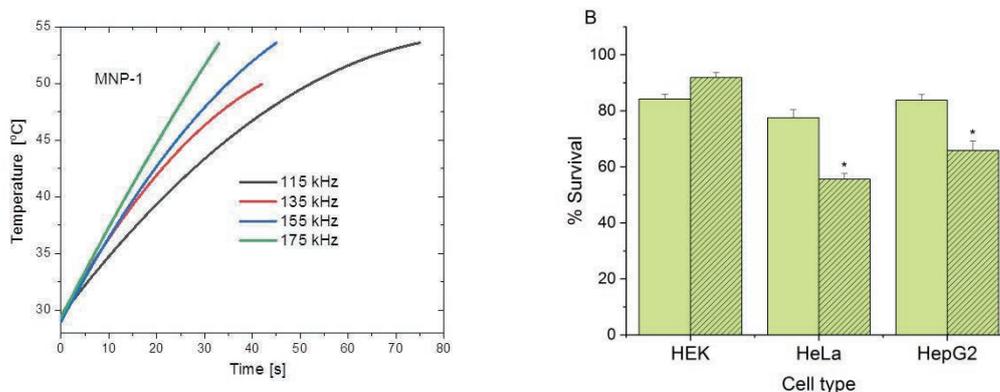


Figure 1. (left) Time dependence of the temperature of magnetic nanoparticles under 12 kA/m magnetic field at the frequencies indicated; (right) cytotoxicity assay of FA-coated MNPs against the low-FR expressing HEK cells and the high-FR expressing FR HeLa and HepG2 cells with (full color) and without (patterned color) magnetic field.

The results show (Fig. 1) that these particles provide excellent performance in magnetic hyperthermia treatment in moderate magnetic fields, and furthermore they show low cytotoxicity, features which make them suitable as a coadjuvant in cancer treatment through hyperthermia.

Keywords: magnetic field hyperthermia, cell viability, folic acid, poly(ethylene-imine)

Acknowledgements: Financial support by Junta de Andalucía, Spain (FEDER Grants No. A1-FQM-341-UGR18, C-FQM-497-UGR18) is gratefully acknowledged.

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Photoswitchable and pH-gated catanionic vesicles for the controlled delivery of a model anticancer drug

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Stimuli-responsive delivery systems provide activation-mediated drug release and hence potential increase in therapeutic efficacy. The stimuli can be either physiological, like pH or redox changes, or exogenous, such as light irradiation [1,2]. Among the myriad nanocarriers studied, mixed cationic/anionic surfactant vesicles offer interesting features, such as facile assembly, long-term stability and composition tunability. [3] Herein, we present work on the design and development of catanionic vesicles sensitive to UV irradiation and acidification, and on their ability to effectively entrap and release the well-known anticancer drug doxorubicin (DOX) (Figure 1). The vesicles are composed of an anionic amphiphile based on a 2-hydroxychalcone as the photosensitive unit, which presents an intricate chemical network [4,5], and a dicationic gemini surfactant. Upon irradiation in acidic media, a vesicle-to-bilayer transition is triggered and a 4-fold increase in release of incorporated DOX is observed compared to the non-irradiated system. The developed vesicles are a proof-of concept for a smart colloidal nanocarrier where the pH can be envisioned as a “lock mechanism”, and light as the trigger. The combination of stimuli works as an “AND” logic gate, conferring higher sensitivity to the drug release.

Keywords: Vesicles; catanionic systems; photosensitivity; drug encapsulation; drug delivery

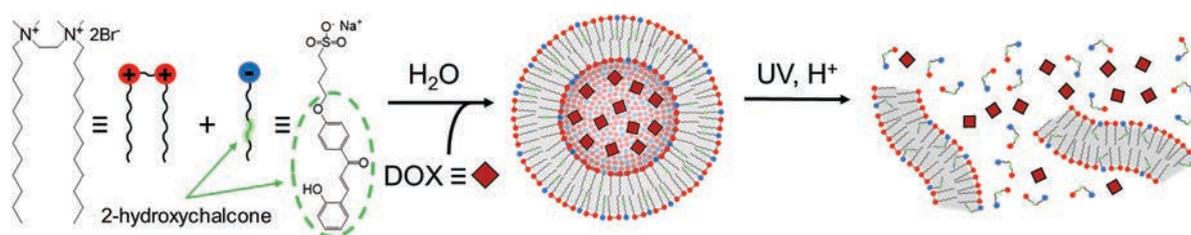


Figure 1. Catanionic vesicle formation and co-encapsulation of DOX with its consequent release via stimuli application.

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EP5.41

Adsorption of pharmaceutical compound from wastewaters onto activated carbon produced from biomass

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The aim of the present study is the synthesis of activated carbon (AC) from different agricultural wastes such as tea and plane tree leaves in order to use them for the removal of pramipexole dihydrochloride (PRM) from aqueous solutions. Two different carbonization and synthetic activation protocols were followed, with the herein-proposed ultrasound-assisted two-step protocol leading to better-performing carbon, especially for the tea-leaf-derived material (TEA(char)-AC). Physicochemical characterizations were performed by Fourier-transform infrared spectroscopy (FTIR), N₂ physisorption, and scanning electron microscopy (SEM). The adsorption evaluation was done by studying the interfacial phenomena between the materials and the molecule (pramipexole compound). TEA(char)-AC presented the highest surface area (1151 m²/g) and volume of micro and small mesopores. Maximum capacity was found at 112 mg/g for TEA(char)-AC at an optimum pH equal to 3, with the Langmuir isotherm model presenting a better fitting. The removal efficiency of TEA(char)-AC is higher than other biomass-derived carbons and closer to benchmark commercial carbons.

Keywords: activated carbons; adsorption; pharmaceuticals; agricultural wastes

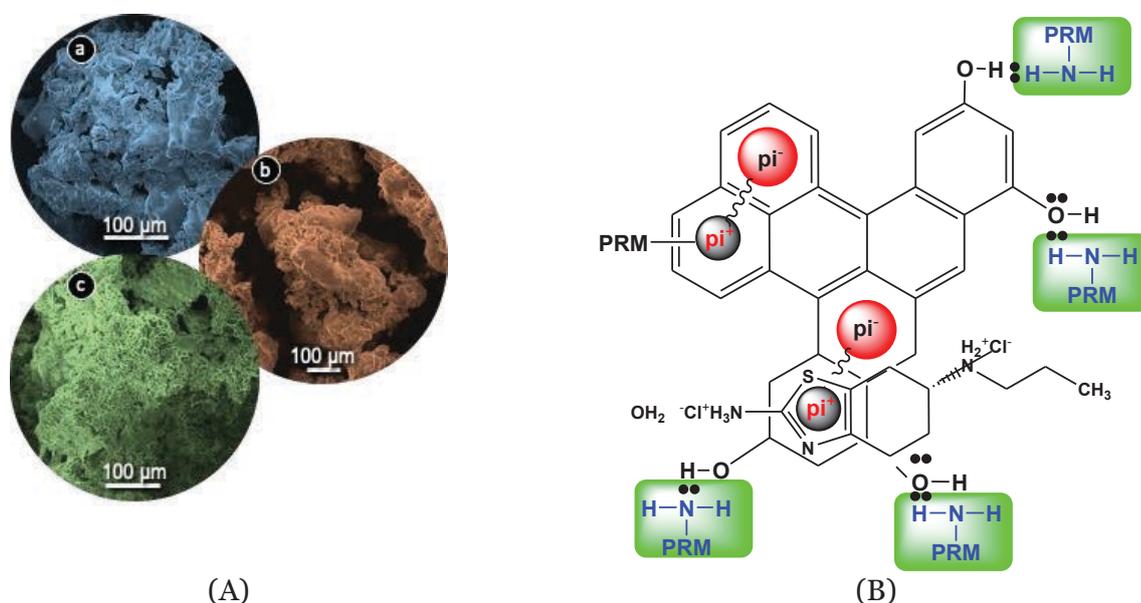


Figure 1. (a) SEM images of TEA(char)-AC (a), PL(char)-AC (b), and TEA-AC (c); (B) Possible interactions between PRM molecules and ACs.

Acknowledgements: This research was funded by the Greek Ministry of Development and Investments (General Secretariat for Research and Technology) through the research project “Research-Create-Innovate”, with the topic “Development of an integration methodology for the treatment of micropollutants in wastewaters and leachates coupling adsorption, advanced oxidation processes and membrane technology” (Grant no: T2EDK-04066).

EP5.42

Biophysical studies of Glycogen Phosphorylase in complex with the cationic polyelectrolyte QPDMAEMA

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Polyelectrolytes in the presence of proteins may form a great variety of nanostructures with different stoichiometries, architectures and phase states. Guided by non-covalent interactions (electrostatic, hydrophobic and Van der Waals interactions), this kind of complexes holds significant biotechnological potential while numerous interdisciplinary methodologies are employed for their analysis and interpretation. Their applications range from food science, biomaterials and biosensors to novel approaches related to drug delivery, enzyme immobilization, protein purification and stabilization [1].

Glycogen Phosphorylase (GP) is an allosteric enzyme with a pivotal role in glycogen metabolism controlling the rate of its phosphorolysis and consequently the circulating glucose levels in the blood stream. Therefore, GP (Fig. 1a) has been utilized as a molecular target for the structure-based design of potential antidiabetics [2]. Motivated by the physicochemical and biophysical properties of the ionic strength-responsive cationic quaternized poly 2-(dimethylamino) ethyl methacrylate (QPDMAEMA) (Fig. 1b), we used it to create electrostatic complexes with GP [3].

Our aim was to utilize GP and QPDMAEMA to carry out a complete physicochemical characterization (Fig. 1c) of the newly formed nanostructures, investigating both the GP interaction with QPDMAEMA and the morphology, properties and potential for applications. GP–QPDMAEMA complexes were successfully formed in the presence of two buffers with different composition and ionic strength. The formed nanostructures do not affect the secondary conformation of GP while their size and composition changes by changing buffer composition or polymers' concentration.

Keywords: Glycogen Phosphorylase (GP), cationic polyelectrolytes, QPDMAEMA, Polymer analysis and characterization techniques

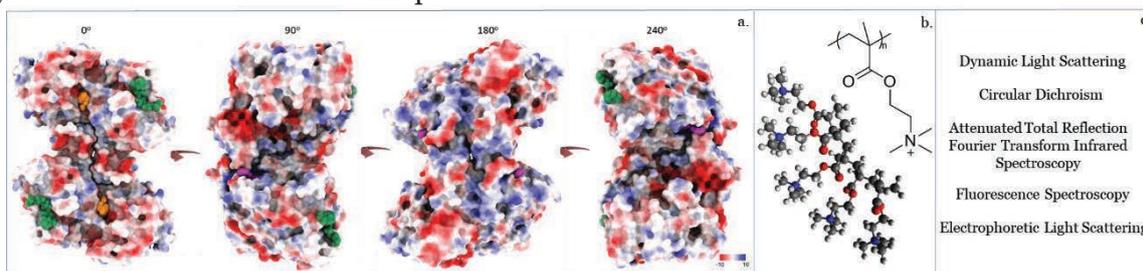


Figure 1. GP coulombic surface coloring (a), QPDMAEMA molecular representation (b), methods for biophysical behavior characterization of GP-QPDMAEMA complexes (c).

Acknowledgements: We acknowledge support of this work by the project “INSPIRED” (MIS 5002550), under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020). We especially acknowledge Dr Angeliki Panagiotopoulou for her assistance in taking the CD measurements using the facilities at NCSR-“Demokritos”, which are part of the national research infrastructure Instruct-EL/INSPIRED.

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EP6.1

Foam-Based Cleaning of Historical Surfaces

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The historical surfaces of artistic and cultural assets are often soiled as a result of long-term exposure to environmental influences. Cleaning these objects is a great challenge as each surface requires a tailor-made cleaning method to remove dirt without damaging the artwork. Our goal is to develop new, innovative foam-based cleaning methods. We were able to reveal that foams have great potential as suitable cleaning agents for several reasons. Firstly, the amount of detergent can be reduced by up to 90%. Secondly, foams allow covering hard-to-access surface shapes and last but not least they generate additional physical cleaning mechanisms, namely imbibition and wiping [1]. These mechanisms can be optimized when working with foams with the “right instability”: the foams need to be sufficiently stable to maintain imbibition, while they need to be sufficiently unstable to ensure an optimal “bubble-wipe”[1]. The combination of imbibition and wiping is so efficient that it is sufficient to simply let the foam sit on the surface for a while before removing it by vacuuming. No additional mechanical action is needed: Less is More! [1] Having shown this fundamental principle on model surfaces, we are now testing our cleaning foams on real historical objects that are difficult to clean. Our goal is to clean the historic carriages of kings and emperors of past centuries in the “Marstallmuseum” in Nymphenburg Palace in cooperation with the “Bavarian Administration of State-Owned Palaces, Gardens and Lakes”. First cleaning tests with foams on historical, gold-plated surfaces showed a successful cleaning result (Figure 1). Using foams for cleaning, one can also clean rough and vertical surfaces without additional mechanics.

Keywords: Cleaning with Foams, Imbibition, Wiping, Historical Surfaces



Figure 1. Historic wooden carved and gold-plated shell on the drawbar of the Renaissance sleigh of King Ludwig II of Bavaria (left) before cleaning, (centre) during cleaning with foam and (right) after cleaning [2].

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Cleaning corroded bronze with pHEMA/PAA and pHEMA/PVP SIPNs: effect of pH and chelators

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Even though bronze artifacts constitute a fundamental portion of cultural heritage, effective methodologies for the removal of corrosion layers, such as those produced by the "bronze disease" are currently missing [1].

We propose hydrogels of poly(2-hydroxyethyl methacrylate) (pHEMA) semi-interpenetrated (SIPN) with polyacrylic acid (PAA) or polyvinylpyrrolidone (PVP), loaded with tetraethylenepentamine (TEPA), for the removal of corrosion products. SIPNs can be applied and simply removed in one piece without mechanical stress or removal of original components from the treated surface. These features are particularly advantageous on corroded surfaces that are usually brittle and mechanically weak, and where the removal or peeling of surface layers (e.g. using film-forming polymeric dispersions [2]) might be risky.

Alkaline pH causes the ionization of carboxyl groups in PAA increasing the swelling and the porosity of the pHEMA/PAA SIPNs. In pHEMA/PVP case, the increase of pH leads to the co-presence of enol and enolate forms of VP, along with significant changes in the macroporosity and a decrease in the mesh size characteristic of the hydrogels. 2D FTIR imaging indicates that TEPA interacts with carboxylates in PAA, and with polar or charged CO groups in PVP. The kinetics of Cu(II) ions uptake by the SIPNs showed that the ion-matrix interaction is stronger for pHEMA/PAA.

Upon application of the TEPA-loaded gels onto corroded bronze, copper oxychlorides dissolve and migrate inside the gel matrix. Cu(II) ions probably form ternary complexes with TEPA and carboxylates in PAA or carbonyl group in PVP. The application of the SIPNs on aged artifacts allowed the gradual and effective removal of oxychlorides, leaving unaltered patinas of cuprite that are needed to passivate bronze against corrosion. Loading the SIPNs with TEPA provides a much higher cleaning efficacy than traditional EDTA, opening new perspectives in the restoration of bronze works of art.

Keywords: hydrogels, pHEMA SIPNs, cleaning, patina, corroded bronze

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EP6.3

Micro-sized cleaning gels as innovative tool for the preservation of paper materials

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Since most of the cultural heritage is preserved on paper material, it's essential to develop appropriate conservation strategies. Degraded paper artworks necessitate restoration treatments to preserve their important historical value and to slow down irreversible degradation processes [1].

Wet cleaning (common restoration procedure) can be efficiently ensured by opportune hydrogels [2-4]. Among those reported in literature, rigid hydrogels (macrogel) based on the deacylated polysaccharide Gellan gum and calcium acetate (Gg), as effective paper cleaning agent, has been widely characterized. These macrogels, indeed, are able to gradually release water and also to absorb water-soluble degradation products present on the paper. However, due to their rigidity hydrogels may not clean efficiently, due to the lack of contact between them and paper materials that have an intrinsic roughness. Knowing in depth its behavior, characteristics and its effects on paper material, the use of Gellan gum based microgel particles, as innovative paper cleaning agent to improve the efficiency of current cleaning procedures, was proposed for the first time.

Compared to established protocols (hydrogels), these colloidal particles, having reduced size can penetrate inside paper's pores and carry out their cleaning action in a shorter amount of time (few minutes). Moreover, experimental results obtained show a higher cleaning efficiency of proposed Gellan microgels (respect to Gellan gum hydrogel and water bath), on two different kind of paper materials, that differ in period of manufacture and constituent raw materials. In detail, non invasive and micro-invasive techniques like SEM, FTIR-ATR and UV-Vis reflectance spectroscopy and HPLC demonstrate that they are able to remove degradation products of cellulose performing an overall whitening action on the paper material, without altering the mechanical properties of samples.

Keywords: Gellan gum, microgels, paper cleaning

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EP7.1

Soft-core colloidal particles with competing interactions near confining surfaces: computer simulations and field theory approach*T. Patsahan¹, I. Kravtsiv¹, M. Holovko¹, and D. di Caprio²**¹ Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine**² Institute of Research of Chimie Paris, CNRS - Chimie ParisTech, 11, rue P. et M. Curie, 75005 Paris, France**Presenting author e-mail: tarpa@icmp.lviv.ua*

Models of colloids with competing interactions, which are characterized by short-range attraction and long-range repulsion (the so-called SALR pair potential) [1], have been the focus of extensive research due to their ability to describe spontaneous emergence in a homogeneous fluid of mesostructured phases of different morphologies [2]. A popular SALR model is that of a two-Yukawa hard sphere fluid. Such a potential provides a reasonable description of dispersions of charged colloidal particles in the presence of a depletant, and it is possible to tune its interaction parameters by varying physical conditions [3]. In contrast, in this work we propose to study colloids interacting with a three-Yukawa potential (3Y model) of the SALR form. Such a model with a soft core takes into account the possibility of partial overlap between two particles. Examples of respective systems include, but are not limited to, protein molecules, soft colloids, polymer grafted nanoparticles, star and branched polymers, microgels. A soft-core potential also has the advantage of making it possible to perform analytical calculations.

We report a study of the 3Y SALR model for soft-core colloids in the bulk and near a confining flat surface using both simulation and theoretical approaches. Using computer simulations, we have examined the system under consideration in a wide range of density and temperature values. We show that at low temperatures various well-known mesostructures, such as lamellar and gyroidal phases, hexagonally packed cylindrical phases, cubically ordered and disordered clusters are formed. In the case of the system near confining surfaces or between two walls, the self-assembly effects become more pronounced and may be observed at temperatures that are noticeably higher than in the bulk.

To describe structural properties of a 3Y SALR colloids at high temperatures, a classical field theory [4,5] is employed. Explicit analytical expressions for the pair correlation function and the density profile are derived. These expressions contain only parameters of the pair potential and the thermodynamic state, thus providing a link between microscopic parameters of the system and respective measurable quantities. Thermodynamic conditions for the applicability of the theoretical approximations employed are discussed. The results found are tested against computer simulations data.

Keywords: soft-core colloids, competing interaction, confinement

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EP7.2

The cell model of ion-exchange membrane: capillary-osmotic coefficient

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The capillary-osmotic coefficient of an ion-exchange membrane is calculated based on the cell model of a charged membrane previously proposed by the author [1]. Various special cases of the obtained exact analytical formulas, including the binary symmetric electrolyte and the ideally selective membrane, are investigated.

In [1], a cell model of an ion-exchange membrane was created, the problem of finding kinetic coefficients was formulated and solved in a general form, and an exact algebraic formula for the hydrodynamic permeability L_{11} of a charged membrane was obtained. In [2], the electroosmotic permeability L_{12} and the specific electrical conductivity L_{22} of the cation-exchange membrane were determined. And in [3], the diffusion permeability L_{33} and the electrodiffusion coefficient L_{23} were determined. In [4, 5], the cell model was successfully verified on the experimental data obtained for the cast perfluorinated membrane MF-4SC and its modifications with halloysite nanotubes, functionalized by platinum and iron nanoparticles, in aqueous HCl solutions, as well as for the extrusion membrane MF-4SC in various 1:1 electrolyte solutions (HCl, NaCl, KCl, LiCl, CsCl).

The calculated electrokinetic coefficients L_{ij} applying the cell method can be successfully used to characterize new ion-exchange materials.

Keywords: ion-exchange membrane, the cell model, electrokinetic coefficients, capillary osmosis.

Acknowledgements: This work was supported by the Russian Foundation for Basic Research (grant # 20-08-00661).

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EP7.3

Broadening of analyte bands in electroosmotic flow through microchannels with different zeta potentials of walls. Pre-asymptotic regimes

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The problem of broadening of analyte bands in micro- and nanoscale channels is central for microfluidic devices that are used for analytical and bio-analytical purposes. In rather long (compared with their thickness) micro- and nanochannels the band broadening is determined by a hydrodynamic dispersion, which causes much faster expansion than due to purely molecular diffusion in the solution. The present study is focused on the transient modes of analyte band behavior in electroosmotic flow through slit channels, whose walls have different zeta potentials. The problem of convective diffusion of analyte in a long flat channel was solved numerically, and the results were compared with known analytical solutions for limiting cases. The simulations demonstrated that, during the transition times before the Taylor-Aris asymptotic regime is established, the variance non-linearly depends on the band displacement. Simultaneously, the solute distributions within the channel cross-sections experience substantial transformations during the pre-asymptotic regime: the initially uniform distributions become strongly non-uniform with well expressed maximums or minimums that decrease with time. It is shown that, in transient modes before the establishment of a quasi-stationary concentration distribution, an increase in the Péclet number can provide a decrease in the variance and the plate height when the band is shifted by the same distance.

Keywords: electroosmotic flow, hydrodynamic dispersion, broadening of analyte bands, slit channels, transient modes

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Performance of different molecular models in characterizing the structure and dynamics of ethylammonium nitrate

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From a molecular modelling perspective, ionic liquids (ILs) are a much more complex than “classical” liquids because their ions have more complex chemical structures, stronger Coulomb forces are present in the system, many ILs show extensive H-bonding, etc. The selection of an appropriate force-field model that provides valid results on the structure and dynamics in molecular simulation is a challenging and crucial task, which, unfortunately, is not always achieved with the currently available molecular models. Many molecular force-field models are optimized to reproduce the correct thermodynamic properties, which does not necessarily mean that other properties of the system are also well described by the model in question. We are particularly interested in the structure and the dynamical properties of IL systems. Therefore, we checked the performance of some established molecular force-field models in the case of ethylammonium nitrate (EAN). We used the ‘complemented-system approach’ method [1] to calculate the small- and wide- angle X-ray scattering (SWAXS) intensities and compared them directly with the experimental SWAXS data. We also compared the transport properties such as self-diffusion coefficients, conductivity and ionicity of the modeled molecules and compared them with the experimental literature data. The methodology used in this study has already proven to be beneficial and informative for many simple liquid systems [2-3].

Keywords: SAXS, Molecular Dynamics, Ionic Liquids, Structure, Transport properties

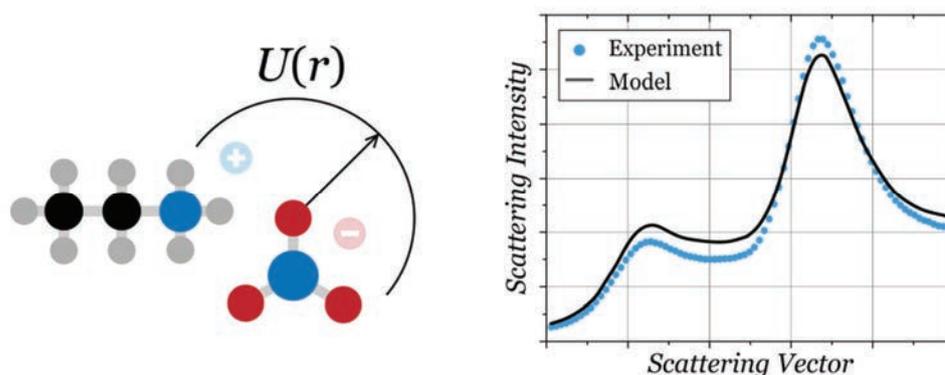


Figure 1. Schematic representation of EAN molecular model and SWAXS data.

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Ion-specific peaks in electrode capacitance and electrode energy determined by ionic steric interactions

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When a conventional nonlinear Poisson-Boltzmann description of electrolytes is applied to electrochemical systems, it predicts an electrode capacitance that increases indefinitely as potential difference is increased and which is indifferent to the specific identity of ions forming the electrolyte. But experimentally a maximum in capacitance is measured [1], and the measured response depends on the specific electrolyte used. The phenomenon arises due to the formation of an ionic steric layer at the electrode interface with an ionic concentration cap driven by steric interactions. The formation of such a steric layer has been attributed as an indirect consequence of solvent entropy [2]. We show that it may be alternatively be derived from a direct steric interaction that contributes to the chemical potential of each ion, independently from the solvent. We interpret the steric effect as a kind of representation of ion-ion correlations in the framework of mean-field theory, which otherwise neglects correlations. The effect is ion-specific, depending on the size of the counterion, with capacitance weakening as ion size increases (Figure 1). We show that the steric interaction provides a contribution to the total free energy of a supercapacitor which at large voltages ($>0.2V$) becomes comparable to the electrostatic free energy. Consequently, the stored energy of a supercapacitor cannot be described solely by the electrostatic energy nor by the conventional formula $\frac{1}{2}CV^2$.

Keywords: capacitance, steric interaction, specific ion effect, energy storage

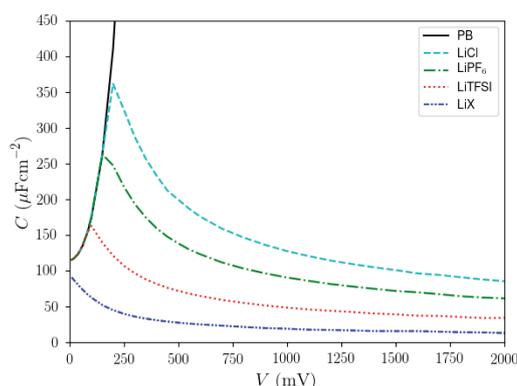


Figure 1. Calculated capacitance as a function of potential difference for supercapacitors with 1.2M electrolyte, showing the effect of counterion size

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EP7.6

Revealing the origin of the specificity of counterion binding to adsorption monolayers of anionic surfactants

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The studied anionic surfactants linear alkyl benzene sulfonate (LAS) and sodium lauryl ether sulfate (SLES) are widely used key ingredients in many home and personal care products. These two surfactants are known to react very differently with multivalent counter-ions, including Ca^{2+} . This is explained by a stronger interaction of the calcium cation with the LAS molecules, when compared to SLES. The molecular origin of this difference in the interactions remains unclear. In the current study, we conduct classical atomistic molecular dynamics simulations to compare the ion interactions with the adsorption layers of these two surfactants, formed at the vacuum-water interface. Trajectories of 150 ns are generated to characterize the adsorption layer structure and the binding of Na^+ and Ca^{2+} ions. We found that both surfactants behave similarly in the presence of Na^+ ions. However, when Ca^{2+} is added, Na^+ ions are completely displaced from the surface with adsorbed LAS molecules, while this displacement occurs only partially for SLES. The simulations show that the preference of Ca^{2+} to the LAS molecules is due to a strong specific attraction with the sulfonate head-group, beside the electrostatic one. This specific attraction involves significant reduction of the hydration shells of the interacting calcium cation and sulfonate group, which couple directly and form surface clusters of LAS molecules, coordinated around adsorbed Ca^{2+} ions. In contrast, SLES molecules do not exhibit such specific interaction, because the hydration shell around the sulfate anion is more stable, due to the extra oxygen atom in the sulfate group, thus precluding substantial dehydration and direct coupling with any of the cations studied.

Keywords: Anionic surfactants, atomistic molecular dynamics, adsorption monolayers, surfactant-counterion binding.

Acknowledgements: Fatmegyul Mustan acknowledges the financial support from the program “Young scientists and Postdoctoral candidates” of the Bulgarian Ministry of Education and Science, MCD No. 577/17.08.2018. Part of this work was supported by computational time granted from the Greek Research & Technology Network (GRNET) on the National HPC facility ARIS under project “VI-SEEM”, grant agreement no. 675121, application Surf_prop.

Electrical origin of the geometrical factor in Helmholtz-Smoluchowsky equation: Implications in the zeta potentia

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One of the ways to determine the zeta potential of large surfaces is through potential-current measurements using electrokinetic cells with parallel surfaces [1-3]. In this type of experiments, the dimensions of the channels: length L and cross-section S , are necessary to obtain the zeta potential from the Helmholtz-Smoluchowsky equation and are used to obtain other parameters such as the porosity of the material [4]. However, the value of the zeta potential obtained should not be a function of the dimensions of the channels, but only of the surface to be electrically characterized and the electrolyte in which it is immersed.

This work shows that the zeta potential of a large surface taken as a model is greatly affected by the value of the L/S factor when this is calculated with the data belonging to the geometry of the channels (changes that can be of the order of 80%). However, when this factor is calculated taking into account the electrical characteristics of the channel, i.e. based on the resistance and conductivity of the cell, the values of the zeta potential are similar regardless of the electrokinetic channel of the measuring cell.

3D printing has allowed us to work with the same material where we have customized the electrokinetic channels under study by modifying the length, cross-section, and number of channels. The results of this investigation may explain why different values of the zeta potential for the same material are found in the literature. In addition, authors propose a way of obtaining the zeta potential with the lowest deviation by working with an optimum conductivity zone of the electrolyte used.

Keywords: Zeta potential, Surface characterization, Geometric factor, 3D printing

Acknowledgements: The authors gratefully acknowledge financial support from “Ministerio de Economía y Competitividad” (PCIN-2016-146), project RTI2018-096862-B-I00, supported by FEDER (Fondo Europeo de Desarrollo Regional “Una Manera de hacer Europa”), Ministerio de Ciencia e Innovación del Gobierno de España, Agencia Española de Investigación and, “Junta de Extremadura-FEDER: European Regional Development Fund” (IB16117, TE-0033-19 and GR18153).

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EP7.9

Rationalization of fragrance release from micellar systems at molecular level using COSMO_{mic}

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Fragrances are a major component of cosmetic, home care, and personal care products. However, its oily character does not favor its compatibility with water-based products. Surfactants have been added to formulations as cleansing compounds but also as solubilizing agents. Indeed, the aggregation of surfactants in micelles forms hydrophobic areas which are suitable for solubilizing fragrance. The surfactant/fragrance interactions alter inevitably the release of fragrance from the product.[1] Nevertheless, it has been shown that modifying the polarity of the micellar system allows controlling the fragrance release but no explanation at a molecular level has been proposed so far.[2]

For this reason, a comparison between two common anionic surfactants used in detergency has been investigated. Sodium dodecyl sulphate (SDS) and sodium lauryl ether sulphate (SLES) have close molecular structure but show different fragrance release by headspace chromatography analysis. To explain such behavior, NMR DOSY experiments has been made to measure the partition coefficient of fragrance between the micelle and the bulk. The latter has been correlated at a molecular level using a new modelling software COSMOmic for anisotropic system as micelles and membranes.[3] Based on quantum chemistry and statistical thermodynamic, the positioning of the fragrance in micelle can be predicted. Thus, a modification of the solubilizing site within the micelle was proposed to explain the different fragrance release.

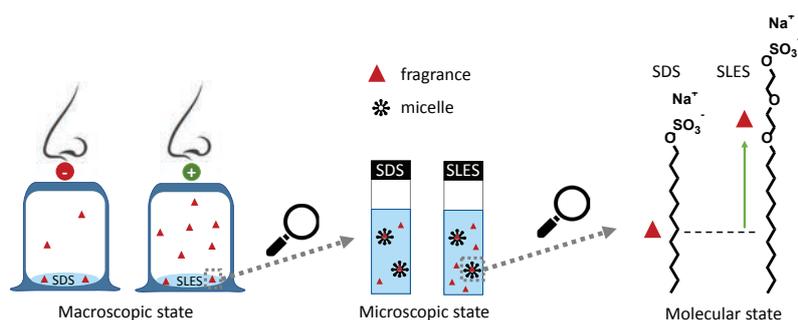


Figure 1: Schematic explanation of the fragrance release between SDS vs. SLES

Keywords: Fragrance, Surfactant, Modelling, Solubilization, Headspace

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Effect of intermolecular van der Waals interactions on local dielectric response in nanosystems

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Basing on the recently developed approach [1] for the calculation of local nanoscopic electric susceptibility and dielectric permittivity tensors we have studied alteration of dielectric response in nanosized systems. This approach self-consistently considers many-body interactions in the framework of Coupled Dipole Method and allows one to analyse how the surface forces originated due to spatial confinement cause boundary layer formation in 2D- and 1D-periodic structures (thin films and nanowhiskers) as well as in nanoparticles.

It was shown that the deviation from bulk properties and dielectric anisotropy arising on the surface may penetrate deep inside the body. Thus, even at the center of relatively big non-polar nanodroplet, an interplay of confinement-induced dispersion forces will cause a notable variation of dielectric response with the droplet size (Figure 1). For nanowhiskers, the same effect causes the formation of “tails” with anisotropic properties near the ends of nanowhisiker (Figure 2). Finally, the analysis of thin film boundary layers formation allowed to explain deviation of dependence of film excess energy on it’s thickness from the macroscopically predicted law.

Keywords: Coupled dipoles method; nanoparticles; boundary layers; dielectric response; permittivity anisotropy.

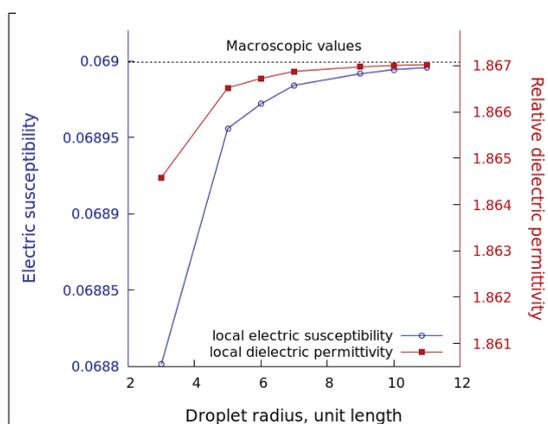


Figure 1. Dependences of the local nanoscopic electric susceptibility (open circles, left axis) and relative dielectric permittivity (filled boxes, right axis) at the center of hexane drop with different radii.

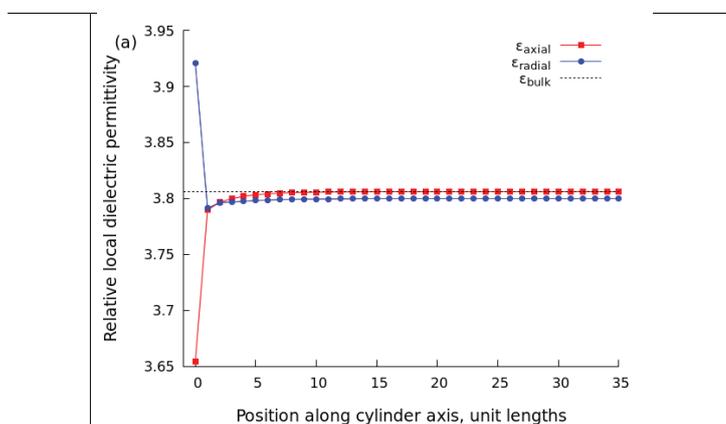


Figure 2. Dependences of the components of the relative local nanoscopic dielectric permittivity tensor at the center spot of the nanowhisiker with radius of 4 and length of 80 unit lengths on the distance from the edge.

Acknowledgements: The work was supported by the Ministry of Science and Higher Education of the Russian Federation.

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Aggregation kinetics and photodynamics of photocontrollable surfactant AzoTMA: a molecular dynamics study

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Photocontrollable surfactants are attractive molecules for their possibility of inducing self-assembly and disassembly upon light irradiation. Potential applications range from industry in for example the modulation of flow properties and triggered gelation to pharmacy in the encapsulation and controlled release of drugs. In this study we investigated the aggregation kinetics of the photocontrollable azobenzene-containing surfactant, abbreviated AzoTMA, in its trans state and further morphological changes that occur in the micelle upon light irradiation using all-atom molecular dynamics. The surfactant displays a fast initial aggregation into small pre-micellar clusters from an initial random distribution in solution, but further aggregation is then slow due to the high energy barrier for fusion of the small clusters. The energy barriers for fusion of micelles and exchange of single surfactants was investigated using umbrella sampling and direct comparison of simulated micelles with experimental small angle X-ray scattering data [1] revealed the average aggregation number for an equilibrated trans-AzoTMA micelle. The energy barriers for fusion were found to be much too high for a fusion event to occur on the timescale of an all-atom simulation, even for micelles smaller than 10 % of the equilibrium aggregation number.

The trans-to-cis isomerization was emulated by temporarily modifying the torsion potential to approximate the excited state energy. Different quantum yields were used on micelles of varying aggregation number. Fission of micelles is found to occur only with high quantum yields for larger micelles. Direct comparison with experimental SAXS data reveal that the required high quantum yields for micelle fission are beyond experimental limits. Instead, micelle dissolution upon UV-irradiation in water, evidenced by an increase in the CMC, is likely a result of slow expulsion of single surfactants from the aggregates, which retain their micellar structure avoiding large morphological transitions.

Keywords: photocontrollable, photoswitch, surfactant, kinetics, molecular dynamics

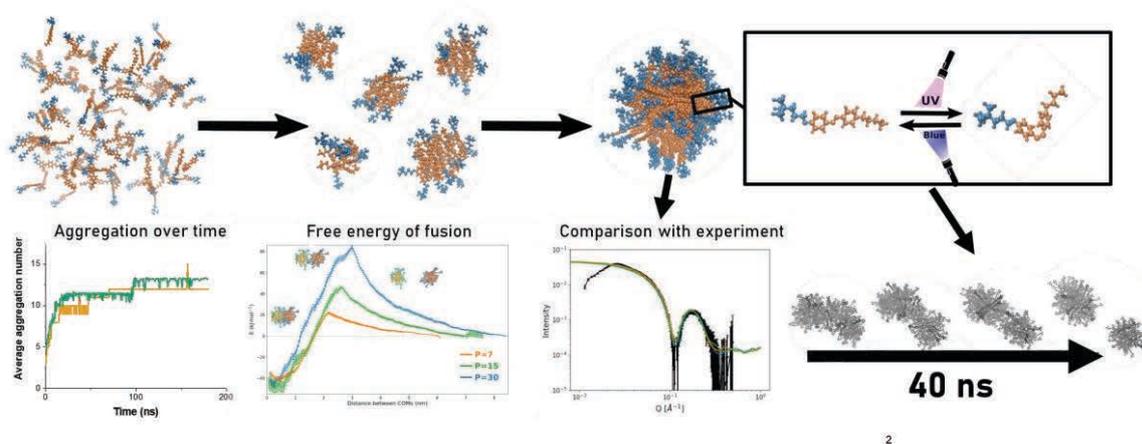


Figure 1. Illustration of how the aggregation kinetics and photodynamics of the surfactant AzoTMA has been investigated.

EP8.1

Synthesis of polymer-functionalized nanoparticles and development of smart fluids for enhanced oil recovery*Ch. Ntente^{1,2}, Z. Iatridi^{1,2}, M. Theodoropoulou¹, G. Bokias^{1,2} and Ch. Tsakiroglou¹**¹Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences, studios street, Platani, 26504 Patras, Greece**²University of Patras, Department of Chemistry**Presenting author e-mail: chntente@iceht.forth.gr*

Linear and comb-type terpolymers were synthesized through free radical polymerization (FRP), while, amphiphilic graft terpolymers comprising an anionic backbone, grafted with hydrophobic alkyl chains, were prepared by grafting reaction based on carbodiimide chemistry. The characteristic structural units chosen for polymer synthesis can be classified in 2 categories: (i) hydrophilic, anionic monomers like 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and acrylic acid (AA) that offer a hydrophilic character to the final copolymers, and are stable in the presence of salts in aqueous media; (ii) hydrophobic monomers like dodecyl methacrylate (DMA) and hydrophobic grafting chains like dodecylamine (DDA). The synthesis of polymer-coated nanoparticles (PNPs) was accomplished by post-grafting and surface initiated free radical polymerization (FRP) on silica nanoparticles. The polymers were characterized by Proton nuclear magnetic resonance (¹H NMR), acid-base titration and attenuated total reflection (ATR), and gel permeation chromatography.

Dilute dispersions of polymers and PNPs were mixed with salts (NaCl, CaCl₂, MgSO₄), and their static and dynamic surface tensions were measured by the Du Noüy ring and pendant drop method, respectively. The microscopic stability of suspensions was monitored by detecting the particle size distribution with dynamic light scattering. Oil-in-water Pickering emulsions were prepared by dispersing n-dodecane in PNP-colloid with ultrasound probe, and their stability was evaluated at three scales: (i) macroscopically, with optical inspection of the transient changes of phase volumes inside a volumetric tube; (ii) microscopically, by measuring the oil drop size distribution with image analysis under a stereoscope; (iii) mesoscopically, by determining the static and dynamic n-C₁₂/aqueous phase interfacial tension. Moreover, the wettability of all fluid systems to glass or plastic (PMMA, polystyrene) surface was quantified by measuring the contact angle. The most stable and viable PNP-based fluids (dispersions, emulsions, foams) were chosen and tested them as agents of enhanced oil recovery with displacement tests in glass- or plastic-etched pore networks.

Keywords: AMPSA, polymer-coated nanoparticles, enhanced oil recovery, aqueous suspension, Pickering emulsion, Pickering foam

Acknowledgements: The research project was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “1st Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment” (Project Number: HFRI-FM17-361, acronym: EOR-PNP).

EP8.2

The comparison of stabilizing and flocculating properties of fucoïdan in different oxide/electrolyte systems

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Stability of colloidal systems is a very important research problem due to the wide range of applications of such systems in many fields of industry and science. Depending on the application, either stabilization or flocculation is considered desirable. Due to the environmental and health concerns it is important to research and develop natural alternatives of synthetic polymers used for this purpose. In the following studies fucoïdan is proposed as a stabilizing or flocculating agent. Fucoïdan is a natural anionic polysaccharide containing sulphate groups in its structure. Its particularly valuable features include anti-inflammatory, antiviral, antioxidant, anti-cancer, and regenerative properties on the skin.

The aim of this study was to investigate and compare the stabilizing and flocculating properties of fucoïdan in different oxide/electrolyte systems. To gain insight into studied systems stability, adsorption and electrokinetic studies were conducted. Furthermore, the analysis using scanning electron microscope (SEM) and optical microscope were carried out. In the case of the adsorbents used in the experiments, three different oxides were selected: aluminum(III) oxide, titanium(IV) oxide and zinc(II) oxide.

It was established that fucoïdan can act either as stabilizer or flocculant in the systems depending on the used electrolyte. In the presence of sodium chloride stabilizing properties were observed, whereas in the case of calcium chloride the flocculation was observed. The obtained results offer new insight in the use of natural polysaccharides used in the production of cosmetics and pharmaceuticals. They also show that depending on the conditions, fucoïdan can be used in the wastewater treatment, with good efficiency of removal Al₂O₃, TiO₂ and ZnO oxide nanoparticles.

Keywords: polysaccharides, electrosteric, depletion, electrolyte, TSI

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EP8.3

Regularities of coagulation and heterocoagulation in polydispersed oxide hydrosols

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Currently, dispersions and powders of various oxides are widely used to produce polycrystalline optical and structural ceramics, high-performance catalysts and various functional coatings. The high practical significance of multicomponent oxide dispersions requires fundamental research in the field of colloidal chemistry of nanoscale dispersed systems and is a powerful impetus to the development of existing theoretical ideas about their stability and coagulation.

Electrokinetic properties and aggregate stability of diluted polydispersed alumina, ceria, zirconia nanosols and their mixtures at different pH and NaCl concentrations are studied. The difference in pH values of the mixed nanosols is allowed us to consider both positive and negative surface potential sign and, therefore, the cases when interacting heterogeneous particles are either the same or oppositely charged.

The colloid-chemical behavior of mono- and bicomponent sols was studied by turbidimetry, dynamic light scattering and Doppler laser electrophoresis. The thresholds of slow and fast coagulation, size, zeta-potential of the oxide particles and the position of the isoelectric point are determined. The theoretical study of hydrosols was carried out within the framework of the classical and extended DLVO theories, the extended theory of heterocoagulation (the theory of interaction of heterogeneous particles taking into account the structural component of the particle interaction energy). The pair interaction energies of identical and heterogeneous particles, the stability factors, the deceleration rates of heterocoagulation, the Hamaker constants for composite particles and particle aggregates, taking into account their non-monolithicity, are calculated. The parameters of the structural component for the interaction of heterogeneous particles are determined and the need to take into account three types of possible interactions in mixed sols (at the initial stage) is shown, even in the case of an intensive process of mutual coagulation. The impact of the ratio of particle number concentrations on the stability is studied.

Keywords: coagulation, heterocoagulation, DLVO, alumina, ceria, zirconia

Microglobule formation during the phase transition of poly(N-isopropylacrylamide)

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Poly-(N-isopropylacrylamide) (PNIPAM) is well known for its lower critical solution temperature (LCST) behavior in water. Making it interesting for various applications, e.g. in drug delivery and sensor design [1-2]. Surprisingly, the mechanism of the phase transition from the water-swollen to the collapsed state is yet not fully understood. It is thought that the main driving force is the hydrophobic interaction. Recent research points to the direction, that a combination of collapsed and swollen regions exists during the phase transition process [3]. The investigation of this regions is challenging due to a low x-ray contrast and in the case of microgels an inhomogeneous network structure.

This work will show that there is still information in small angle x-ray scattering (SAXS) data that can be used to get a valuable insight into the phase transition. We are in particular interested in exploring the influence of polymer concentration and the end-groups with respect to microglobule formation. This data will then be used for comparison with the swelling behavior of microgels. Through this a universal mechanism can be shown.

The difference in x-ray scattering for the same sample below and above the phase transition is shown in Figure 1. The most apparent change is the evolution of a pronounced correlation peak at around 4 nm^{-1} . Light scattering experiments have also been carried out to further investigate the effect of the end-group on the phase transition.

Keywords: SAXS, scattering, phase transition

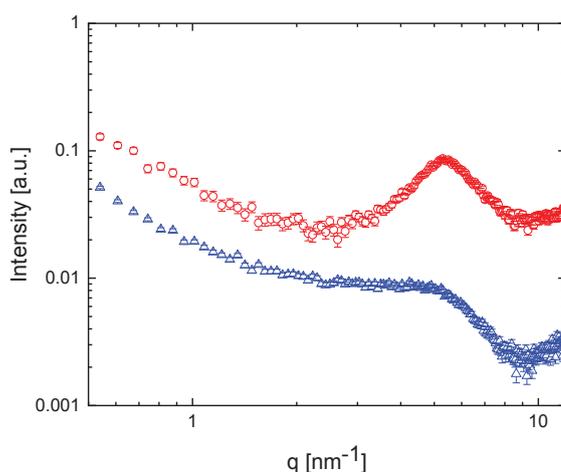


Figure 1. SAXS measurement of PNIPAM (10 wt%) in the high q region. Below (blue triangle) and above (red circle) the phase transition temperature. Data is shifted for better visualization.

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EP8.5

Phase separation of saturated micellar network and its potential applications for nanoemulsification

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Phase separation of saturated micellar network, as a result of cross-linking of branched micelles, is established in mixed solutions of the anionic surfactant sodium lauryl ethersulfate (SLES) and the zwitterionic cocamidopropyl betaine (CAPB) in the presence of divalent counterions: Ca^{2+} , Zn^{2+} , and Mg^{2+} . The saturated network appears in the form of droplets, which are heavier than water and sediment at the bottom of the vessel. In the case of Mg^{2+} , the sedimented drops coalesce and form a separate multiconnected micellar phase – a supergiant surfactant micelle. For this phase, the rheological flow curves show Newtonian and shear-thinning regions. The appearance/disappearance of the Newtonian region marks the onset of the formation of a saturated network. The addition of small organic molecules (fragrances) to the multiconnected micellar phase leads to an almost spontaneous formation of oil-in-water nanoemulsion. The nanoemulsification capacity of the multiconnected micellar phase decreases with the rise of the volume of the oil molecule. A possible role of the network junctions in the nanoemulsification process can be anticipated. The properties of the multiconnected micellar phases could find applications in extraction and separation processes, in drug/active delivery, and for nanoemulsification at minimal energy input.

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Rheological properties of rotator and crystalline phases of alkanes

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Rotator phases (R) are intermediate phases between the fully ordered crystalline phase and completely disordered, isotropic liquid phase. They are observed for several classes of long chain linear molecules, including alkanes, alkenes and alcohols [1,2]. Molecules arranged in rotator phases form layered structure, but the individual molecules within the layers are not fixed and may rotate/oscillate around their long axis. Long chain alkanes ($20 \lesssim n \lesssim 50$) and short chain alkanes with odd-number of C-atoms form one or several consecutive rotator phases upon both cooling and heating. The specific molecular arrangement in R phases presumes a complex viscoelastic rheological behavior. Although the rheological properties of alkanes are of major importance for the characteristics of various cosmetic products (vaseline, creams), lubricants in industry, and important processes in living nature, these properties remain poorly understood.[1,3]

Usually, the phase transitions among the R phases are studied by X-ray scattering and differential scanning calorimetry. In the current study, we develop a method for detection of the rotator phases using rheological measurements upon shear. The rheological properties of both rotator and crystalline phases of alkanes with chain-lengths between 15 and 28 C-atoms were studied. The results from the performed experiments can be summarized as follows: (1) Stepwise increase in the viscoelastic moduli is observed upon first order phase transitions between the liquid and rotator phases, and between the rotator and crystalline phases. (2) The storage (G') and loss (G'') moduli measured for the different rotator phases upon shear are ≈ 0.5 -3 MPa and ≈ 0.2 -0.4 MPa, respectively [3]. The specific values of the G' and G'' moduli is not determined primarily by the type of rotator/crystalline phase, but from the subcooling of the specific system below its melting temperature.

Keywords: rotator phase, rheology, shear moduli, alkane, phase transition

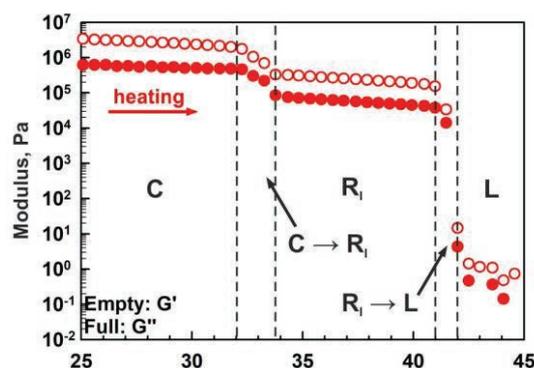


Figure 1. Storage and loss modulus measured upon heating of heneicosane.

Acknowledgements: The authors acknowledge the financial support from the Bulgarian Ministry of Education and Science for participation in the European Cooperation in Science and Technology (COST) action Chemobrionics 17120 (project KP-06-COST-10); project 2852.

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A depolarized dynamic light scattering study on gold nanorods functionalized with thermoresponsive ligands

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Isotropic particles are analyzed by dynamic light scattering (DLS) to determine their translational diffusion coefficient D_t in dilute dispersion. Thus, particle dimensions can easily be calculated. The autocorrelation curve of anisotropic particles by contrast is influenced by the translational as well as the rotational motion, making it not possible to determine particle dimensions by standard DLS. Here depolarized DLS (DDLS) offers a great tool to decouple the translational and rotational diffusion coefficient D_t and D_r , respectively and to determine the coefficient values precisely.

In this work, gold nanorods functionalized with high molecular weight, thermoresponsive poly-*N*-isopropylacrylamide (PNIPAM) ligands are analyzed by a combination of DLS and DDLS [1]. Measuring at temperatures below and close to the lower critical solution temperature (LCST) of the PNIPAM ligands enables the determination of temperature dependent diffusion coefficients, see Figure 1. Isotropic scattering of polymer decorated spherical gold nanoparticles is used as a reference to estimate the ligand thickness. The effective aspect ratio, the length and the diameter of the polymer decorated rods can then be determined as a function of temperature. The measurements reveal that the ligands collapse with increasing temperature resulting in an increase of the effective aspect ratio. At low temperature the particle diffusion is best described by a model for prolate spheroids changing to a more cylindrical like model at high temperature.

Keywords: gold nanorods, depolarized dynamic light scattering, PNIPAM ligand shell

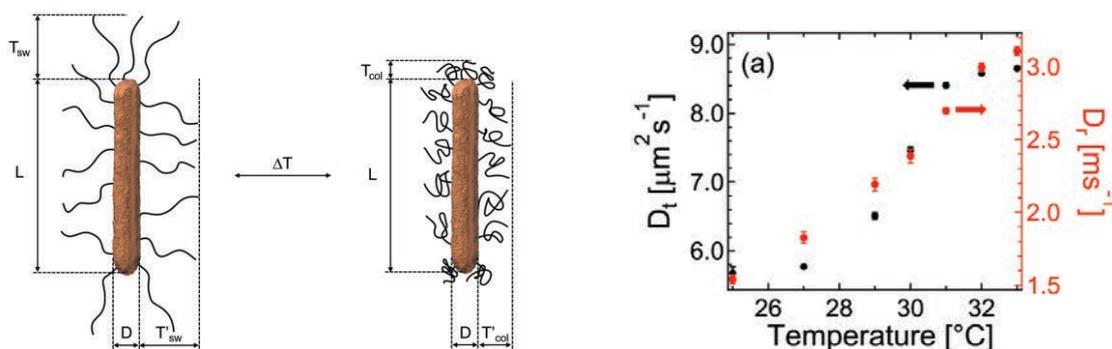


Figure 1. Schematic illustration of a gold nanorod decorated with PNIPAM ligands showing the LCST behavior. *Sw* refers to the swollen ligands and *col* refers to the collapsed ligands. *L* refers to the rod length, *D* refers to the rod diameter. *T* and *T'* refer to the ligand shell thickness at the tips and the sides of the rods, respectively (left). Temperature dependent D_t and D_r extracted from DLS and DDLS measurements (right).

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Shape stability vs shapes in motion: the role of the surfactant adsorption layer

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Governed by the ubiquitous energy-minimization law in nature, emulsion droplets usually have spherical shapes. Interestingly, recent studies have revealed that micrometer-sized alkane drops, dispersed in appropriate surfactant solutions, break symmetry upon cooling, transforming into a series of regular fluid shapes.^[1,2] The “self-shaping” phenomenon occurs at positive interfacial tension and is characterized by a ca. 2-to-10-fold increase in particle surface area. Denkov et al. proposed that an enthalpy gain due to the arrangement of alkane molecules in multilayers of metastable rotator phase next to the drop surface compensates the increase in the system’s interfacial energy.^[1,2] This theory is supported by recently obtained structural data.

Until now, however, it has remained unclear whether the non-spherical fluid shapes are thermodynamically or, rather, kinetically stable. To investigate the problem, the following model experiments were performed: monodisperse emulsions were cooled until a particular shape in the evolutionary scheme was reached. Then, a constant temperature was established and the particles’ behavior was observed. Based on the obtained results, the following could be argued: (1) The stability of the obtained non-spherical fluid particles is governed mainly by the composition of the surfactant adsorption layer. A preservation of the initial particle shape could be achieved with surfactant molecules with narrow compositional variations (such as oil-soluble fatty alcohol ethoxylates). In contrast, the use of technical-grade surfactants (e.g., polysorbates), containing molecules with varying alkyl chain lengths and a wide distribution of ethoxylate units, leads to an ongoing shape evolution. Therefore, the dynamic behavior of the adsorption layer promotes further nucleation of rotator phase with sufficient mechanical strength to stretch the particles’ surface; (2) The kinetics of the shape transitions depends both on the subcooling of the system and on the size of the confinement; (3) We demonstrate for the first time that an universal dimensionless rate of plastic phase growth can be extracted from the experiments with elongating fluid rod-like particles. The currently revealed approach opens the possibility for systematic investigation of the factors determining the rotator phase nucleation and growth.

Keywords: rotator phase, plastic phase, self-shaping drops, shape stability

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Structure and dynamics of concentrated protein mixtures – a colloid approach

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An ability to characterize and predict the phase behavior and the related structural and dynamic properties of concentrated protein mixtures such as those in living cells is crucial for our understanding of the cellular machinery or various cell-related pathologies. Here we focus on the mammalian eye lens, which contains a concentrated aqueous mixture of lens proteins, the so-called crystallins. Within the lens fluid, three major protein fractions exist: α , β and γ crystallin. The high concentration of these proteins combined with their specific inter-protein interactions provides the requirements for the eye's function: a high index of refraction, transparency and flexibility. In the presence of pathologies, e.g., cataract or presbyopia, the proteins can undergo condensation, aggregation, an arrest transition or liquid-liquid phase separation causing vision impairment. Thus, it is vital to understand how these proteins interact at high concentrations in the eye lens cells.

Here we investigate the structural and dynamical properties of binary lens protein mixtures of α and γ crystallin as a function of volume fraction. We combine a variety of scattering experiments (i.e., static and dynamic light scattering, small angle X-ray scattering, neutron spin echo measurements) with microrheology measurements, and interpret the results with a colloidal approach to proteins.

There have been attempts in the past to develop theoretical models capable of reproducing the phase behavior and key thermodynamic variables using statistical physics-based colloid models. However, while providing considerable insight for binary mixtures, such an approach is prohibitive for more complex multicomponent systems. We show that we can use simpler phenomenological colloid-inspired mixing rules to predict the behavior of protein mixtures based on the known properties of the individual components. We also point out the limits of such an approach for more local dynamic properties such as local motion on length scales of the protein size.

Keywords: Protein mixtures, protein phase separation, crowding, microrheology, quasielastic scattering

Collective dynamics of active rotating colloids

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We report a study on collective dynamics of self-propelling, rotating Lennard-Jones (LJ) particles in two dimensions using Brownian dynamics simulations. Previous work on self-propelling LJ particles showed re-entrant phase behavior as self-propulsion speed (Pe) is increased for a given attraction strength due to attractive interaction driven aggregation at low Pe and self-propulsion driven dynamic clustering at high Pe [1]. Another study on self-propelling, rotating hard discs showed suppression of dynamic clustering as angular velocity (w) is increased [2]. Our study combines the role of attraction, self-propulsion and angular velocity on the collective dynamics of particles. Our results converge to that of Ref [1] and Ref [2] when $w=0$ and Pe is very high, respectively. Our simulation shows that the fraction of particles in the clusters first decreases and then increases with Pe for a finite w , showing a non-monotonic trend. The study shows that cluster size can be controlled by Pe , w and attraction strength.

Keywords: active matter, self-propulsion, Brownian dynamics

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The development and understanding of indirect oil structuring method by using zein stabilized ethanol-based emulsion

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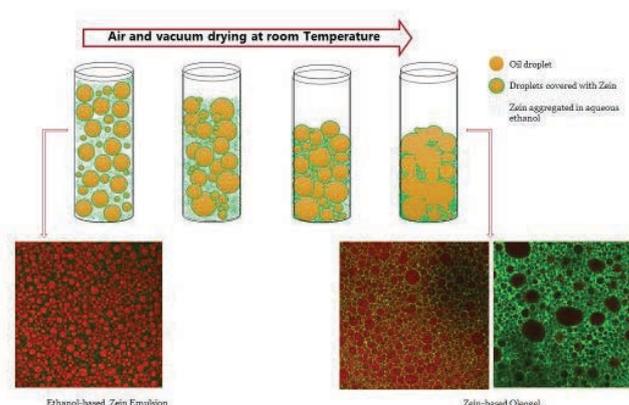
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Food oleogel is soft solid containing dispersed gelator network with a continuous phase of vegetable oil [1]. Among all the gelator molecules which have been used to stabilize oleogels, proteins offer great potential. Especially plant proteins raised great interest in food structuring due to their availability, low price and sustainability. Zein (corn seed protein) is soluble in aqueous ethanol as more than half of its amino acid residues are hydrophobic. By taking advantage of unique physicochemical properties and self-assembly ability of zein, we have developed an emulsion-template approach to structure oil [2].

The aim of this study is to understand the relationship between zein stabilized oil in ethanol-water emulsion and the properties of the obtained oleogel after drying. We examined the effect of zein concentration (0.4-12%w/v) and initial ethanol content (50-90%v/v) on droplet size and stability of emulsions during 14 days by using Coherent anti-Stokes Raman Scattering Microscopy (CARS) and light scattering method. The stability and gelling properties of samples were observed visually. To characterize the structural properties of oleogels, oil holding capacity (OHC) and CARS imaging were assessed. The results showed that increasing zein concentration resulted in smaller droplet size, while there was not any linear relationship between ethanol content and emulsion stability. No visual instability in emulsions with higher than 8%w/v zein in 70%v/v ethanol were observed. This may be due to unabsorbed proteins in continuous phase, forming gel-like structure. These emulsion-gels resulted in an oleogel with high OHC and more compact gel structure. Smallest droplet size was achieved in 4%w/v zein in 70% v/v ethanol, however emulsions containing 50% and 60%v/v ethanol resulted in more stable oleogels with higher OHC.

Keywords: Zein, Oleogel, CARS microscopy, Ethanol-based emulsion, Plant-based protein

Figure 1. Schematic diagram of the formation of oleogel by evaporation of continuous phase of Zein stabilized oil in ethanol-water emulsion and CARS Images of the emulsion and resulted oleogel after drying.



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Brownian Dynamics simulations of shear-induced clustering of electrostatically-stabilized colloidal suspensions with hydrodynamic interactions

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In this work, the aggregation kinetics of charged polystyrene particles exposed to shear flow has been investigated using Brownian Dynamics simulations with the Rotne–Prager–Yamakawa (RPY) approximation of the long-range Hydrodynamic Interactions (HI) over a wide range of particle volume fractions (Φ), Peclet number values (Pe), which measures the relative importance of shear forces with respect to diffusion, and surface potentials (ψ_0). The strength of the repulsive electrostatic interactions has been quantified by means of the Fuchs stability ration (W).

It has been observed that, for high values of W and low Pe number values, the aggregation rate is insensitive to the shear rate $\dot{\gamma}$, being the process dominated by repulsion forces among particles, similarly to what is observed under reaction-limited cluster aggregation (RLCA) regime. As the values of Peclet number increase, the resulting shear is sufficient to overcome the energy barrier to aggregation resulting in a sharp increase in the aggregation dynamics and radius of gyration, consistently with the available experimental results and theoretical predictions¹.

Similar results have been obtained as particle concentrations increases under a given shear rate $\dot{\gamma}$ and for a specific W. Simulations predict that the larger the volume fraction, the higher the collision rate, and the more intense is the disturbance in the flow field induced by particles, which promotes the mobility of the clusters and enhances the resulting aggregation rate. It was also observed that for high values of the Pe number, the curve describing the dimensionless time evolution of the number concentration of clusters for different Φ are almost overlapping throughout the whole simulation time, most likely indicating a similar aggregation mechanism, where concentration instead of shear rate plays a predominant role in determining the process dynamics.

Furthermore, in the early stages of the process, when aggregation occurs mostly between primary particles and small clusters, simulations neglecting HI and employing a pure BD algorithm lead to faster aggregation kinetics if compared to the method which includes the long-range hydrodynamics contributions. However, in the subsequent stages, the process is dominated by particle-cluster and cluster-cluster interactions and the long-range hydrodynamics term becomes predominant, resulting in a rapid increase of the aggregation rate and radius of gyration after a given time. This indicates that the inclusion of long-range HI can reveal unique features of the phenomenon and provide a more exhaustive description of the complex interplay between DLVO-interactions and hydrodynamics under shear flow conditions.

Keywords: colloidal aggregation, shear-induced aggregation, hydrodynamic interactions

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Novel bottom-up active matter

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We report a novel type of active matter, self-assembled from the bottom-up. It consists of emulsion oil droplets subjected to temperature changes. It is driven by a unique interfacially based phase transition, which gives rise to elasticity and is capable of repeated action and recharging from environmental fluctuations. This type of energy harvesting is usually reserved for living systems, but our 3-component abiotic system is simple and possible to understand in great physical detail. We quantify deformation and movement mechanisms and reveal potential analogies to the movement of living organisms. Macroscopic observation and quantification of the behavior is used to provide estimates of molecular level transitions and physical properties that are otherwise very hard to measure. The system is also biocompatible, made by mixing inexpensive materials (cost < \$0.02 /ml) and easy to study in any lab equipped with a simple optical microscope. It will enable a large number of investigations on interactions between abiotic and living active matter in physiological conditions.

Keywords: Bottom-up, active matter, emulsions, phase behaviour, dynamics, complex fluids

Self-assembly of colloidal cubes with critical Casimir attractions

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The structure of self-assembled materials is determined by the shape and interactions of the constituent building blocks. Recent advances offer unprecedented control over these parameters, allowing us to explore the relationships between shape, and provide a means to guide assembly towards desired structured materials. Here, we investigate the self-assembly of colloidal ‘superballs’, i.e. cubes with rounded corners, by temperature-tunable critical Casimir forces. For this unique particle shape already rich phase behavior, including solid–solid phase transitions in 3D [1], as well as different dense packings in quasi 2D have been observed [2,3].

The critical Casimir force is a completely reversible and controllable attraction that arises from the confinement of solvent fluctuations in a near-critical solvent between the particle surfaces[4]. By dispersing the cubes in a near-critical mixture of water and lutidine and heating it close to the critical temperature, attractions between the superballs are induced. Using confocal microscopy and particle tracking, we follow the self-assembly dynamics and structural transition in a quasi-2D system. At low density, we observe the formation of small clusters with simple-cubic symmetry. When the attraction strength is increased, a transition to a rhombic Λ_1 -lattice is observed, explained by the increase in surface contact. At high concentration, we find that large network-like structures form, that maintain their simple-cubic lattice structure even at high attraction strengths. Our results reveal that the coupling between the cubic shape and surface attraction plays a crucial role for the superstructures that form.

Keywords: Critical Casimir Forces, Self-Assembly, Superballs, Colloidal Crystals, Phase transitions

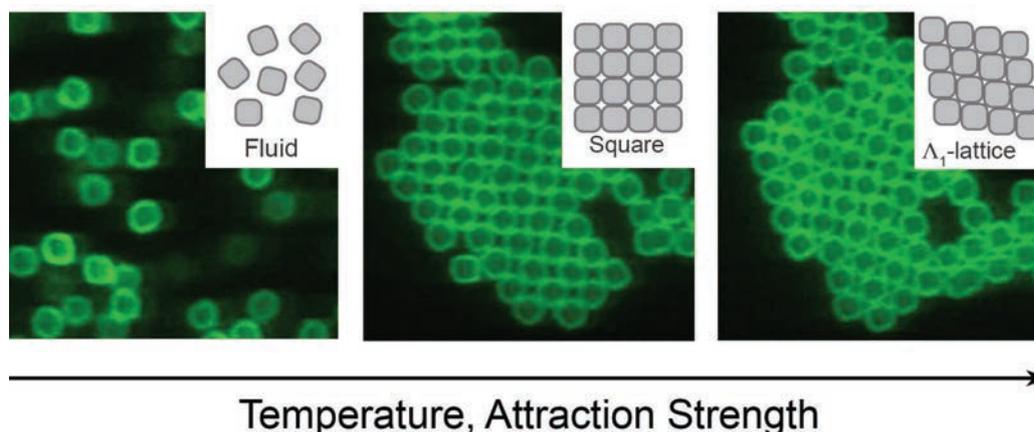


Figure 1. Confocal microscopy images of different self-assembled structures formed by the superballs with increasing attraction strength due to the critical Casimir attraction.

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The effect of alternating electric current on the energy-storage properties of the mixture $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} - \text{Na}_2\text{MoO}_4$

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One of the critical tasks of modern power engineering is to increase the service life of heat-storage materials operated in a wide range of temperatures. One of the classes of substances that meet technological, economic and environmental requirements is the crystal hydrates of alkali metal salts, in which the process of heat accumulation is carried out due to a phase transition [1]. On the other hand, an essential condition for the functioning of heat-accumulating mixtures is preserving a constant thermal background, so the development of methods for intensifying heat transfer is relevant. The paper purposes of establishing the modes of intensification of the process of accumulation of thermal energy. In this regard, studies were conducted on the effect of alternating electric current (AEC) on the melt of the mixture $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} - \text{Na}_2\text{MoO}_4$. For the processing of alternating current with a 50 – 5000 Hz frequency, a generator of the GZ-112 brand was used. Two platinum plates with an area of 1 cm², located at a distance of 1 cm, served as a working electrode. The latent heat of melting was calculated according to the method [2]. Regression equations are obtained that model the relationship between the specified parameters (temperature, AEC frequency, processing time) and the latent heat of melting of the mixture.

The results of the studies are shown in Figure 1. The increase in the latent heat of fusion of the mixture is associated with the electrical conductivity dispersion. Thus, the intensification of heat accumulation by crystal hydrate melts is achieved by processing AEC with a $5 \cdot 10^4$ Hz frequency for 40 minutes.

Keywords: crystal hydrates, alternating electric current, frequency, latent heat of fusion

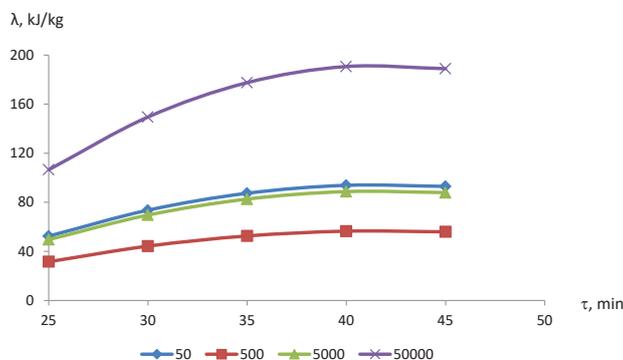


Figure 1. Influence of alternating electric current on the heat-storage properties of crystal hydrates mixture.

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Shape Matters in Magnetic-field Assisted Assembly of Colloidal Ellipsoids

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An anisotropic colloid shape in combination with an externally tunable interaction potential results in a plethora of self-assembled structures with potential applications towards the fabrication of smart materials. Here we present our investigation of the influence of an external magnetic field on the self-assembly of hematite-silica core-shell ellipsoidal colloids for different aspect ratios (ρ). Our study has brought to light a rather counter-intuitive but interesting phenomenon, where prolate anisotropic colloids self-assemble into oblate liquid crystalline (LC) phases. With an increase in the concentration of particles with smaller ρ , a sequence of LC phases involving para-nematic, nematic, smectic and oriented glass phase is observed. The occurrence of a smectic phase in colloidal ellipsoidal systems has been neither predicted nor reported before. Quantitative shape analysis of the particles and a comparison with extensive computer simulations indicates that not only ρ but a subtle deviation from the ideal shape dictates the formation of this highly unusual sequence of field-induced structures. Our study unequivocally demonstrates the power of combining anisotropic building blocks and external fields as a route towards field-directed self-assembly of novel structures with externally tunable properties together with the ramifications that the subtle changes in the particle shape have on the resulting self-assembled structures.

Keywords: Directed self-assembly, Magnetic anisotropic colloids, liquid crystals, SAXS, MC simulation, Particle shape-analysis

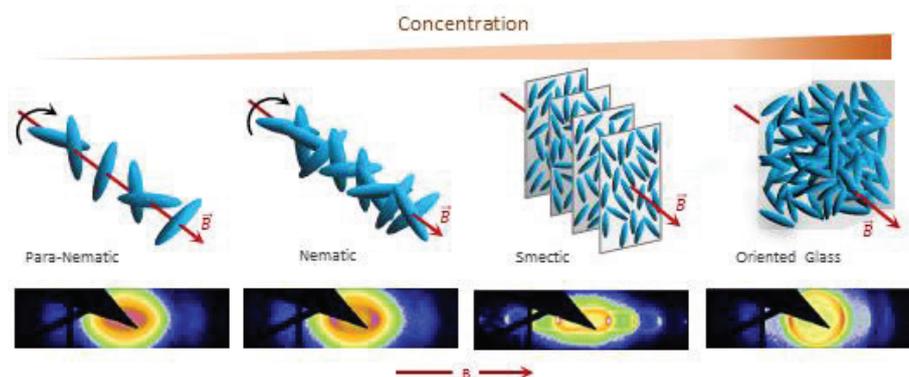


Figure 1. Magnetic field induced different oblate LC phases formed by colloidal ellipsoids as a function of concentration.

Phoretic dynamics of colloids in phase separating critical solvent mixtures

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Colloids suspended in binary liquid mixtures exhibit fascinating features near its coexisting region [1,2]. An important feature of these systems is that the interaction between particles can be tuned by varying the temperature and proximity to the critical point. Recently, these systems are used to realize active motions [3].

Here we have investigated the dynamics of colloids in near-critical liquid mixtures undergoing phase separation by X-ray photon correlation spectroscopy [4,5]. Two types of colloidal systems were studied, charge stabilized silica [6] and silica-nickel Janus particles [7], which showed a strikingly different phase behavior in the vicinity of the lower critical temperature of the solvent [4]. The out-of-equilibrium dynamics of colloids was found to be strongly influenced by the magnitude of the temperature jump into the two-phase region. For relatively large temperature jumps, the particle dynamics is dominated by velocity fluctuations induced by the concentration fluctuations during the spinodal decomposition of the solvent mixture. The effective diffusion coefficient was significantly enhanced from the Brownian limit with an anomalous wave vector dependence. For Janus particles, the induced dynamics slows down subsequently by clustering effects near the liquid-liquid interface. For smaller temperature jumps, the velocity fluctuations displayed a Gaussian distribution with silica and Janus colloids manifesting qualitatively different characteristics (active colloids).

Keywords: colloid dynamics, phase separation, XPCS, USAXS

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Sol-Gel Transition in Dispersions of Molybdenum Blue. Effect of the reducing agent.

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Molybdenum blues - dispersions of molybdenum oxide clusters are promising materials and are actively used as precursors for catalysts, drug delivery, sensors, and membrane devices [1,2,3].

This paper presents the results of measurements of the rheological characteristics of dispersions (hydrosols) obtained using several organic reducing agents: glucose, hydroquinone, and ascorbic acid. All synthesized dispersions were aggregative stable in the acidic range ($0.8 < \text{pH} < 2.5$). The dispersed phase is represented by molybdenum oxide clusters of the Mo_{154} family [4]. For research, we synthesized dispersions with different pH values and dispersed phase concentrations.

From the viewpoint of rheology hydrosols, synthesized using ascorbic acid and hydroquinone are Newtonian liquids. Their viscosities depend on the concentration of the dispersed phase. The dependence of specific viscosity on concentration is linear and obeys Einstein's law. At high values of the concentrations ($C = 18 \text{ wt}\%$), a deviation from Einstein's law is observed due to the appearance of electro-viscous effects. At concentrations of more than 18 wt. %, a transition from sol to gel is observed. It was assumed that the formation of a gel is the result of the appearance of constrained conditions leading to the overlap of particle surface layers and the fixation of particles at certain distances, since at small sizes of clusters, their partial concentration in sols is quite high.

The flow curves and viscosity curves of molybdenum blue synthesized using glucose are non-linear. Dispersions have a very high viscosity - due to structure (up to $1500 \text{ mPa}\cdot\text{s}$ for $C = 7.5 \text{ wt}\%$), however its destruction occurs at very low values of shear stress (less than 1 Pa). The sol-gel transition in systems obtained using glucose is observed at significantly lower concentrations of the dispersed phase of the order of 8 wt. %.

Keywords: molybdenum blue, dispersion, rheological properties

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Modification of the colloidal structure of the bitumen induced by several aging cycles with and without a new green surfactant

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This paper deals with the potentialities of a rejuvenating agent (green surfactant) in conferring an appreciable resistance against the effects caused by several artificial aging cycles on a given bitumen. Bitumen is a colloidal system formed by asphaltenes (micelles) enveloped in a maltene phase. The asphaltenes are the polar part dispersed in the continuous oil phase (maltene). The present investigation clearly evidences the fact that artificial aging, realized here by the use of the pressure aging vessel (PAV) test induces important structural modifications which are observable by several physical chemistry characterization techniques employed in this study. It is well known that the asphaltenic part of bitumen is the part susceptible to oxidation and a part of this study exploits that fact by taking a closer look at these asphaltenes via a variety of techniques. Both neat and aged bitumen samples were analyzed and compared to analogous samples modified with fluxing agent. Control samples containing a vegetable oil as softening agent were also tested for comparison. The tested samples were subjected to three aging cycles. Structural differences between the samples were tested and observed mainly through Rheological (DSR) and Differential Scanning Calorimetry (DSC) techniques. In addition, dynamic rheological analyses were conducted to determine the dependence of the mechanical moduli on temperature and of the gel-sol transition temperature on both the type of additive and aging process. Images obtained via Atomic Force Microscopy (AFM) allowed to monitor the structural changes induced by additives and the aging processes. The rejuvenating agent restores the initial bitumen structure despite several aging treatments while the fluxing agent just softens the oxidized bitumen. In this study, calorimetry has been demonstrated to be a useful tool to distinguish between rejuvenator and simple vegetable oil as additives in the modification and improvement of bitumen and its properties.

EP8.21

Phase behavior of quinoa protein isolates and maltodextrin for the microstructure engineering of plant-based foods

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Water-in-water (W/W) emulsions are mainly formed by a protein and a polysaccharide mixture that separates to different phases when both polymers present the same net charge. These systems are used for the creation of many microstructures in the food industry and recent studies have been exploring plant proteins, instead of animal proteins, as phase-forming biopolymers. In this research, the phase behavior of native (N-) and heat denatured (HD-) quinoa protein isolates (QPI) in mixture with maltodextrin (MD) was studied. QPI was extracted from quinoa flour at pH9, precipitated and lyophilized. It was then resuspended at pH7 and the soluble fraction (N-QPI) was separated by centrifugation. HD-QPI was prepared by heating N-QPI at 55°C for 30 min. Both suspensions were used separately for the creation of mixtures with MD of dextrose equivalent 2 in 0.1 M NaCl pH 7 at 22°C. The mixtures were centrifuged, and phase diagrams were constructed based on analytically obtained biopolymer concentrations in each phase.

The binodals of both phase diagrams differed from the classical W/W emulsion separation behavior, where the curve approaches each axis as the main polymer concentration in each phase increases. Instead, the curves approximated the MD axis at low biopolymer concentrations and shifted away from the axes as concentrations increased. HD-QPI presented a higher incompatibility with MD than N-QPI. Although literature proposes that the heat treatment of globular proteins before mixing with a polysaccharide can lead to W/W emulsions, due to structural change [1], this did not apply to our system. We hypothesize that the bimodal molecular weight distribution of MD contributed to the phase separation behavior [2] and conclude that microstructure engineering approaches relying on a W/W emulsion microstructure are not applicable to this system.

Keywords: plant proteins; water-in-water emulsion; phase diagrams.

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Effect of long-range ordering in diffusion of globular macromolecules

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The dynamics of colloidal particles at infinite dilution is commonly described with Brownian motion [1]. Classical description of diffusion does not hold when particles move in a crowded environment: one main example is provided by the dynamics of macromolecules inside living cells, where anomalous diffusion occurs due to macromolecular crowding [2]. In our research, we focused our attention on the impact of structural organization on the diffusion of globular macromolecules, which is still be unclear and less investigated nowadays.

We investigated the effect of long-range ordering on diffusion of globular macromolecules performing Monte Carlo simulations of hard-core spherical tracers dispersed in a bath of hard board-like particles (HBPs). HBPs proved to be ideal to model the effect of long-range ordering on the capability to form many liquid crystals phases, depending on their shape and packing fraction [3, 4].

More specifically, we employed our recently developed Dynamic Monte Carlo simulation technique [5] to model the diffusion of globular macromolecular in isotropic and nematic LC phases of colloidal HBPs. From our results, spherical tracers showed anisotropic diffusion whereas the structural organization of the bath was anisotropic, due to the formation of temporary cages along specific directions.

Keywords: Colloids, Brownian Motion, Diffusion, Liquid crystal

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The Road Less Travelled – Icosahedral or Decahedral Symmetry in Spherical Confinement?

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Icosahedral or decahedral symmetries are frequently observed in nano- and micro- scale objects such as atomic clusters, supramolecular assemblies, nanoparticles and their superlattices. These five-fold multi-twinned structures, unfavorable in bulk, are often the free energy minimum configurations when the number of building blocks is finite. Despite their abundance, the competition between icosahedral and decahedral symmetry is not well understood. Here, we investigate structure formation of colloidal particles confined in emulsion droplets in simulation and in-situ experiments using structural color. We find unprecedented large icosahedral and decahedral colloidal clusters consisting of up to 100,000 particles. Although free energy calculation indicates that both clusters are thermodynamically preferable in alternating regions of system sizes, decahedral clusters are disproportionately rare in simulation and experiment. We show that crystallization kinetics disfavors decahedral clusters under spherical curvature and the pathway towards decahedral symmetry is hindered at a surprisingly early stage during cluster formation.

Keywords: self-assembly, confinement, cluster, crystallization pathway, structural color

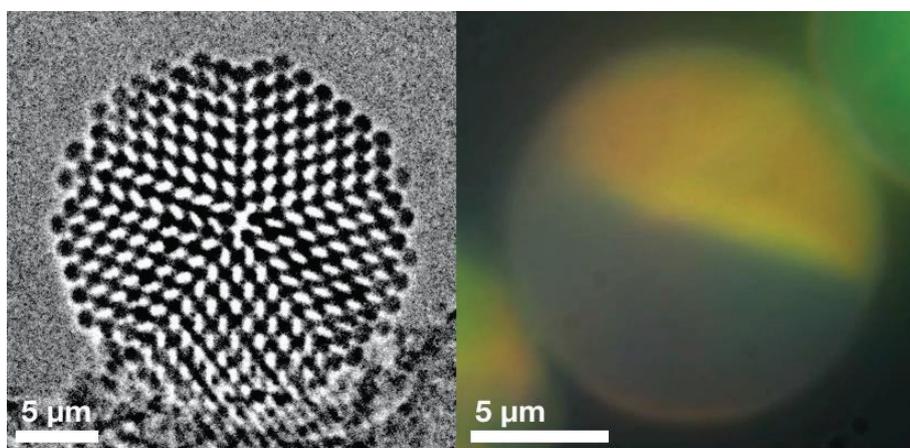


Figure 1. Observing the formation of decahedral colloidal cluster in emulsion droplet using structural color.

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Response Times in Field-induced Uniaxial-to-Biaxial Nematics Switching of Hard Colloidal Cuboids

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Rapid response times are crucial to optimise the refresh rates of liquid crystal displays (LCDs) for the enhanced display performance. One way this can be achieved is by incorporating biaxial nematic liquid crystals (N_B) in displays, as they are predicted to achieve fast switching through a minor-axis switching mode in an external field [1]. In our recent work on colloidal cuboids, we have shown that transient N_B phases can be stabilised by forcing particles to reorient in a uniaxial nematic phase (N_U) with an external field [2]. This finding consequently opens up an avenue to study the dynamics of uniaxial-to-biaxial nematics switching in an external field. In this work, we employ Dynamic Monte Carlo (DMC) simulation [3] to study the reorientation dynamics in field-induced $N_U \rightarrow N_B$ switching when an external field is switched on, and $N_B \rightarrow N_U$ relaxation when the external field is removed. We detect a strong correlation of anisotropy with the response times. In particular, the self-dual shape, despite theoretically considered to be the most optimal geometry to promote phase biaxiality [4], has shown switching performance that are less satisfactory compared to rod-like particles.

Keywords: Colloidal Liquid Crystals, Biaxial Nematic Phase, Dynamic Monte Carlo

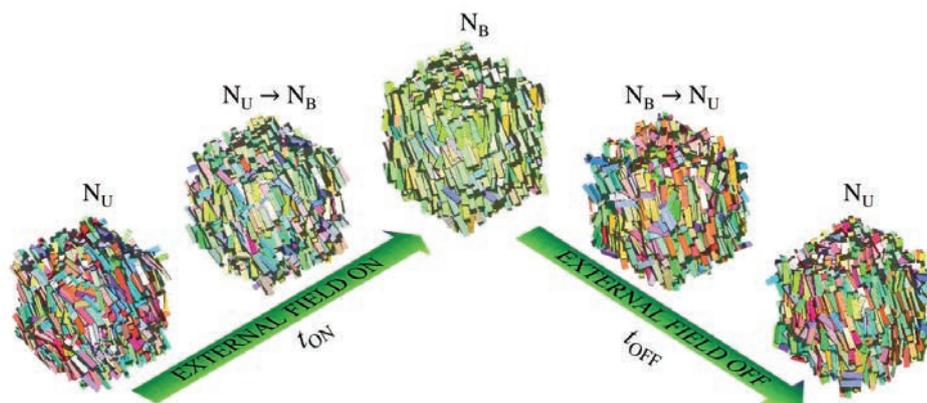


Figure 1. Schematic of a $N_U \rightarrow N_B$ switching when an external field is applied, and $N_U \rightarrow N_B$ relaxation when it is removed.

Acknowledgements: EMR would like to thank the Malaysian Government Agency Majlis Amanah Rakyat for funding his PhD at the University of Manchester. AP and LT acknowledges the financial support from the Leverhulme Trust Research Project Grant RPG-2018-415. EMR, LT, DC and AP acknowledge the assistance given by IT Services and the use of Computational Shared Facility at the University of Manchester. Finally, we thank Gerardo Campos-Villalobos (Utrecht University) for his assistance in generating the snapshots in Figure 1.

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Colloidal dynamics in confined and crowded environments

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Complexity in cells arises, in part, from the fact that most of their biochemical processes occur within an environment where the free volume accessible for molecules and supramolecular objects diffusion appears strongly limited as result of two aspects: (i) confinement, and (ii) crowding [1]. The former is associated with the existence of the cell membrane, which avoids the leakage of the cytoplasmic content, and provides mechanisms for the entrance of nutrients and other compounds to the inner cellular region and the expulsion of residues. Therefore, the cell membrane constrains most of the dynamic processes occurring within the cell to the cytoplasmic region. On the other side, the crowding arises from the high density of organelles, supramolecular structures and biomacromolecules that exist in the cytoplasm, occupying up to 40% of the cell volume [2]. The understanding of the impact of confinement and crowding on the dynamic of macromolecules plays a central role on the elucidation of many processes of physiological relevant. However, the complexity of the problem makes necessary to use model systems for deepening on the understanding of the diffusion of biomacromolecules within the cytoplasm [3]. This work proposes to use videomicroscopy for tracking the trajectories of spherical colloidal microparticles diffusing within the internal cavity of giant vesicles obtained by the electroformation technique, assuming this model as a simplified picture of that what happens in real cells [4]. The study is focused on providing an experimental framework to understand the diffusion in confined and crowded environments, facing for such purpose four different aspects: (i) particle diffusion; (ii) effect of the available volume, (iii) the chemical nature of the vesicle membrane, and (iv) the chemical nature of the encapsulated volume.

Keywords: colloid, cells, confinement, crowding, dynamics

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Laning, thinning and thickening of sheared colloids in a two-dimensional Taylor–Couette geometry

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Understanding the dynamics of confined particulate systems under external deformations is relevant for many industrial and technological processes. A classical yet versatile approach is based on the use of the Taylor–Couette (TC) geometry, where complex fluids are confined and sheared between two coaxial cylinders [1]. In this talk I will explain recent results obtained with circular colloidal clusters that are continuously sheared by magnetic and optical torques in a two-dimensional (2D) Taylor–Couette geometry [2,3]. By varying the two driving fields, we investigate the dynamics and rheological properties of this strongly confined colloidal system. We obtain the system flow diagram and report the velocity profiles along the colloidal structure. We then use the inner magnetic trimer as a microrheometer, and observe continuous thinning of all particle layers followed by thickening of the third one above a threshold field. Experimental data are supported by Brownian dynamics simulations [2]. Our approach gives a unique microscopic view on how the structure of strongly confined colloidal matter weakens or strengthens upon shear, envisioning the engineering of rheological devices at the microscales.

Keywords: Colloids, Micro-Rheology, External fields

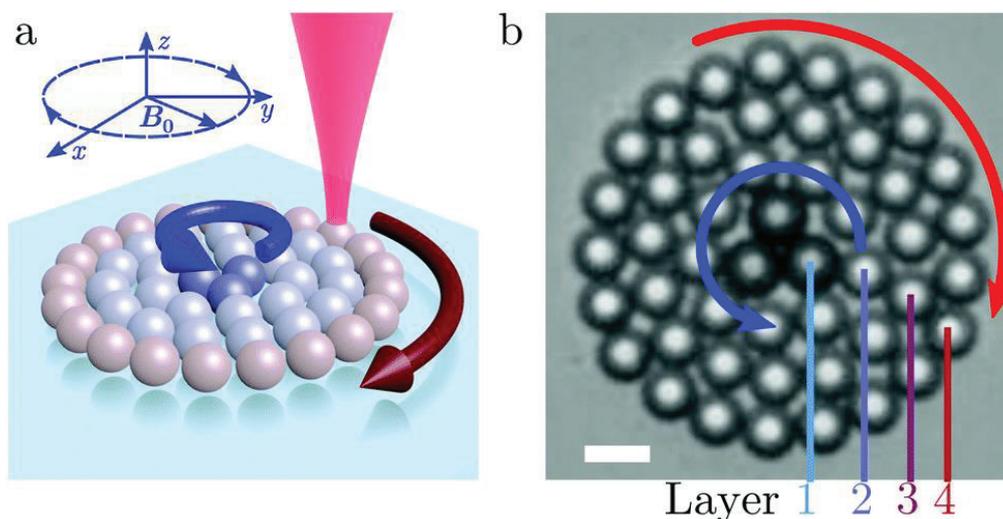


Figure 1. (a) Scheme of the experimental system where a cluster of 48 particles is confined by 21 time-shared optical traps and three inner paramagnetic colloids are rotated by an in-plane rotating field. (b) Microscope image of one colloidal cluster.

Acknowledgements: This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 811234).

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Role of asphaltenes in the structure of the interfacial film in bicontinuous microemulsions studied by Small Angle Scattering (SANS/SAXS) and cryo-TEM.

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In the context of Enhanced Oil Recovery, the use of Winsor III microemulsions is one of the most effective method so far. An optimal formulation is injected into the reservoir rock and forms a bicontinuous microemulsion when in contact with the crude oil. This leads to lower the interfacial tension with the crude down to almost zero, allowing the fluids to flow out. However, the optimal formulation is usually defined based on an equivalent alkane which is probably not representative of real crude systems. Compounds such as asphaltenes could play an important role due to their surface-active properties. Therefore, to optimize processes, there is a crucial need to understand the impact of these crude-indigenous surfactants on the bicontinuous microemulsions.

It is well-known that asphaltenes do adsorb at the oil/water interfaces by creating a rigid network and stabilizing emulsions [1]. But up to date, no systematic studies were performed to assess the impact of such complex compounds on the structure of the interfacial film in bicontinuous microemulsions. We performed SAXS/SANS experiments on a model microemulsion [2] containing different types of asphaltenes. The samples were studied without affecting their internal structure. In particular, we extracted the contributions of both interfacial film and asphaltenes using the method of contrast matching. Together with cryo-TEM images (ie **Figure 1**), we show that asphaltenes have an impact on the domains sizes and the volume fraction of interface. We suspect that the asphaltenes aggregates are included into the SDS interfacial film as it was already reported in the case of polymer-surfactant systems [3].

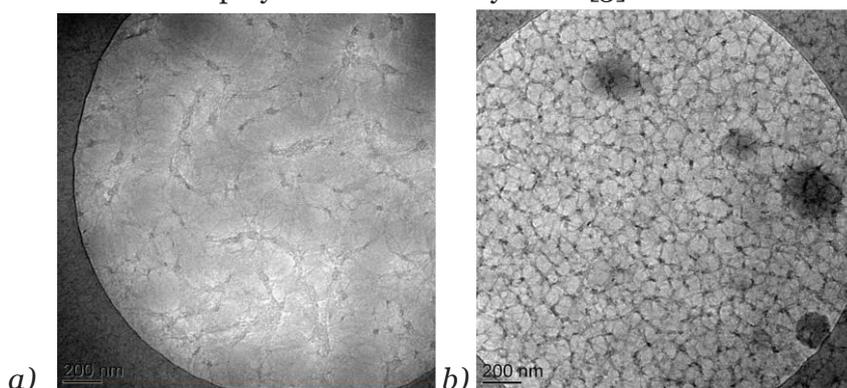


Figure 1. Cryo-TEM images of the studied bicontinuous microemulsions a) without asphaltenes; b) with 2%wt of C6-asphaltenes in oil phase

Keywords : Microemulsion, Bicontinuous, Asphaltenes, film, contrasts.

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EP9.1

Phase behaviour and rheology of multi-responsive soft microgels

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Multi-responsive microgels are widely studied hybrid systems that combine the properties of polymers and colloids. They can be considered very good models for the understanding of the general problem of dynamic arrest, since their larger tunability not only with respect to atomic systems but also to hard colloids, due to their intrinsic interpenetrability that leads to very complex-phase diagrams.

The behaviour of microgels becomes even more interesting if during the synthesis two different homopolymeric chains are interpenetrated, as in the case of Interpenetrated Polymer Network (IPN) microgels obtained by adding poly (acrylic acid) (PAAc), sensitive to pH, to a preformed PNIPAM microgel, responsive to temperature [2,3]. However, due to their complex synthesis procedure and morphology the microscopic interactions, viscoelastic properties and phase diagram of these soft particles are quite completely unknown.

Here we report a rheological investigation, accompanied by dynamical and structural measurements, of IPN microgels as a function of weight concentration and PAAc content across the VPT. The viscoelastic properties are derived and a preliminary phase diagram is obtained.

Keywords: soft matter, rheology, microgels

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EP9.2

Single microgels in limited solutions of oppositely charged amphiphilic drug

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Cationic-amphiphilic molecules are widely used in pharmaceutical field such as antihypertensive, antimicrobial, antidepressive and anticancer drugs. They vary in size and complexity from simple molecules to more complex peptides [1]. Microgels, on the other hand, are polyionic hydrogels consisting of cross-linked polymers that possess a negative charge. They can be used as a drug delivery system by loading a large amount of drug inside and then controlling the release by a triggering factor such as pH, ionic strength and temperature. They have the ability to protect the drug from degradation or denaturation especially in the case of biomolecules [2].

The loading of oppositely charged amphiphilic drugs or peptides inside these microgels makes them deswell while during the release the gel tend to reswell. The deswelling/swelling concept of microgels is fundamental for designing a theoretical loading and release model [3].

We have investigated single polyacrylate microgels at intermediate drug loads, equilibrated in amitriptyline solutions at both high and low ionic strength. For this purpose, a new microscopy technique in a small liquid volume was used to investigate the distribution of the drug inside single microgels at intermediate loading levels (figure 1). This allowed us to determine binding and swelling isotherms, and to study the phase behavior, in particularly if the drug redistributes or not inside the gel after equilibration.

In summary, we succeeded in building a specially designed microscopy cell that enabled us to study different volume regions for a single microgel in equilibration with small volumes of cationic amphiphilic drug solutions.

Keywords: Microgels, Amphiphilic drugs, Swelling isotherm, Deswelling

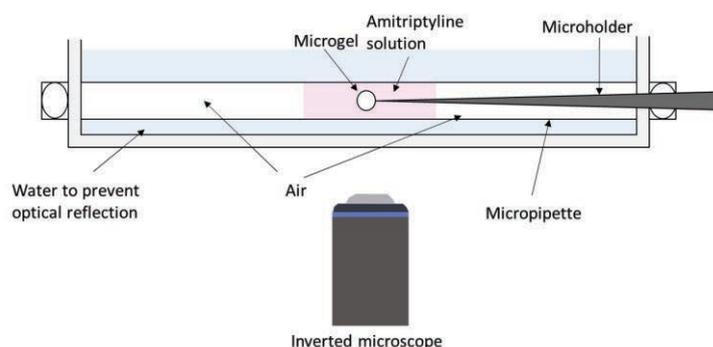


Figure 1. Schematic illustration of the small-volume method. One single polyacrylate microgel hold by a micropipette equilibrated in a limited volume of amitriptyline solution

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EP9.3

Synthesis and characterization of amphiphilic graft copolymers with improved environmental footprint as potential fragrance encapsulation systems.

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Coating material plays a fundamental role in the development of nano/microcapsules to protect the bioactive compounds against external factors. Type of encapsulation process and applied capsule wall material exert a direct impact on encapsulation efficiency, solubility, stability, surface permeability, and release profile of desired bioactive compounds. Particular attention should be paid to fragrances, they have a limited lifetime as their constituents evaporate and degrade before or during use. Innovations in the field are rare and many products still have downsides such as complex encapsulation technology or the use of non-biodegradable materials. Of the many polymeric materials, synthetic biodegradable polymers with good self-assembling capabilities are promising candidates for developing encapsulation devices [1]. The objective of the present work was to synthesize and characterize potential fragrance encapsulation systems using biocompatible and biodegradable polymers with synthetic origin.

To achieve the synthesis of copolymers with self-assembled structures, hydrophilic poly (ethylene glycols) (PEGs) of different molecular weights, hydrophilic and hydrophobic monomers like thermoresponsive N-vinyl caprolactam (VCL) and/or vinyl acetate (VAc), have been used. Amphiphilic copolymers were obtained through a radical polymerization method using peroxide as an initiator. Different molecular weights (lengths of the chain), grafting densities as well as various chemical moieties have been investigated [2-3].

The chemical structure and composition of the copolymers were confirmed by FTIR and ¹H-NMR spectroscopy. The molecular weights were determined by gel permeation chromatography (GPC). The copolymer's thermal stability was analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition, thermoresponsive behavior has been studied by visual measurements of the cloud point.

Keywords: amphiphilic polymers, self-assembly, encapsulation, radical polymerization

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EP9.4

Evaporative self-assembly of semi-crystalline polymer in confined geometry

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The drying of polymer solutions is a facile method to generate a variety of self-assembled patterns. Here, we report the self-assembly of Poly(ethylene oxide) into an intriguing concentric ring deposition pattern solely achieved by evaporating the polymer solution in confined geometry. The sphere-on-flat plate confinement geometry was achieved by fixing a glass bead onto the flat glass plate. The formation of concentric rings is understood by taking into account the regular stick-slip motion of the three-phase contact line of the drop during the course of evaporation [1]. Besides, the effect of solvent quality, the molecular weight of the polymer, concentration of the polymer in the solution, size of the droplet, and the curvature on the self-assembled pattern are systematically investigated. We found that the dried deposit pattern is strongly related to the molecular weight and the concentration of the polymer in the solution [2]. The width of the concentric rings and the spacing between the rings can be controlled by tuning the concentration of the polymer. A transition from a concentric ring-like deposit pattern to a single ring resembling a flower petal-like distribution of polymers with nearly equal angular separation is observed by solely tuning the molecular weight of the polymer. Moreover, the presence of fingering instability, which once again strongly depends on the molecular weight of the polymer, is observed for the rings located near the central region of the deposit and will be discussed in detail.

Acknowledgements: *We are grateful for the financial support from IIT Madras through Institutions of Eminence (IoE) Scheme, the Ministry of Human Resource Development, Government of India.*

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EP9.5

***Rhodococcus opacus* FCL1069 strain as a source
of extracellular polymeric substances**

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Rhodococcus strains are known due to their physicochemical and biological properties which can be applied in industry, pharmacy and medicine. These bacteria belong to the Actinobacteria family, consisting of strains with antibacterial, antiviral, antifungal and antioxidant properties [1]. Actinobacteria present the remarkable adaptability to various environmental conditions (extreme pH, wide temperature range, presence of heavy metals) and can be found in soil, water, plant roots, deserts, Arctic and Antarctic glaciers. Many of mentioned strains are able to produce extracellular polymeric substances (EPS) consisting of proteins, polysaccharides, lipids and nucleic acids [2]. Due to diverse chemical composition, exopolymers are known by various properties, such as biodegradability, hydrophobicity, biofilm formation, the ability to adsorb metal ions and organic compounds. Therefore, EPS participate in mineralisation, sorption and flocculation processes. The exopolymers production depends on multiple factors such as pH value and temperature of the culture broths, the growth phase of the microorganism, the type of carbon and nitrogen sources and their concentrations. These factors affect not only the yield of the exopolymers, but also their activities. All studies in this field are aimed to obtain products with the highest biological activities by the most efficient method of purification.

In this study, *Rhodococcus opacus* FCL1069 strain was tested due to its biological and physico-chemical properties. Analyses were performed with post-culture broths and with the extracellular substances obtained during the secondary metabolism of bacterial strain. Factors affecting the growth and the amounts of extracellular polymers were analysed. Additionally, the flocculating activity of post-culture broths was determined by the kaolin test.

Keywords: exopolymer, *Rhodococcus*, bacteria, flocculation

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Glycidyl methacrylate-based multifunctional amphiphilic copolymers with self-association capabilities

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Glycidyl methacrylate (GMA) is a low cost and highly reactive hydrophobic monomer which can be easily copolymerized with a variety of hydrophilic monomers, leading to amphiphilic materials. Moreover, GMA can serve as a precursor of multifunctional polymers, since its pendant epoxy group can react with nucleophiles (e.g. amines, carboxylic acids, thiols, etc.), creating new polymeric architectures with additional functionalities or responsive abilities.

Taking advantage of the reactivity of GMA-based copolymers towards acrylic acid units or amine groups, the preparation of coatings for potential antimicrobial or antifouling applications is elaborated in our laboratory during the last years [1-3], while through the combination with collagen, the preparation of hydrogels as potential biofertilizers has been recently explored [4].

In the present work, the self-organization in aqueous solutions of GMA-based copolymers is investigated by means of techniques including turbidimetry, fluorescence probing, dynamic light scattering, ζ -potential and viscometry/rheology, as well as microscopy techniques (scanning electron microscopy or transmission electron microscopy). The copolymers are prepared through free radical copolymerization of GMA with a variety of monomers, including the anionic sodium styrene sulfonate (SSNa), the nonionic hydrophilic N,N-dimethylacrylamide (DMAM), the nonionic sparingly water-soluble 2-hydroxyethyl methacrylate (HEMA) or the poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) macromonomer. In addition, it is shown that these copolymers form mixed associates with surfactants such as sodium dodecyl sulphate (SDS) or cetyltrimethylammonium bromide (CTAB) through hydrophobic interactions, eventually combined with electrostatic interactions. Finally, the reactivity of GMA towards amine functionalities was exploited in some cases, to introduce additional characteristics such as thermoresponsiveness in these structures.

Keywords: amphiphilic copolymer; glycidyl methacrylate; surfactant; functionality; self-assembly; stimuli-responsiveness

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Insights into hybrid orthosilicic acid/hyperbranched polyethylene/silver nanoparticle formation and gelation mechanisms

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Orthosilicic acid is the most common precursor of gel synthesis. Consequently a lot of research is performed on the different gelation mechanisms with dendritic polymers. Among them hyperbranched poly(ethylenimine) (PEI) possesses biomimetic potential for silica formation and metal ion reduction. In this context silver nanoparticles well known for their antibacterial and catalytic properties were initially formed into the cavities of variable MW PEIs. Then combined silica hydrogels were produced from these hybrid nanocomposites. These materials, optionally dried to xerogels proved ideal active ingredient carriers. They were applied as coatings to solid surfaces (metals, ceramics, leathers, glasses) and researched for potential uses, for instance to antifouling orthopedic implants, catalytic reactors, antibacterial hospital equipment and water filtering devices.

The optimization of gels composition for each specific application requires a thorough understanding of silver nucleation and silica-PEI hydrogen bond network formation mechanisms. Herein, Dynamic Light Scattering Spectroscopy and Zeta Potential kinetics data and conclusions on the two processes are presented.

Keywords: sol-gel, hydrolysis, dendritic polymers, hyperbranched poly(ethylene imine)

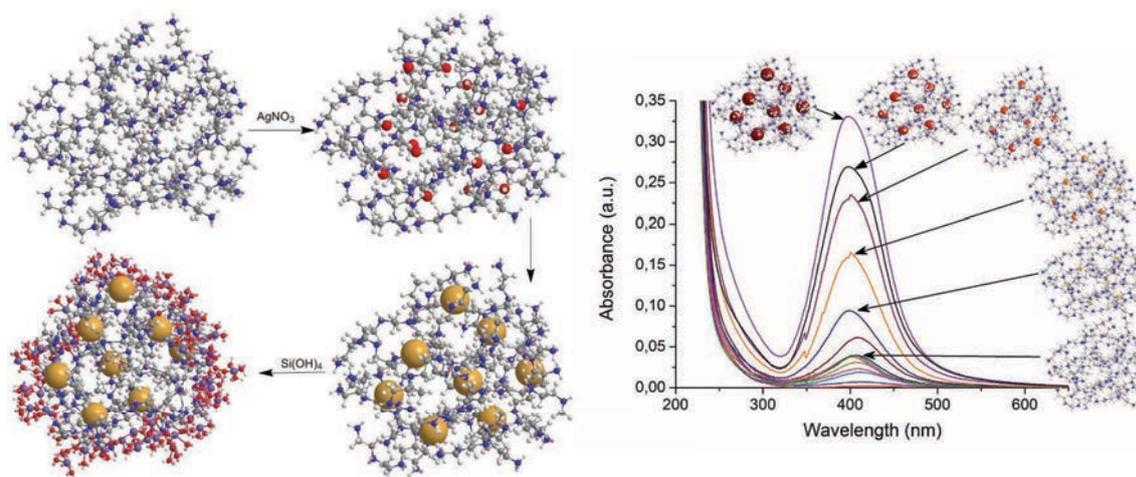


Figure 1. Silver nanoparticle/Hyperbranched polyethylene imine/Silica gel formation mechanism

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Saloplastics as multiresponsive ion exchange reservoirs and catalyst supports

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Processing polyelectrolyte complexes (PECs) by compaction in the presence of large salt concentrations enabled assembling a class of plastic materials, called Compacted Polyelectrolyte Complexes (COPECs) or saloplastics. Polyelectrolyte chains in COPECs are blended at the molecular level, interacting either through reversible intrinsic charge compensation (between polyelectrolytes) or through reversible extrinsic charge compensation (doping) with dissolved counterions.[1] For instance, pH stimuli on a saloplastic composed of poly(methacrylic acid) (PMAA) and poly(allylamine hydrochloride) (PAH) resulted in a tunable density of intrinsic charge compensation sites in the matrix and changed the porosity level and mechanical properties. [2] In this work, the fundamental chemical behavior of COPECs and their potential application as ion reactors for designing catalysts have been comprehensively investigated. The ionic reservoir behavior of saloplastics was exploited for monovalent sodium to multivalent copper cation exchange in order to assemble supported catalytic materials from PMAA/PAH COPECs. Copper ions were chosen as a model of multivalent ions that cumulate excellent capability for forming complexes with PMAA and demonstrated potential for designing cost-effective catalysts for carbon monoxide (CO) oxidation.[3]

Keywords: Compacted polyelectrolytes complexes, hybrid materials, catalyst support.

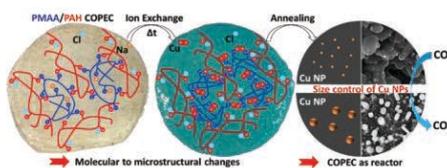


Figure 1: Dynamic aspect of saloplastics allows cation exchange with a tunable molality, enabling designing Cu(o) supported catalysts for CO oxidation.

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Influence of linear charge density parameter on water dynamics in polyelectrolyte solutions

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Thermodynamics of polyelectrolyte solutions is significantly influenced by strong electrostatic interactions. While the extent of Coulombic interactions can be at least for polyelectrolytes that lack notable hydrophobic character rather easily determined either experimentally or theoretically [1], determination of water dynamics is more delicate. It is expected that in strong electric fields formation of more stable hydrogen bonds would occur leading to slower switching of hydrogen bonds while the translational mobility of water molecules should be reduced [2].

The influence of static electric field on relaxation of water protons as a measure of water dynamics was experimentally studied using NMR Relaxometry. The strength of electric field around ionizable polymer molecules was varied by changing linear charge density parameter of the polyion. As a suitable model molecules for such a purpose weakly basic amine-based polyallylamine (PAH) and polyethyleneimine (PEI) were chosen. Aqueous solutions of PAH and PEI were neutralized with trifluoroacetic acid to the selected degrees of neutralization and ¹H relaxation dispersion curves were recorded in magnetic fields between 10 kHz and 30 MHz.

The relaxation rates of water protons were increasing with the increased degree of neutralization up to the full neutralization of PAH and PEI. In over-neutralised solutions, relaxation rates start to diminish in PAH but not in PEI solutions. For PAH solutions a correlation of these changes with the strength and the volume extent of the electric field around the polyions calculated from the solution of Poisson-Boltzmann equation within the cell model [3] was found.

Due to complex influence of the charge of polyions on thermodynamic and transport properties of polyelectrolyte solutions, further investigations of this phenomenon to obtain conclusive answers are needed. Relaxation studies of solutions of fullerene-based polyelectrolytes having rigid structure might help in resolving observed ambiguities [4].

Keywords: NMR relaxometry, polyallylamine, polyethyleneimine

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Tailoring mechanical and transport properties of polyvinyl alcohol based semi-interpenetrating hydrogels

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Hydrogels can be used in a wide range of medical applications, such as wound dressings, controlled drug release, or in production of scaffolds for tissue engineering [1]. Mechanical, and transport properties of hydrogels are crucial for these applications; therefore, the possibility of modifying their performance and relevant material parameters is still being researched [2, 3]. One of the ways to modify the properties of hydrogels is to use semi-interpenetrating (semi-IPN) polymer networks. These hydrogels have a modifying polymer incorporated by mechanical entrapment in the background network structure. By incorporating polymers with specific behavior, mechanical and transport properties of the resulting gels can thus be controlled. Therefore, this work focused on monitoring the influence of incorporated polyelectrolyte components on the resulting mechanical and transport properties of a model hydrogel system.

Due to its wide range of biomedical applications, a polyvinyl alcohol (PVA) hydrogel system has been chosen as a model material. In this work, PVA hydrogels were prepared either via borax - induced crosslinking or by physical gelation (cyclic freezing/thawing of aqueous PVA solutions). In order to modify the properties, polyelectrolytes (sodium polystyrene sulfonate and sodium alginate) were added to the prepared hydrogels.

Mechanical properties were studied with use of oscillatory rheometry. Strain sweep test was chosen as suitable for the description of mechanical properties, this test provides information about the linear viscoelastic region. The transport properties were investigated from a macroscopic point of view, by the diffusion pair method, where the transport process proceeds from the source PVA hydrogel containing a non-zero concentration of diffusion probe (methylene blue or rhodamine 6G) to the receiving PVA hydrogel containing a zero concentration of diffusion probe with either presence or absence (in the case of reference sample) of the interpenetrating polyelectrolyte component.

Keywords: hydrogel, polyvinyl alcohol, rheology, diffusion

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Bacterial Adhesion to Polyelectrolyte Multilayer Coated PVC Catheter Surfaces

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Catheters applied to the urinary tract are associated with nosocomial infections, which are one of the most common types of infections in hospitals and health care facilities and can lead to numerous medical complications. The understanding of the properties of urinary catheter surfaces and their potential modifications are therefore crucial in order to reduce bacterial adhesion.

In our study, we considered polyvinyl chloride (PVC) catheter surfaces and compared their properties with the properties of the same surfaces coated with poly(diallyldimethylammonium chloride)/poly(sodium 4-styrenesulfonate) (PDADMA/PSS) polyelectrolyte multilayers. All surfaces were characterized by means of roughness, hydrophobicity, and zeta potential measurements. The bacterial adhesion extent of uropathogenic *Escherichia coli* on bare and polyelectrolyte multilayer coated surfaces was measured. Our results showed that on non-treated surfaces, biofilm is formed which was not the case for multilayer coated surfaces. The PSS-terminated multilayer showed the lowest bacterial adhesion which could be helpful in prevention of biofilm formation. The analysis of the surface properties showed that the most significant difference is related to the charge (i.e., zeta potential) of the examined surfaces. From our study we can conclude that the surface charge plays the crucial role in the bacterial adhesion on uncoated and coated PVC catheter surfaces.

Keywords: Bacterial adhesion, catheters, Polyelectrolyte multilayers

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Physicochemical aspects of subcutaneous administration of drugs

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There is a growing amount of peptide and protein-based pharmaceuticals with low oral bioavailability. For these biopharmaceuticals the subcutaneous route is often a suitable alternative, but the bioavailability can vary greatly between the different pharmaceuticals. The basic process of absorption from the subcutaneous formulation to blood and lymph is quite well explored, but there is a lack of understanding of how the interactions between pharmaceuticals and the subcutaneous extracellular matrix (ECM) affects the bioavailability. [1] We aim to provide a greater mechanistic understanding of how pharmaceuticals interact with the polyelectrolytes (eg. Hyaluronic acid, Chondroitin sulfate) of the ECM from a physicochemical perspective.

To fulfill this aim a combination of different scattering and spectroscopy methods are used to gain information about the structure and size of interaction complexes. For quantification of interaction strength, microgels consisting of cross-linked polyelectrolytes from the ECM are used. The interactions between these microgels and different biopharmaceuticals in solution are investigated by a number of microscopy techniques. These include visual light, fluorescence, confocal laser scanning microscopy, and confocal Raman microscopy.

The work has thus far resulted in a novel microfluidic-based *in vitro* screening method to investigate interactions between polyelectrolytes from the ECM and biopharmaceuticals. Initial results are promising and further investigation of these interactions will provide the basis for a deeper understanding of the behavior and bioavailability of subcutaneously administered pharmaceuticals. It will also provide the basis for the development of new subcutaneous formulations with microgels as carriers.

Keywords: Microgels, Polyelectrolytes, Subcutaneous injection, Microfluidics

Acknowledgments: This research was performed with funding from the Swedish Drug Delivery Center (Swedeliver).

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Lecithin as internal architecture modifier of hydrogels for model drug delivery systems with tunable properties

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The purpose of this study focuses on the current and still developing topic of micro- and nanosized drug delivery systems, since their usage in treatment procedure offers a variety of benefits compared to conventional drug dosing. In recent years, specific extracellular matrix (ECM) imitating biopolymers carry exceptional properties of biocompatible and biodegradable materials, which are able to form soft or semi-solid networks beneficial for drug incorporation. Recent studies of innovative complex biomaterials have proved the potential of hydrogels usage for fabrication of novel materials, providing appropriate mechanical, chemical and biological characteristic for mimicking ECM for regenerative medicine, fabrication and in situ analyses of drug delivery systems [1-3]. Final properties related to specific application of these materials can be modified not only by polymer and/or crosslinking agent type and concentration, but actively also with other additives influencing inner architecture like phospholipid lecithin, which in water-based solutions forms organized structures [4].

In this proposed study the effect of lecithin additions on hydrogel matrix with various crosslinking principles was investigated. Selected systems were subjected to structural characterization in the form of xerogel as well as freeze dried form using direct visualization technique scanning electron microscopy (SEM). Further, these systems were rehydrated and the kinetics of swelling process was monitored. Changes in inner structure of hydrogels caused by addition of appropriate additive (e.g. lecithin) strongly influence key essential properties related to specific application such as mechanical or transport. Therefore, viscoelastic properties using rheometry as well as transport properties via macroscopic diffusion techniques has been performed. Following experiments consisted of characterization of viscoelastic behaviour via oscillatory rheology of rehydrated samples that were compared with freshly prepared hydrogels, as well as transport properties using macroscopic diffusion techniques, specifically by observing the release of model drug from the gel matrix.

Keywords: hydrogel, lecithin, rheology, SEM, diffusion

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Spontaneous and time-controlled aggregation of nanoparticles in electrostatic self-assembly

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Electrostatic self-assembly has huge importance in synthesizing nanostructures of desired shape and size in an aqueous solution with a narrow size distribution [1,2]. This process is based on coulombic interactions between polyelectrolytes and multivalent organic counterions; a wide range of shapes in nanoparticles for example spheres, rod-like structures, ellipsoids, cylinders, and others can be formed [3]. These self-assembled nanoparticles can be tuned by various external triggers such as pH, light irradiation, ionic strength, concentration ratio, and many more that we are potentially unaware of yet. Anionic azo dyes and cationic dendrimers are the core components used in this study. The isomerization property of an azo dye and pH responsiveness of a dendrimer makes them suitable candidates to alter the structure of a self-assembled particle driven by the number of charges and light irradiation. Herein, we used Acid Yellow 38 (AY38) as an azo dye and generation 4 (G4) PAMAM dendrimer for electrostatic self-assemblies in solution. The mechanism behind the formation of electrostatically self-assembled nanoparticles is difficult to follow as it takes place within seconds[1]. To understand the formation mechanism in detail it is necessary to slow down the particle growth. Therefore, we used different sample preparation methods that prevented nanoparticles' fast growth and helped to understand the particle evolution mechanism in detail using small-angle neutron scattering (SANS), static and dynamic light scattering (SLS and DLS), UV-Vis spectroscopy and ζ -potential.

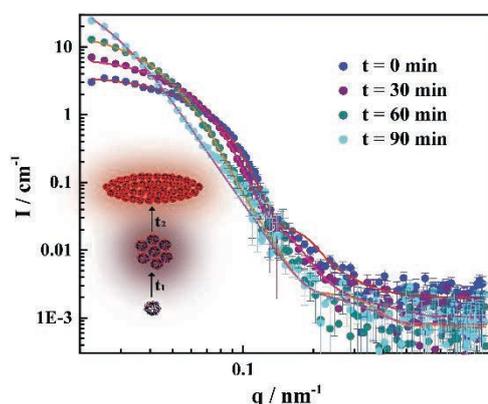


Figure-1: SANS measurement of AY38/PAMAM G4 dendrimer assemblies at different times.

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Influence of aromatic additives on the phase transition behaviour of thermoresponsive Poly(N-isopropylacrylamide) microgels with different cross-linker densities

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Thermoresponsive polymers bear a large potential for drug delivery applications, however, the influence of small molecules on the phase transition is a critical issue. Our work investigates the effects of different additives such as benzene derivatives, employed as model drugs, on the phase transition behaviour of differently crosslinked Poly(N-isopropylacrylamide)/N,N'-methylenebisacrylamide (PNiPAM/BIS) microgels. While the homopolymer PNiPAM has already been studied earlier in the presence of various aromatic additives,[1] in the present work the influence of a selection of additives (dihydroxybenzenes, dihydroxybenzaldehydes) on the VPTT of PNiPAM microgels is determined. NMR Spectroscopy, Differential Scanning Calorimetry (DSC) and Dynamic Light Scattering (DLS) are employed to determine the characteristic Volume Phase Transition Temperature (VPTT), transition widths and incorporation/release behavior towards additives.

All additives investigated induce a shift of the VPTT to lower temperatures, consistently observed in all temperature-dependent characteristic parameters. This shift is sensitively dependent on the microgel architecture, as the VPTT shift depends on crosslinking density.

Furthermore, as a result from temperature dependent ¹H-NMR spectra, this work proofs the existence of an incorporated additive fraction at T > VPTT. A quantification of the incorporated additive fraction is achieved. By investigation of the transverse spin relaxation rates R₂ of the aldehyde protons, additive molecular dynamics below and above the collapse temperature of the microgels are clarified.

Keywords: microgel, thermoresponsive, additive, VPTT, phase transition, NIPAM

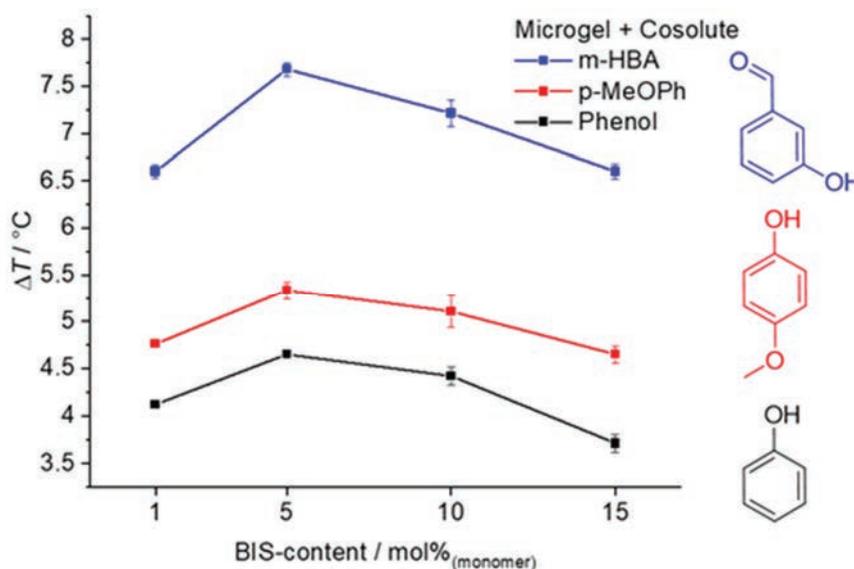


Figure 1. VPTT depression ΔT induced by different aromatic species with the same concentration as determined by DSC in dependency of the crosslinker-content.

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Phycocyanin and Phycocyanobilin Extraction from *Spirulina maxima* and their encapsulation in polymeric hydrogels

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Phycocyanin is a light-harvesting protein complex produced by cyanobacteria. It displays a characteristic blue color, owed to its tetrapyrrole chromophore, named phycocyanobilin, which is covalently bound to the protein via a thioether bond. Phycocyanin has shown potential for several biotechnological applications and has been used as food coloring and as a natural dye in cosmetics, in efforts to use more natural dyes. It has also been extensively studied for its antioxidant activity. As a result, phycocyanin has attracted the interest of the food, cosmetics, and pharmaceutical industries. Because of its inherent sensitivity to environmental variables, encapsulation presents a suitable means of maintaining the protein's beneficial properties. (1)

In this work, phycocyanin as well as the phycocyanobilin chromophore, are extracted from *Arthrospira maxima* biomass and subsequently immobilized in polymeric hydrogels. Hydrogels represent a simple and affordable tool for the creation of an environment that maintains the properties of biologics (2). They consist of three-dimensional networks, generated by hydrophilic polymers. These networks enclose high water content, allowing the encapsulation of hydrophilic molecules. Thus far, the encapsulation of phycocyanin in hydrogels created by natural biopolymers like chitosan and cellulose has increased the stability of the color associated with the protein, against increased temperatures, extreme pH and light-induced color loss. Upcoming work will aim to validate protein stability in hydrogel systems via evaluation of its antioxidant properties by Electron Paramagnetic Resonance (EPR).

Keywords: Cyanobacterial biologics, Hydrogels, Antioxidant activity

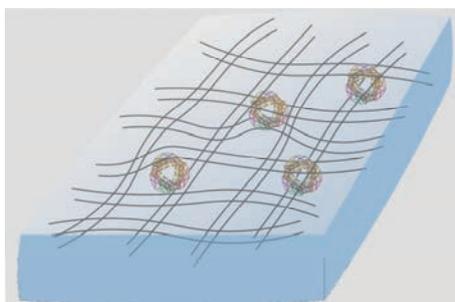


Figure 1. Encapsulated phycocyanin into hydrogel scaffold.

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Hyperbranched H-[P(OEGMA-co-LMA)] random amphiphilic copolymers as self-assembled nanocarriers for curcumin

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Amphiphilic copolymers have attracted significant research interest over the last years since they find potential applications in targeted drug delivery, nanomedicines and many other fields. This is mostly due to their ability to self-assemble into nanostructures in aqueous media. The copolymers molecular architecture and composition are the main influences to their self assembling behavior. [1-3]

In our study, innovative amphiphilic hyperbranched random copolymers, namely H-[poly (ethylene glycol) methyl ether methacrylate-co-lauryl methacrylate] (H-[P(OEGMA-co-LMA)]), with variable hydrophobic content, were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in combination with the divinyl monomer, ethylene glycol dimethacrylate (EGDMA) as a branching agent. Molecular characterization by size exclusion chromatography (SEC) and proton nuclear magnetic resonance (¹H-NMR) spectroscopy indicated the success of the polymerization, whereas self assembling behavior in aqueous media was investigated by light scattering techniques and fluorescence spectroscopy. Copolymer composition and degree of branching seem to affect the characteristics of the aggregates formed. In addition, the model hydrophobic drug, curcumin, was used in order to investigate the H-[P(OEGMA-co-LMA)] copolymers drug encapsulation ability. Curcumin was successfully loaded into the polymeric nanoparticles, as confirmed by dynamic light scattering and UV-Vis spectroscopy. Interestingly, curcumin incorporation contributes to more structurally defined self assembly, consisting of small size nanoparticles (<100nm) which exhibit relatively high uniformity and stability.

Overall results signify that the biocompatible H-[P(OEGMA-co-LMA)] nanostructures could potentially serve as nanocarrier systems for hydrophobic drug delivery applications.

Keywords: amphiphilic copolymers; hyperbranched; RAFT; drug loading

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Modification of flat Ti/TiO₂ surface with strong polyelectrolytes

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Titanium is a widely employed material in the aerospace industry, biomedicine and dentistry due to the combination of favorable mechanical properties, great corrosion resistance and good tissue compatibility. Some of the titanium properties are attributed to the passive oxide layer, which spontaneously forms on the titanium surface in an oxygen-containing environment. The protective oxide layer, few nanometers thick, mainly consists of amorphous TiO₂ [1, 2].

Many properties of titanium can be improved by introducing polyelectrolyte films on its surface. For example, polyelectrolyte coatings offer a new way for antibacterial protection of titanium dental implants [3]. Properties of such films are controlled by the interplay of various interactions between surface and adsorbed polymer molecules. A comprehensive understanding of these interactions may enable very fine-tuning of titanium surface properties.

In this study, the surface properties of Ti/TiO₂ substrate before and after the adsorption of polyelectrolytes were investigated. As a model polyelectrolytes, strongly charged polycation poly(diallyldimethylammonium chloride) (PDADMA) and strongly charged polyanion poly(sodium 4-styrenesulfonate) (PSS) were used. First, the bare titanium substrate was characterized by means of ellipsometry, atomic force microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. It was shown that the substrate surface is very flat with an average roughness of only 2.3 nm and oxide layer thickness of 3.8 nm. Furthermore, electrochemical measurements revealed a good corrosion resistance of Ti/TiO₂ substrate. After the adsorption of polyelectrolytes, coated titanium surface was again examined using the above-mentioned methods. Enhanced anticorrosion characteristics were observed for surfaces fabricated by both polyelectrolyte films, while the surface roughness didn't significantly change. These results lead us to the conclusion that polyelectrolyte molecules form a stable nanofilm on Ti/TiO₂ surface that partially or fully covers the surface. Our previous work made on the adsorption of PSS to rutile surface [4] strongly corroborates these findings.

Keywords: titanium/titanium dioxide surface, polyelectrolytes, ellipsometry, atomic force microscopy, cyclic voltammetry, electrochemical impedance spectroscopy

Acknowledgements: Croatian Science Foundation financially supported the research under the project POLYMIN2 (IP-2020-02-9571).

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Collective transitions in pH-sensitive hydrophobic polyelectrolytes

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Hydrophobic polyelectrolytes (HPE) are polymers containing both hydrophobic and ionizable chemical groups. These groups will, on average, be homogeneously distributed across the chain. As for any polyelectrolyte, the degree of ionization will affect the conformation of the chain in aqueous solutions. The presence of hydrophobic groups in these chains can however lead to more abrupt changes in conformation and therefore solubility [1]. In general, the competition between the two chemically opposing groups leads to sharp changes between “oily” and “aqueous” states. Examples of HPEs are poly(styrene-co-maleic acid) and poly(ethylacrylic acid) [2,3].

We propose that this sensitivity to ionization state and therefore pH can be explained through an analytical 2-state statistical mechanical model based on the principles of the Monod-Wyman-Changeux allosteric model. The sharpness of a transition scaling with the number of ionizable groups on a polymer chain. The polyelectrolyte poly(acrylic acid-co-n-butyl acrylate) was synthesized and modified with a clicked-on UV probe, and its partitioning between water (“aqueous” state) at different pHs and dichloromethane (“oily” state) was followed using UV-Vis absorption. Aggregation in a single aqueous phase was also investigated through turbidimetry. The experimental results are in good agreement with the analytical model.

This class of highly pH sensitive polymers show great promise for chemical and biological sensing [4], for targeted drug delivery into tissues with pH gradients, such as cancerous tissue [5], and they are also extensively used in the solubilization of cell membranes allowing for the characterization of proteins in their native environment [6]. Validation of the proposed model will lead to useful predictive power on the behavior of HPEs in these applications, as well as further elucidating the physical origin of sharp transitions that are very common in biology.

Keywords: polyelectrolyte, pH, allostery, collective behavior, oil-water interfaces

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3D printed Polylactic Acid (PLA) scaffolds: Surface modification and Biocatalytic Applications

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Additive manufacturing or 3D printing is a layer by layer manufacturing process based on computer data that has met fast development and recognition in a great variety of applications, from engineering and architecture to environmental applications and biomedical industry¹. Polylactic acid (PLA) is a biocompatible and biodegradable polyester made from feedstock. Its large range of mechanical and physical properties allows its engineering to suit different applications².

Biomolecules immobilization on the surface of 3D printed PLA can be achieved by generating hydrophilic functionalities and/or graft hydrophilic polymers on its surface. Combining these perspectives, we present a method to modify the surface of 3D printed PLA scaffolds under the scope to immobilize different enzymes for biocatalytic applications. Proteolytic and oxidoreductive activities have been explored for the biotransformation of different bioactive compounds of natural origin.

Expanding the potential of polymeric scaffolds, rapid prototyping offers the capability to design complex microstructured devices, like microfluidic reactors and lab-on-a-chip devices that could be properly modified with several biological activities for a wide variety of biotechnological applications.

Keywords: 3D printing, polylactic acid, enzymes, biotransformation, natural compounds

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The Hidden Secrets of Cosmetic Colloids

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Biomimetic liquid crystalline systems are widely used in skin care cosmetics and topical pharmaceutical preparations intended to treat dry skin conditions. Such products are formulated with the intention that when exogenously applied to the skin surface they form lamellar structures that mimic those within the underlying stratum corneum – the outermost layer of the skin [1]. By this means it is proposed that the applied products provide an occlusive barrier that acts to reduce water loss and so helps promote skin (re-)hydration [1]. Our ability to design such formulations rationally, however, is hampered by our incomplete understanding of their molecular architecture.

In the studies reported here, we use polarized light microscopy and small-angle and wide-angle X-ray scattering to probe the molecular architecture and properties of a barrier formulation prepared from distearoylphosphatidylcholine mixed with long-chained fatty acid and alcohols, with and without antimicrobial pentanediols. The nature and composition of the various (liquid crystalline lamellar) phases identified are determined through small-angle neutron scattering studies using chain-deuterated components, and the detailed structure and dynamics of the gel network lamellae are determined through molecular dynamics simulations.

The formulations show molecular ordering with long and short periodicity lamellar phases (Figure 1) which mimic the lamellar organisation of the *stratum corneum*. There is little change in these structures caused by changes in temperature, drying, or the application of shear stress. The diol-free formulation is demonstrated to be self-preserving, and the added pentanediols are shown to distribute within the interlamellar regions where they limit availability of water for microbial growth. In culmination of these studies, we develop a more complete picture of these complex biomimetic preparations, and thereby enable their structure-based design.

Keywords: Colloidal systems; Liquid Crystalline Structures; Bio-mimetic skin creams

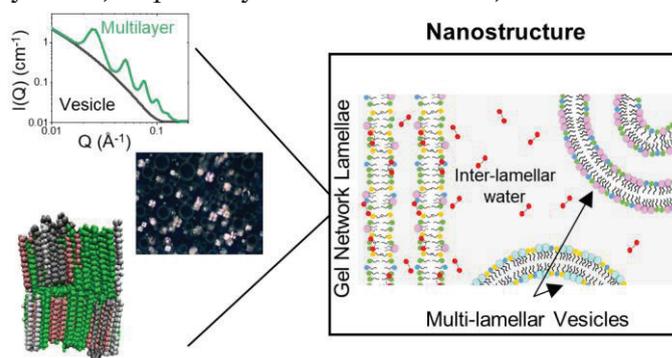


Figure 1. Schematic displaying the nanostructure of a lipid-based biomimetic skin care formulation derived through the synthesis of findings from experiments performed using a range of techniques.

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pH and thermo responsive schizophrenic self-assembly of PDEGMA-b-PDIPAEMA copolymers in aqueous media

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Many modern functional materials, nanostructures, and devices have polymers as integral parts. In recent years polymer research has focused on materials that respond to external stimuli such as pH, [1,2] temperature,[2,3] and ionic strength [4], thus named as responsive, “smart,” [5] and environmentally sensitive polymers.

The aim of this work is to study the schizophrenic self-assembly of a series of doubly responsive poly(di-[ethylene glycol] methyl ether methacrylate)-b-poly(2-[diisopropylamino] ethyl methacrylate) (PDEGMA-b-PDIPAEMA) diblock copolymers synthesized by RAFT polymerization. The homopolymer of di(ethyleneglycol) methyl ether methacrylate (DEGMA) is a hydrophobic polymer above its T_{cp} (around 27°C), and becomes hydrophilic below the T_{cp} . The 2-(diisopropylamino) ethyl methacrylate (DIPAEMA) homopolymer is a pH-responsive polymer with a pK_a of around 6.2. PDIPAEMA is water-soluble as a cationic polyelectrolyte, due to the protonation of the side amino groups and is transformed into a highly hydrophobic polymer at and above neutral pH, where deprotonation of the tertiary amine groups takes place. By using light scattering and fluorescence spectroscopy techniques it was possible to elucidate the self-organization of the block copolymers into nanoassemblies in aqueous media as a function of pH and temperature. The PDEGMA-b-PDIPAEMA copolymers form aggregates of increasing hydrophobicity as solution pH increases due to the deprotonation of the PDIPAEMA blocks and to a lesser extent as temperature increases due to the LCST behavior of the PDEGMA blocks. Composition of the copolymers also affects the size and mass of the nanoscale aggregates formed under different solution conditions. The increase of solution ionic strength affects the structural properties of the PDEGMA-b-PDIPAEMA aggregates at pH 3, where they are met in the form of strong polyelectrolytes, leading to the formation of aggregates of larger dimensions and mass at the highest ionic strength values investigated.

Keywords: double responsive copolymer, light scattering, ionic strength, RAFT polymerization

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Complex Coacervate based systems for Advanced Materials

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Complex coacervation is a self-assembly phenomenon arising from electrostatic interaction of oppositely charged macro-ions (e.g. proteins, dendrimers, polyelectrolytes, polypeptides, etc.) resulting in a liquid–liquid phase separation between one polymer rich aqueous phase and one polymer poor phase [1]. The dense phase relies mainly on electrostatic interactions and its composition and physical properties can drastically change depending on the salinity of the medium. Indeed, for a given polyelectrolyte couple, the material can transition from a free-flowing viscoelastic fluid to a rigid and brittle polyelectrolyte complex (PEC) solid [2]. This outstanding versatility has made complex coacervates good candidates for a wide range of applications [3].

In the Kamperman group in Zernike Institute for Advanced Materials at the University of Groningen, we are dedicated to improve and engineer complex coacervates to introduce novel advanced functional materials. To this aim, we have been either developing fully synthetic polymers imparted with carefully chosen additional chemical moieties or made use of natural polymers.

In this poster, the aim is to introduce our strategies to develop complex coacervate based underwater adhesives [4], double network hydrogels, 3D printing bioinks and responsive Pickering emulsifiers micelles.

Keywords: complex coacervation, polyelectrolytes, underwater adhesive, double network gels, 3D bioprinting, micelles

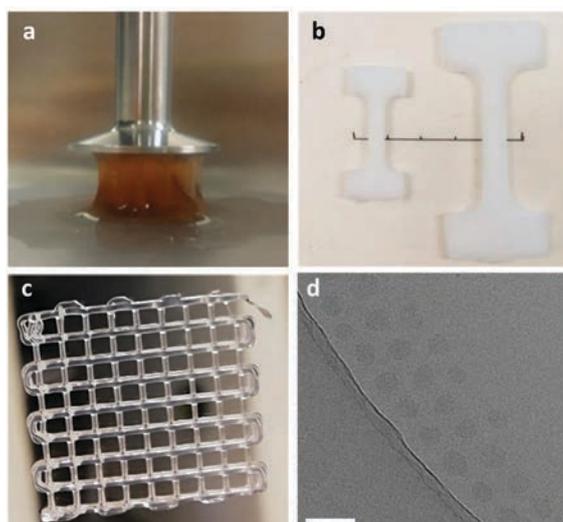


Figure 1. Applications of complex coacervates as a) underwater adhesive, b) sacrificial network for double network gels, c) ink for 3D bioprinting and d) emulsion stabilizer micelles. Scale bar is 100 nm.

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Novel Near-Infrared Conjugated Polymers for Photoacoustic Imaging

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The need for new or improved imaging probes without hazard effects for in vivo testing is always a bet for the researcher worldwide. Photoacoustic imaging (PA) is a noninvasive technique with many benefits in biological imaging, especially in the near-infrared (NIR) region, as it provides deep tissue penetration and high spatial resolution [1]. Thus, pathological tissue can be easily detected and visualized, taking advantage of the photoacoustic effect.

Conjugated polymers (CPs) are a type of macromolecules with an extended π -conjugated system which due to their highly electron-delocalized structures and efficient coupling between optoelectronic segments can absorb light energy in the NIR regions and effectively transformed it into photoacoustic energy [2]. Since CPs are generally hydrophobic, we implemented strategies to enable solubility in aqueous media. In this study, we examine the potential use of novel water-soluble conjugated polymers nanoparticles as photoacoustic imaging probes in-vitro. Under this scope we synthesized two novel π -conjugated polymers in donor-acceptor (D-A) structure, consisting of indacenodithiophene (IDT) (phenyl or benzyl substituted) as electron-donating and thiadiazoloquinoxaline (TDQ) as electron-deficient building blocks. The nanoparticles were formed *via* the encapsulation method by using the amphiphilic polymer *m*PEG-PLGA in order to be soluble in an aqueous solution.

Keywords: conjugated polymers, photoacoustic imaging,

Acknowledgements: This work was funding by the Helmholtz European partnering program for the cooperation between German Cancer Research Center (DKFZ) and National Hellenic Research Foundation (NHRF) to built the Athens Comprehensive Cancer Center (ACCC).

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Hexanoyl-modified Chitosan for Metal Ion Adsorption

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The N-acylation of chitosan with hexanoyl chloride is a known pathway for hydrophobization of this otherwise comparatively polar, biobased polymer(1). The majority of applications is located in the field of drug delivery, whilst only few investigations target the use as an absorber of pollutants such as metal ions(2). Hypothesizing that the same physical properties, such as self-aggregation and improved pH stability in solution, which are beneficial for drug delivery, may also endorse adsorption characteristics, we investigated hexanoyl chitosan (H-chitosan) for its adsorption capacities of Cd²⁺ and Al³⁺ (Figure 1).

Therefore, we chose a simple and cost-effective synthesis in water, which we subjected to a thorough investigation(3,4). By utilizing and comparing various analytical methods such as ¹H-NMR, ATR-FTIR and colloidal titration the degree of substitution (DS%) was determined. Further, the different reaction parameters were investigated. Especially, the pH of the reaction solution played a vital role in product formation regarding appearance and DS%.

Additional investigations showed that the DS%, and therefore the pH of the synthesis, has a great influence on the amount of adsorbed Cd²⁺ ions (differences between 0 to 91%). For Al³⁺ the modified chitosan exhibited higher adsorption than native chitosan. Thus, H-chitosan exhibits promising adsorption characteristics with great potential for application.

Keywords: hexanoyl chitosan; chitosan modification; substitution degree; pH variation; metal ion adsorption

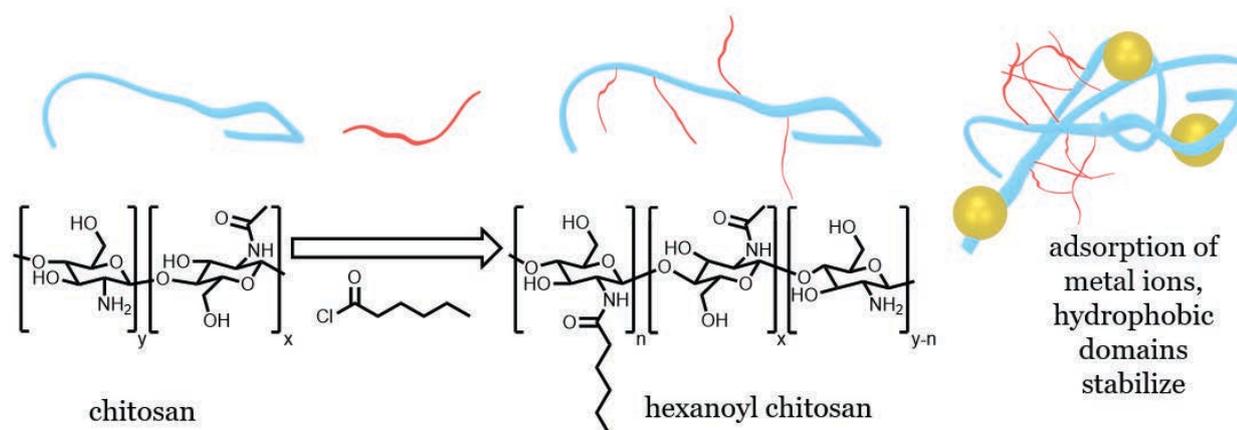


Figure 1. Modification of chitosan and subsequent adsorption of metal ions.

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Nanostructured Lipid Liquid Crystalline Films for Trapping Extracellular Vesicles (EVs)

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Extracellular vesicles (EVs) are natural nanosized vesicles, which represents essential regulators of intercellular and inter-organism communication. Due to their intrinsic circulation and targeting abilities -arising from their biological function- EVs are naturally endowed with extraordinary medical potential in fields such as drug delivery [1]. Understanding and controlling the interaction of EVs with biological barriers, such as cell membranes, is the key to develop engineered nanovesicles with optimized medical properties.

To this purpose, recent studies have focused on the interaction of EVs with biomimetic surface, mimicking the most common configuration encountered in cell membranes; on the contrary, almost nothing is known on their interaction with non-lamellar structures of higher complexity, such as “cubic membranes”, which are surprisingly common in cells under selective conditions. [2] Here we investigate the interaction of artificial cubic membranes based on glycerol monooleate (GMO) with EVs, by building-up complexity from biomimetic to natural EVs from milk and *Ascaris* source. This interaction has been characterized both in dispersion and at a surface level, by combining structural (i.e. Neutron and X-Ray Small Angle Scattering) and surface (e.g. Quartz Crystal Microbalance) techniques with microscopies (e.g. Confocal Laser Scanning and Cryo-Electron Microscopy).

By systematically varying the composition and surface charge of cubic phases, we demonstrate that EVs and their mimics can either adsorb or fuse with cubic membranes, provoking a dramatic rearrangement of the structural organization of the cubic membrane.

Keywords: non-lamellar cubic phase, extracellular vesicles, biomimetic systems

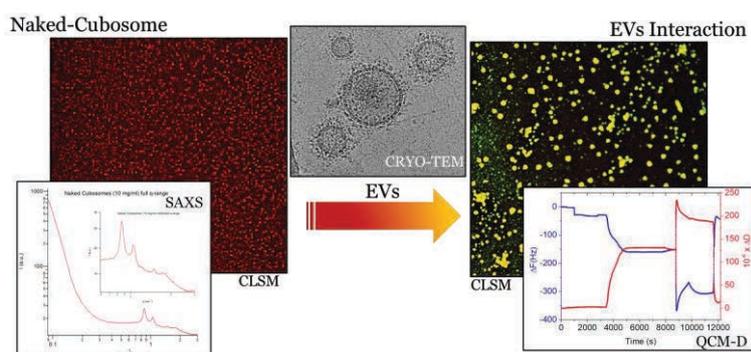


Figure 1. Chemical-Physical characterization of the EVs and naked-cubosome interaction

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A Self-Reporting Adduct for Real-time Fluorescence Monitoring of Molecular Imprinting Polymerization

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Understanding the mechanisms of formation of molecularly imprinted polymer (MIP) and MIP-ligand recognition can provide useful guidance to design better-performing MIP. Fundamental research based on *in silico* strategies, electronic structure methods and molecular dynamics simulations has brought in valuable insight into molecular imprinting systems. These techniques have allowed to study molecular interactions between functional monomer and template in pre-polymerization mixture as well as the characteristics of MIP-template recognition. However, monitoring molecular interactions during polymerization in real time has not been realized.

In this work, we use Alizarin Red S (ARS) as a model template and vinylphenylboronic acid (VPBA) as functional monomer to synthesize MIP. By monitoring the fluorescence of the ARS-boronic acid adduct, we are able to investigate the status of molecular complexation during the polymerization process as well as in the finished MIP.

ARS-imprinted polymers prepared by precipitation polymerization display high affinity and selectivity. The kinetics of ARS binding and release are monitored by separation-free fluorescence assay. Experimental results indicate that ARS binding with the imprinted polymer reaches equilibrium within 20 min, and the bound ARS can be released by adding fructose to the polymer. The interactions between ARS and VPBA/the growing polymer chains are also studied in real time. The boronate ester bond between ARS and VPBA is stable during the polymerization process, and the imprinted polymer starts to form within 20 minutes. This work opens new possibilities to study molecular imprinting in real time. The experimental approach will help to develop new MIP with better performances.

Keywords: molecular imprinting, real-time monitoring, fluorescence

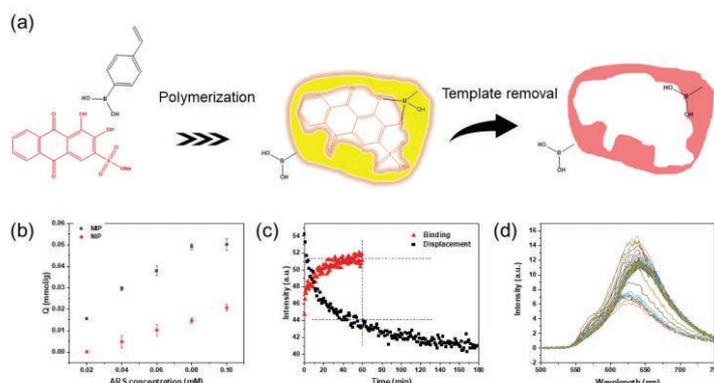


Figure 1. (a) Synthesis of ARS-imprinted polymer particles, (b) binding curve of ARS on MIP and NIP particles, (c) kinetic curves of binding and displacement of ARS in MIP, (d) the fluorescence spectrums of ARS imprinting polymer acquired at different times.

The impact of molecular architecture of block copolymers on lubrication efficacy in non-aqueous media

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Transportation consumes 27% of global energy. Most of the energy is lost *via* exhaust and cooling processes; a staggering 33% is lost to friction when the energy is converted to mechanical power. Recent studies suggest that in the short term (~8 years) 620MtCO₂ and 9.1EJ could be saved in the transportation sector alone per annum if advanced tribological techniques and materials are applied^[1]. Consequently, it is important to minimise friction by developing new additives that operate in the boundary regime between rubbing surfaces.

In collaboration with Infineum (a world-leading engine-oil additive company), novel, custom designed polymers of varying molecular architectures (random, diblock, multiblock and homopolymer) consisting of polar, hydrophilic blocks and non-polar, hydrophobic blocks in *n*-dodecane solvent (model oil) will be compared. Both the normal and shear forces are measured using the surface force apparatus (SFA, Fig.1), from which the structure and lubrication mechanisms can be elucidated^[2]. Furthermore, complementary data from small-angle neutron scattering (SANS, Fig. 2) and adsorption isotherms provide complementary understanding of their properties in the bulk solution and at the interface. Such fundamental studies will assist rational design of future polymeric friction-modifying additives for mechanical lubrication, which is of immense environmental and economic importance.

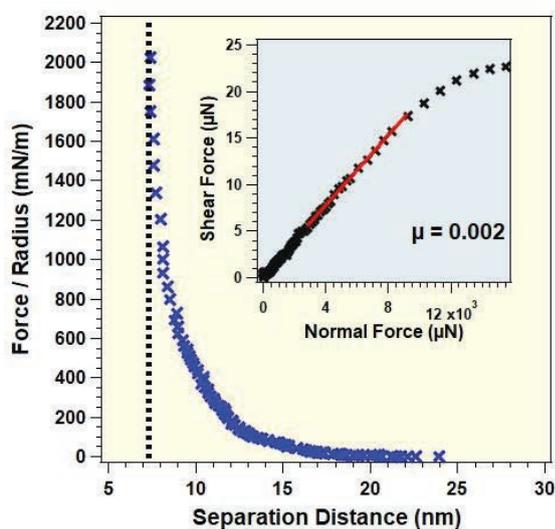


Figure 1. SFA measurements of 1wt% diblock copolymer dodecane solution revealing ultra-low friction.

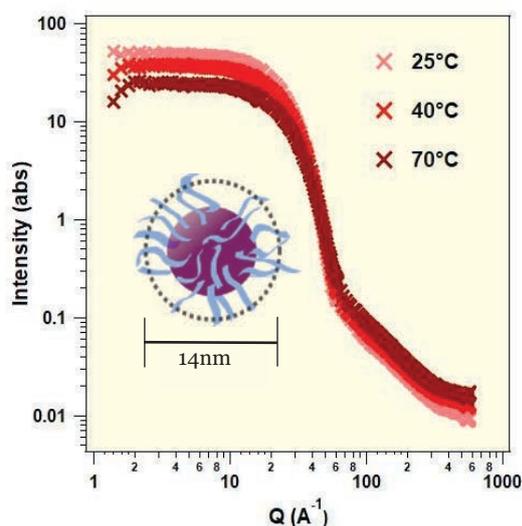


Figure 2. SANS of 1wt% diblock copolymer in dodecane at different temperatures.

Key Words: Polymers, Surface Forces, Friction

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Backflow of P-atic topological defects

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Topological defects are ubiquitous in nature. They appear, for example, as cosmic strings/domain walls in cosmology, vortices in superfluid helium and, finally, as dislocations/disclinations of various charges in liquid crystals. They strongly affect the relaxation dynamics of their physical systems, and in two dimensions they provide a remarkable mechanism for phase transitions (Berezinskii–Kosterlitz–Thouless, 2016 Nobel Prize in Physics).

The study of the effects of external flows on liquid crystals through hydrodynamics has been a long-term endeavor. However, less light has been shed on the self-generated flow of defects (backflow), which significantly affects their trajectory. In previous work [1], this effect had only been studied in the case of nematic liquid crystals, but even for nematics the precise origin of the flow has yet to be pinpointed.

By solving the Navier-Stokes equation coupled to the evolution of the order parameter analytically and numerically, we quantify the relevance of all sources of backflow in systems with p-atic orientational order; for any $p \geq 2$, where $p = 2$ corresponds to nematics. Finally, we explain how these findings may lead to an experimentally verifiable prediction of the elusive flow alignment parameter. This study helps set the foundation for the emerging field of active p-atics, which will enrich our understanding of morphogenesis and metastasis of epithelial tissues [2].

Keywords: Liquid crystals, Phase transitions, Rheology, Biophysics.

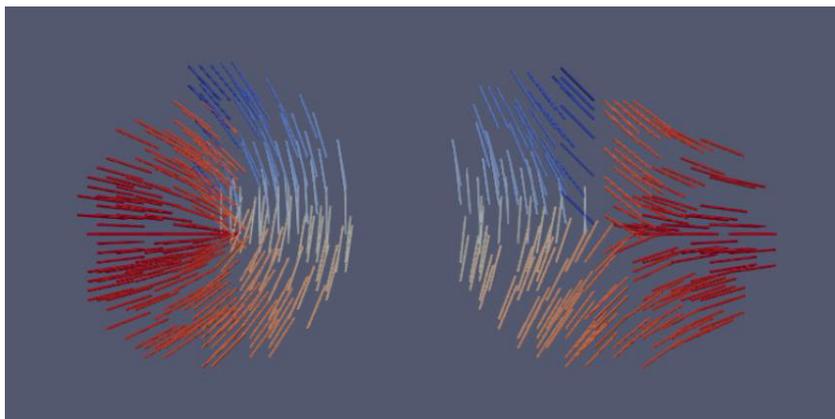


Figure 1. The director field of $+1/2$ and $-1/2$ nematic defects.

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EP9.31

Thermoresponsive heavy metal-mopping magnetic nanoparticles for the treatment of wastewater

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With this work we present a comprehensive experimental, theoretical, and computational study aimed at designing macromolecules able to adsorb a cargo at the nanoscale. Specifically, we focus on the adsorption properties of star di-block copolymers, i.e., macromolecules made by a number f of H-T di-block copolymer arms tethered on a central core; the H monomeric heads, which are closer to the tethering point, are attractive toward a specific target, while the T monomeric tails are neutral to the cargo. Experimentally, we exploited the adaptability of poly(2-oxazoline)s (POxs) to realize block copolymer-coated nanoparticles with a proper functionalization able to interact with heavy metals and perform a thermoresponsive behavior in aqueous solution.

EP9.35

**Sugar-boronate organogels:
structure, rheology and water-sensitivity**

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Physical organogels are obtained by adding a small amount of a small molecule (less than 5% wt) called organogelator into an organic solvent, and are known as a promising source of soft materials with applications in medicine, food industry or analytical chemistry.

Sugar-based derivatives are already known for their potential as remarkable organogelators.^[1]

Here we describe a new class of organogelators obtained by esterification of a glycolipid with an aromatic boronic acid. A series of sugar-boronate derivatives is synthesized: on one side, the length of the alkyl chain (originating from the glycolipid) can be varied, as well as the aromatic part on the other side (originating from the boronic acid).

Our experiments show the ability of these derivatives to gelify different organic solvents (toluene, cyclohexane, ethyl myristate...), evidencing their strong potential as organogelators.

The produced organogels are then fully characterized - from the macroscopic scale to the molecular one - by rheometry, electron microscopy (SEM) and X-ray diffraction, and the impact of chemical structure on the organogel properties are discussed.^[2]

Moreover, thanks to the boronate function, our organogels are water-sensitive, and get back to a liquid state in contact with water. We also demonstrate here that the chemical structure of the organogelators sets the behavior and dynamics against this hydrolysis.

In addition some members of this organogelator family can bear fluorescent properties, and the potential of this new feature is also discussed.

Keywords: organogel – sugar-boronate – multiscale characterization - water-sensitivity - fluorescence

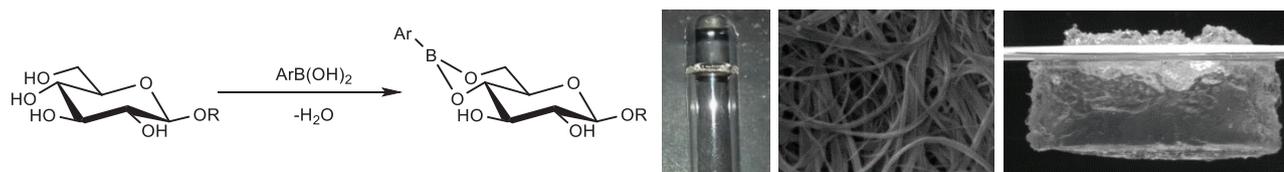


Figure: Synthesis of arylboronate glucosides, gelation in toluene, SEM image of the fibrillar network and hydrolysis of the *n*-butyl derivative.

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Phase changes within interpenetrated bioamphiphile/biopolymer hydrogels: responsive elastic properties and improved strength

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Hydrogels are materials of high interest for many applications. Their mechanical properties and behavior regarding external stimuli directly depend on their components. Recent research is devoted to the development of interpenetrated hybrid hydrogels. Indeed, the ones involving an amphiphilic molecule and a polymer would benefit from their respective fast phase change and good mechanical properties. According to a safety-by-design approach, our goal is to develop stimuli-responsive hydrogels from entirely biobased components.

The phase behavior of bioamphiphiles, also known as biosurfactants, strongly depend on physicochemical stimuli and the variety in their phase behaviour under dilute conditions is impressively large. (1) Fast phase change can then be an interesting tool to modulate the elastic properties of polymeric hydrogels, and in particular of biopolymers.

In the present work, we will show how the elastic properties of well-known biopolymers, e.g., gelatin, at a concentration >1wt%, can be controlled through an externally induced micelle-to-vesicle-to-fiber phase changes of the same selected bioamphiphile. In the micelle or vesicle region of the bioamphiphile phase diagram, the elastic properties of the biopolymer hydrogel are either not affected or completely disrupted. In the fiber region of the phase diagram, the elastic properties are, on the contrary, enhanced.

Keywords: biosurfactant, stimuli-responsiveness, interpenetrated network, hydrogel

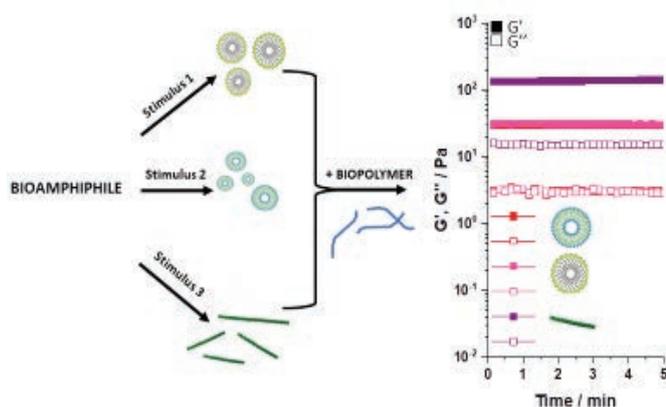


Figure 1. Mechanical properties of the G-C18:1 phases combined with gelatin

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Rheology of Fish Gelatin Hydrogels Modified with Sodium Alginate

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Fish gelatin is widely used in food, pharmaceutical, cosmetic, and biomedical fields, and it can be utilized as a substitute for mammalian gelatin, which was criticized for many years [1]. Nevertheless, compared with mammalian gelatin, fish gelatin possesses inferior rheological properties (low gelling and melting temperatures, gel strengths), which limits its practical application. One of the most promising strategies for improving the rheological properties of fish gelatin is its modification with natural polysaccharides. One of the commonly utilized compounds for this purpose is sodium alginate. The interaction between gelatin and sodium alginate leads to the formation of polyelectrolyte complexes. At a certain biopolymer ratio, pH, and ionic power of the medium, these complexes become gels. As fish gelatin has a different structure, composition, and rheological properties to that of mammalian gelatin, further research is required to better understand the mechanism of such modifications and expand the application of fish gelatin.

Viscoelastic properties of gels formed by polyelectrolyte complexes comprising cold-water fish gelatin (G) and sodium alginate (SA) in a wide range of mass ratios Z ($Z = C_{SA}/C_G$, g_{SA}/g_G) were investigated using oscillatory rheology. The maximum values of sol-gel transition temperature, elastic modulus, and viscosity of the gels were observed at a characteristic mass ratio $Z^* = 0.06$, and this ratio quantitatively correlates with the concentration of ionic groups in the components of the complexes.

The interaction of gelatin with sodium alginate was investigated using UV-spectroscopy. At low Z , less than the characteristic value Z^* , the structure of the system is homogeneous; it consists of stoichiometric SA-gelatin complexes and unbound gelatin macromolecules. At larger mass ratio values, the system is characterized by a heterogeneous structure, arising from the presence of non-stoichiometric complexes. This leads to the distinct behavior between systems with low and high Z .

Keywords: fish gelatin, sodium alginate, polyelectrolyte complexes, gel-liquid transition, rheology, viscoelastic media

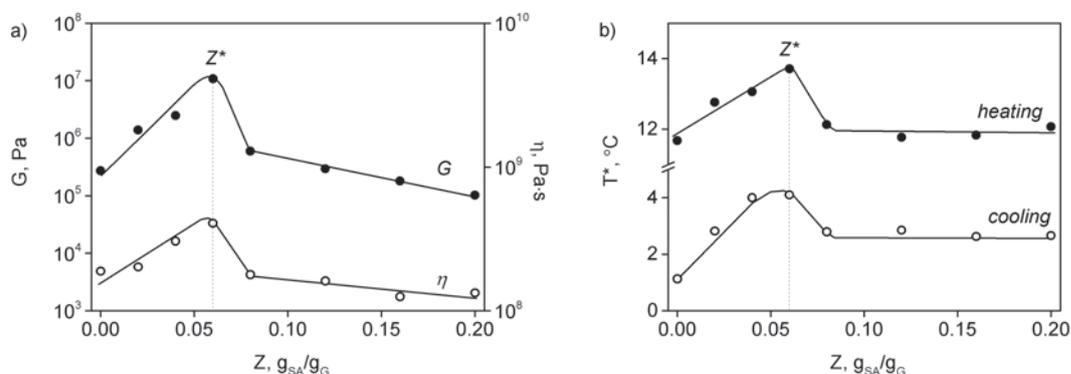


Figure 1. (a) Elastic modulus and shear viscosity dependency on Z at $\sigma = 5$ Pa and 4 °C. (b) Transition temperature T^* dependency on Z for cooling and heating at temperature ramp of 1 K/min.

Acknowledgements: This work was supported by the Russian Foundation for Basic Research (project no. 19-016-00118).

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HPMC and chitosan film as an enzyme carrier

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The use of polymers in the form of hydrogel films has been proposed as an alternative solution to acquire a biocatalyst with good mechanical properties¹. In this frame, the present work reports on the use of a hybrid blend of biopolymers that provides enhanced immobilization capability, biodegradability and flexibility². Simultaneous blending of HPMC with chitosan could expand their potential usages. The two biopolymers were combined in order to formulate a promising enzyme carrier for the synthesis of propyl laurate. The biocatalyst was studied in terms of its capability to provide an appropriate environment where lipase from *Mucor miehei* will maintain its activity and stability in organic media. Several parameters were examined in order to optimize the conditions to a model esterification reaction.

According to our findings, the highest efficiency regarding the synthesis of propyl laurate was achieved using the system with polymer ratio 2:1 HPMC to chitosan, respectively. By increasing the amount of the enzyme entrapped in the matrix of the film the initial rate of the reaction increases, showing diffusion restrictions. Moreover, the use of ultrasound significantly accelerates the catalysis. The highest lipase activity was observed in isoctane and hexadecane. The reuse of the biocatalyst was studied presenting excellent results. The enzyme maintained its full activity for 35 uses. Finally, Atomic Force Microscopy (AFM) was conducted for surface examination of the biocatalyst and Small Angle X-ray Scattering (SAXS) was used in order to clarify the possible alterations that may be provoked in the film matrix after enzyme incorporation.

Keywords: biocatalysis, biopolymers, SAXS, AFM

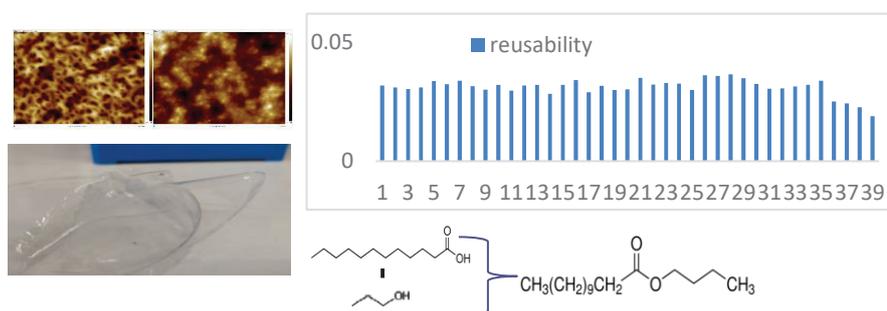


Figure 1. HPMC and chitosan film for the entrapment of lipase from *Mucor miehei*. Operational, structural and morphological study.

Acknowledgements: The authors thank Prof. Frédéric Nallet, from CRPP for his help in the analysis regarding the SAXS results; Mr. Hassan Saadaoui and Gilles Pecastaings from CRPP for their help on AFM experiments.

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Mikto-arm star cationic polyelectrolytes as insulin nanocarriers

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The complexation of proteins with nanoparticles of self-assembling polyelectrolytes is attractive for applications in biotechnology and nanomedicine [1]. Star copolymer polyelectrolytes combine properties of self-organizing macromolecules with architectural integrity. However, relevant literature is limited. In this presentation the investigation of the star copolymer containing mixed arms of the hydrophilic poly(oligo ethylene glycol methacrylate) and the cationic polyelectrolyte poly(2-(dimethylamino)ethyl methacrylate) (star-PDMAEMAx-POEGMAy) and their electrostatic complexation with the protein-drug insulin are discussed. The star copolymers were synthesized by RAFT polymerization [2] whereas the pH responsive PDMAEMA arms are also modified to a QPDMAEMA cationic polyelectrolyte by a quaternization reaction. Both mikto-arm stars showed stability in water with aggregate sizes in the order of 100-150 nm and ζ -potential at 20-40 mV. Complexation with insulin led to an increase in the mass of the aggregates. Interestingly, increasing salt concentration resulted in increased mass and size at intermediate ionic strengths for high insulin content, whereas the effect was diminished at physiological salt conditions (Figure 1). This work motivates the use of mikto-arm star polyelectrolytes in protein and drug delivery.

Keywords: star polyelectrolytes; amphiphilicity; light scattering; insulin

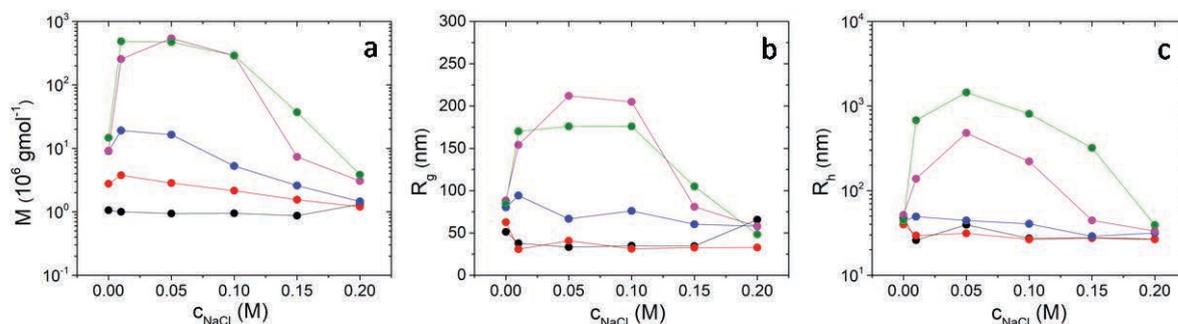


Figure 1. (a) Molar mass (b) radius of gyration and (c) hydrodynamic radius at 0 (black), 0.125 (red), 0.250 (blue), 0.375 (magenta) and 0.500 (green) mgmL $^{-1}$ INS for star-PDMAEMAx-POEGMAy at 0.5 mgmL $^{-1}$.

Acknowledgements: This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Reinforcement of Postdoctoral Researchers - 2nd Cycle” (MIS-5033021), implemented by the State Scholarships Foundation (IKY).



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Cellulose model surfaces as an approach to study the interaction between fibers and additives in paper

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Paper, as a functional material, has a high importance in a variety of sectors: packaging, print media and speciality papers. The multilateral use is especially crucial with regard to reducing plastic use and waste and replacing it with renewable and biodegradable resources.[1] The modification of papers is done through functional additives, e.g. wet-strength increasing polymers. The interactions of cellulose fibers with the additives have been investigated in the past with respect to the mechanical properties of the resulting paper.[2-4] Yet, a systematic understanding of the effects of the chemistry and structure of the polymer on the properties of the fibers is still missing and would lead to an exhaustive knowledge of the functionalization of paper.

In the present study, cellulose model surfaces were prepared from trimethylsilyl cellulose (TMSC). The model surfaces were characterized with regards to film thickness and morphological properties. We used the model surfaces to study the interaction with two different polymeric additives. In the first instance, a cross-linkable polymer is deposited onto the model surface and the change in swelling behavior is studied. The crosslinking between the additive and paper fibers would in future allow for a semi-irreversible increase in wet-strength.

In the next step, the cellulose surfaces are coated with core-shell particles. The shell consists of a pH-responsive polymer bearing positive charges, leading to an adsorption to the partially negatively charged cellulose surface. The adsorption is characterized by the density of particles and the influence of parameters such as pH-value and concentration of the particle solution is studied. The use of these core-shell particles allows the functionalization of fibers to create elastic papers with a wide range of applications.

Keywords: cellulose model surface; paper functionalization; wet-strength; elastic paper

Acknowledgements: The authors gratefully acknowledge funding by the DFG.

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Microbial glucolipids: new stimuli, new phases, new properties.

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Microbial surfactants are a kind of biosurfactants entirely produced by a microbial fermentation processing. They are made from sugar and vegetable oils, they have an excellent bio-compatibility and they are biodegradable.

The yeast *S.Bombicola* Δ ugtB1 is known to mainly produce glucolipids. At room temperature, these molecules reversibly undergo a micelle-to-vesicle or a micelle-to-lamellar phase transition in water, depending on pH and saturation of the aliphatic backbone. [1] For neutral/acidic conditions, saturated glucolipid stabilize lamellae while monounsaturated glucolipids self-assemble into vesicles. In the former case, gelation spontaneously occurs by the presence of defect at different scales into the lamellar domains. [2] At basic pH, both compounds form a micellar phase. Both the micellar and vesicle phase has no remarkable elastic properties.

In this presentation, we show how the micelle-to-vesicle phase transition of monounsaturated glucolipids can be shifted to a micelle-to-fiber transition by playing on the type of counterions. The novel phase spontaneously and immediately displays thickening of the solution and hydrogels formation at water content as high as 98%. We study the elastic and structural properties monounsaturated glucolipids hydrogels by associating rheology and small angle X-ray scattering (rheo-SAXS) as well as cryo-TEM.

Keywords: Hydrogels, self-assembly, biosurfactants

Acknowledgements: Sophie Roelants (Ghent University) to provide the glucolipids within the framework of the APPLISURF Project.

Javier Perez (Soleil Synchrotron) is kindly acknowledged for his assistance on SAXS experiments. This work is funded by French ANR, SELFAMPHI Project.

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Incorporation of Dopamine Methacrylamide into PNIPAM microgels for increased adhesion

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Microgels are colloidal particles, which are highly swollen in a solvent like water. One of the most commonly studied microgels is poly(N-isopropylacrylamide) (PNIPAM). As a stimuli-responsive microgel, it undergoes a volume phase transition (VPT) when heated above its lower critical solution temperature (LCST) at 32°C.

The co-polymerization of PNIPAM is a well-defined technique to achieve unique microgel systems. Dopamine methacrylamide (DMA) is a catechol-based monomer, which can be found in marine organisms like mussels. It has been identified to be main responsible for the unique adhesive properties of these organisms. A co-polymerization of PNIPAM with DMA bears a huge potential especially in the field of biological and medical engineering.

In literature the formation mechanisms of the microgel network are shown, while using [1-2]. Furthermore, it is well-known that such catechol-based monomers like DMA have a high radical scavenging ability [3] and thus cross-link the microgel [1-2]. This counteracts the increasing adhesion ability of microgels at the surface. In order to ensure an increased adhesion ability DMA should be located in the microgel shell, but, so far, a detailed understanding of the DMA co-polymerization is missing.

Therefore, the present study reports a detailed view into the reaction kinetics of DMA during the microgel synthesis. DMA was incorporated into PNIPAM microgels. The consumption of the different components was analysed at different times during the synthesis by mass spectrometry. The built-in DMA was verified by UV-VIS standard addition and NMR spectroscopy. First adhesion test under water will be presented.

Keywords: PNIPAM microgels; reaction kinetics; Dopamine methacrylamide; catechol chemistry; Adhesion

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EP9.43

Use of layer-by-layer coating of electrodes by polyelectrolytes for capacitive deionization of solutions

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When an electric potential difference is established between porous electrodes immersed in an aqueous solution, the migration of ions to their respective counter-electrodes brings about a reduction of the ionic content of the bathing solution, in a process known as *capacitive deionization* of the solution, increasingly identified as a promising tool for (partial) desalination of brine waters [1]. The method performance can be significantly improved if the electrodes are covered by ion-exchange membranes or by polyelectrolyte layers (membrane CDI and soft-electrode CDI, respectively).

In this work, we propose to investigate the deionization achievement of carbon electrodes coated by multilayers of polyelectrolytes of alternating polarity. Using the layer-by-layer method [2], the electrodes were coated with layers of the anionic (cationic) polyelectrolyte polystyrene sulfonate, PSS (poly(diallyldimethyl-ammonium chloride), PDADMAC), following the sequences +/-+/- on one of the electrodes, and -/+/-/+ on the other. Fig. 1 illustrates some results, obtained with one to three layers of polyelectrolyte.

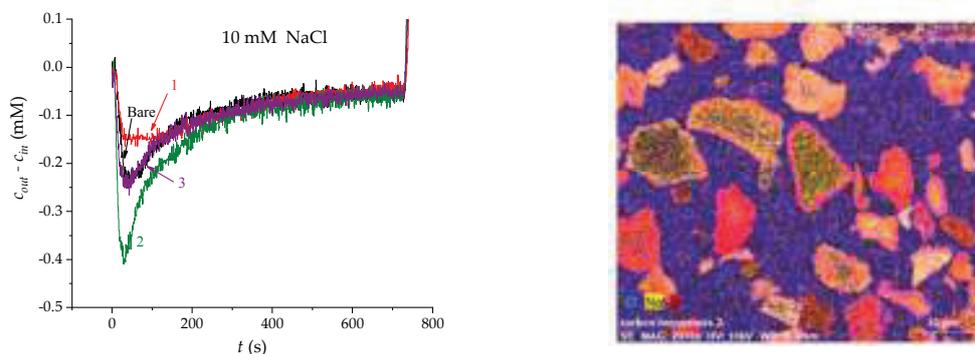


Figure 1. Left: Difference between the initial and exit concentrations of 10 mM NaCl solutions after passing along the inter-electrode channel (500 μm thickness) subjected to 1.2 V potential difference. The number of layers is indicated. Right: EDX image of a PDADMAC/PSS coated electrode. Color code: carbon:cyan; chloride (PDADMAC): blue; sodium (PSS): yellow; sulfur (PSS): red.

As observed, the application of just the first layer does not produce a significant improvement over the amount of desalination reached with bare electrodes. The EDX analysis of the carbons demonstrated in fact that this layer does not penetrate deep into the carbon pores. But the addition of the oppositely charged second layer (observed by EDX, Fig. 1, right) leads to almost 100 % increase in performance, indicating the role of “seed” of the first one for the attachment of the second. No further improvement results from extending the procedure to 3 or 4 layers.

Keywords: Capacitive deionization, layer-by-layer, polyelectrolyte, porous carbon, soft electrodes

Acknowledgements: Financial support by Junta de Andalucía, Spain (FEDER Grant No. B-FQM-141-UGR18) and MICINN, Spain (PGC2018-098770-B-I00) is gratefully acknowledged.

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Enzyme Cross-linked Pectin Microgel Particles for Use in Foods

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We report on a new enzyme-based method for producing permanently cross-linked pectin microgels. We investigate the shape, size and rheological properties of these microgel particles making comparisons to the more traditional design of calcium cross-linked pectin microgels. Both sets of microgel particles were prepared via the 'top-down' mechanical disruption of parent pectin hydrogels in the presence of excess solvent.

The first hydrogel was prepared from low methoxyl pectin (*LMP*) (2 wt.% pectin) cross-linked using Ca^{2+} (8.3 mM CaCl_2). The resulting *LMP* microgels show particle sizes ca. 1 to 100 μm , but are stable only in $[\text{Ca}^{2+}] = 8.3$ mM or above, swelling and/or dissolving rapidly in pure water. The second type of microgel was prepared from sugar beet pectin (*SBP*) hydrogels covalently cross-linked via laccase. Gelation kinetics were investigated by small amplitude oscillatory shear rheometry. The *SBP* microgels resisted dissolution in water for several months. Light scattering measurements suggested that the *SBP* microgel particle sizes were related to the mechanical properties of the parent hydrogels. Various imaging techniques all suggested that *SBP* microgels have highly irregular shapes owing to the top-down technique used for their manufacture. Concentrating the *SBP* microgels (to 35 - 50 wt.% microgel, or 0.6 - 0.8 wt.% overall pectin concentration) resulted in suspensions with rheological properties typical of yield stress fluids. When compared at similar overall *SBP* concentrations, the *SBP* microgel suspensions offer distinct advantages as bulk rheology modifiers compared to *SBP* solutions.

Keywords: Pectin, Microgel, Rheology, Laccase

Theoretical modeling of metal-organic precursor structures on surfaces

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Surface-assisted synthesis of organic nanostructures has been recently recognized as a useful method to create low-dimensional covalently bonded polymers with tailorable structure and functions. In this work the Monte Carlo simulation method [1-3] was used to study the metal-organic precursors of covalent polymers formed in the Ullmann-type coupling reaction of halogenated polyaromatic hydrocarbons (PAHs). To that end a coarse grained model was proposed in which the monomers, represented by a collection of interconnected segments, and two-coordinate metal atoms (one segment) were adsorbed on a triangular lattice mimicking (111) catalytically active crystalline surface. Different distributions of halogen atoms in the monomer molecules were modeled using appropriately assigned directional interactions, sustaining the resulting metal-organic labile links. Depending on the halogen content and distribution in the molecule, the simulations predicted creation of diverse supramolecular connections such as linear and cyclic aggregates, ordered and aperiodic networks and other more complex forms including fractal-like patterns. Moreover, in the case of the prochiral monomers the calculations demonstrated basic structural differences between the enantiopure and racemic assemblies in which chiral separation and mixing was observed. The obtained results can be helpful in directing the surface-assisted polymerization reactions towards organic structures with predefined size, shape, symmetry and connectivity.

Dual-responsive tubule-based hydrogels for protein loading

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Delivery nanocarriers can be designed to selectively change their characteristics in response to intrinsic physiological stimuli or externally applied stimuli [1]. Amino acid-based surfactants are particularly amenable to generate such nanocarriers because of their high biodegradability, reduced human cytotoxicity and multifaceted self-aggregation [2-4]. In this work, we investigated three families of novel anionic double-chained lysine-based surfactants, with variable degree of chain length mismatch [3,4]. The effects of the chain length asymmetry and structural isomerism of the surfactants on their interfacial properties, thermal behavior and self-assembly in water were studied by surface tension, DSC, imaging techniques and SAXS. Below their Krafft temperature, all the amphiphiles self-organize into tubular structures of various morphologies (flat structures, twisted and coiled ribbons, and hollow tubes) [3]. In particular, the tubules consist of long, multilamellar, hollow cylinders that give rise to a swollen entangled network (hence gelation). Besides exhibiting temperature-driven tubule-to-micelle and tubule-to-vesicle phase transitions, these systems are also pH-sensitive, due to a carboxylate group in the surfactants' headgroup [3,4]. The interactions of the tubules with a model protein, lysozyme (LZM), were then investigated with the aim of developing topical applications for the hydrogels (Figure 1) [4]. The gels are efficient in entrapping LZM and display different release profiles, depending on the applied stimulus (T and/or pH). Cytotoxicity studies further show that the hydrogels have good levels of biocompatibility and are thus promising for biological applications.

Keywords: lysine-based surfactants; self-assembly; tubular structures; hydrogels; delivery systems; cytotoxicity.

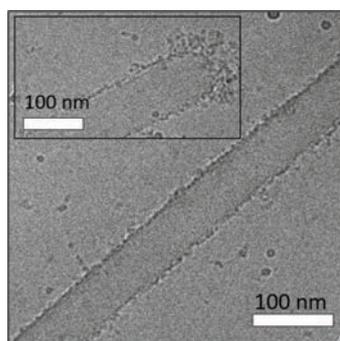


Figure 1. Cryo-TEM micrographs of 10Lys14/LZM system, at 3 mM surfactant concentration and 0.15 mg of LZM.

Acknowledgements: This work was supported by FEDER/COMPETE and FCT through grants UID/QUI/0081/2020, POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028.

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Polymer/surfactant mixtures as dispersants for multiwalled carbon nanotubes: synergism, antagonism and molecular insight

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Surfactants and polymers have been independently investigated as agents to separate, disperse and stabilize carbon nanotubes (CNTs) in water [1-3], yet mixed polymer/surfactant (P/S) systems have been far less explored in that realm. In this work, we investigate the ability of various types of P/S mixtures to effectively separate multiwalled carbon nanotubes (MWNTs) in water, using rigorously controlled processing conditions [3]. We explore two types of mixtures: i) nonionic polymer (polyvinylpyrrolidone, PVP) and ionic surfactant (sodium dodecylbenzene sulfonate, SDBS, or cetyltrimethylammonium bromide, CTAB); and ii) ionic polymer (poly(diallyldimethyl ammonium chloride), PDDA, and sodium polyacrylate, PAS) and nonionic surfactant (TX100). Detailed, high precision dispersibility curves (concentration of dispersed nanotubes vs. total P + S concentration, at fixed S concentration) are presented for four P/S mixtures (PVP/SDBS, PVP/CTAB, PDDA/TX100 and PAS/TX100) and their respective individual components. Quantitative metrics extracted from the dispersibility curves allow for solid comparisons between the systems. Depending on the P/S mixture, either beneficial (synergistic) or detrimental (antagonistic) effects in nanotube dispersibility are observed compared to the individual components. The P/S systems were also investigated per se by surface tension curves, where polymer concentration was fixed at 0.1 wt% and surfactant concentration varied. These studies clearly show strong interactions in the PVP/SDBS and PVP/CTAB and basically no interactions between TX100 and the polyelectrolytes. Zeta potential measurements provide further information on surface charge effects and electrostatic interactions at play in the P/S systems and in the P/S + MWNT dispersions. Morphological characterization of the as-obtained dispersions by scanning electron microscopy (SEM) shows a significant degree of nanotube separation by the P/S systems. The overall results are interpreted in terms of the interplay between the P/S systems and the nanotube surface, on one hand, and kinetic aspects inherent to the mechanism of MWNT exfoliation/separation upon sonication, on the other hand [4,5]. P/S association may not only offer conditions for enhanced CNT dispersibility but also expand the types of noncovalent, reversible functionalization required in many applications, such as the development of hybrid films and coatings.

Keywords: Multiwalled carbon nanotubes; surfactant; polymer; liquid-phase exfoliation

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EP10.1

A multistate adsorption model for the adsorption of C₁₄EO₄ and C₁₄EO₈ at the solution/air interface

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Langmuir was the first who realized that the area occupied by a surfactant molecule at the interface is one of the key parameters in determining the adsorption behaviour of the surfactant. There are, however, many surfactants that can adopt different conformations and, therefore, can occupy different molecular areas at the interface. For example, surfactants with flexible ethylene oxide chains can allow a large variety of conformations of the molecules at the interface. For such surfactants a reorientation model was proposed, which assumes two possible adsorption states. However, there are obviously surfactants for which assumption of only two adsorption states can be insufficient. The aim of the present work was to extend the classical reorientation model to a larger number of adsorption states. This refined adsorption model, considering here up to 10 possible states, was applied for the analysis of the surface tension isotherms for C₁₄EO₄ and C₁₄EO₈ as well as the surface dilational viscoelasticity at a fixed oscillation frequency of 0.1 Hz, all measured by bubble profile analysis tensiometry. It was shown that assuming an entire spectrum of molecular conformations adsorbing in a coexisting way allows a much better representation of the dilational surface viscoelasticity as a function of bulk concentration, than the classical 2-state reorientation model does, while providing the same good accuracy for the surface tension isotherms.

Keywords: Surface tension isotherm, Dilational surface viscoelasticity, Reorientation adsorption model, Multistate adsorption model, Bubble profile analysis tensiometry, Poly(oxyethylene) alkyl ether

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EP10.2

Bulk and Interface behavior of Rhamnolipids

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Rhamnolipids (RLs) are glycolipids produced by bacterium *Pseudomonas aeruginosa*. Due to their high biodegradability their environmental impacts are less. RLs have been increasingly getting attention over synthetic surfactants due to lower toxicity, stability at high temperatures, PH and salinity. RLs are reported to be capable of oil water separation, Membrane interactions and bioremediation. Our study aims at design of RLs for industrial applicationa by fixing the dosage and ambient parameters to optimize the process. In this study we are checking the feasibility of RLs to replace synthetic surfactants. We are using Coarse-Grained molecular simulation to explore the phase behavior of RLs (Both Mono-RLs and Di-RLs) as a function of temperature and concentration. Interface studies are done with air-water and decane water system for surface tension measurements. Mixing of Mono and Di rhamnolipids is giving synergy in significant surface tension reduction at certain concentration. More over Di-Rhamnolipids can exhibit cytokinesis and cause cell wall lysis as experimentally reported. We are giving a molecular level explanation for this phenomena also.

The Diverse Phase Behavior of Lipid Monolayers Containing Glycolipids

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Glycolipids are abundant constituents of biological membranes, which are known to be involved in lipid lateral phase separation [1,2]. There have been great efforts towards an investigation of the transient formation of ordered lipid domains in model membrane systems [3]. Recently it was demonstrated that depending on the tail and saccharide chemistry glycolipids can form highly-ordered 2d-crystalline arrangements involving the alkyl chains and saccharide headgroups ordering and a molecular superlattice formation [1].

In the present study by means of the GIX diffraction, isotherm measurements, and BAM we investigate the phase behavior of Langmuir monolayers containing glycolipids with various saccharide headgroups in mixtures with phospholipids or other glycolipids. The headgroup-dependent structural fingerprint of molecular superlattices in the form of distinct GIX diffraction patterns puts us in a unique position for a systematic structural investigation of glycolipid ordered domains at the molecular scale. The experiments reveal a rich phenomenology, ranging from complete demixing to the formation of mixed-lipid ordered domains or the complete loss of headgroup ordering. The phase behavior is governed not only by the tail but also by the headgroup chemistry. Remarkably, glycolipid-enriched domains can recruit and integrate phospholipids which are otherwise disordered under the imposed conditions, stoichiometric mixed glycolipid molecular lattices are found to occur.

Keywords: Glycolipid, Phospholipid, Langmuir monolayer, grazing incidence X-ray diffraction, lipid domains

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Evaporation Kinetics of Soft Colloids on Hydrophobic Surfaces

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We report a comparative study of the evaporation kinetics of aqueous sessile drops containing hard and soft microgel (crosslinked poly (N-isopropylacrylamide) (p-NIPAM)) particles placed on hydrophobic surfaces. The droplets containing hard colloids typically follow a constant contact angle mode of evaporation on substrates with low contact angle hysteresis [1]. The droplet remains pinned for a brief period initially, and as the evaporation progresses, the contact angle falls below the receding contact angle triggering a continuous slippage of the contact line, thereby leading to the formation of a dot-like central deposit after complete evaporation of the fluid. In contrast, when soft microgel particles replace the hard colloids, the sessile drops remain pinned to the hydrophobic surface and evaporate in the constant contact radius mode. This is understood by taking into account the spontaneous adsorption of soft microgels to the air-water interface and the resulting reduction of the interfacial tension [2]. The magnitude of force acting at the three-phase contact line responsible for the depinning of the sessile drop gets weaker and becomes insufficient to cause depinning of the contact line. Therefore, the sessile drop remains pinned to the hydrophobic surface and finally forms a uniform colloidal deposit after the complete evaporation of the solvent [3,4]. The critical microgel concentrations required to suppress the depinning and the role of crosslinking density of microgels will be presented in detail.

Usually, for hard colloids, sustained pinning of the sessile drop is achieved by increasing the particle concentration [5]. In contrast, we show that reducing the surface tension of the air-water interface of the sessile drop by using surface-active amphiphilic soft microgels can suppress the depinning of the drop despite low particle concentrations.

Keywords: Evaporation, microgel, surface-active, softness, substrate, hydrophobicity.

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Biocidal action of Ag and soap against *Staphylococcus aureus*

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Microbial pathogens (bacteria, viruses, and fungi), which can cause infections and diseases in humans, are one of the leading causes of death worldwide, namely one-fourth of global deaths annually [1]. Therefore, the control and prevention of microbial infections are of utmost importance. To fight with pathogens, many antimicrobial agents have been developed, such as antibiotics, disinfectants, and antiseptics. However, due to mutations, new strains of antimicrobial-resistant microorganisms are emerging, thus making the search of new biocides a substantial challenge.

In our study, we have tested the biocidal action of soaps and silver (Ag⁺) against planktonic and adherent *S. aureus*. Soaps are commonly used in hand-wash formulations and should be able to kill most bacteria within 30-60 s without damaging the skin, however, in many cases they are not very effective alone. We found that the antibacterial properties of soaps improve when their hydrophobicity increases up to 12 carbon atoms. Moreover, when soaps are combined with Ag⁺, we observed a synergistic effect: increased cell permeability due to soap, resulting into higher silver uptake and enhanced biocidal action. Furthermore, using SEM and TEM, we detected the external and internal defects due to the treatment, thus elucidating the mechanism of biocidal action.

Keywords: Bacteria, Biocides, Soaps, Silver

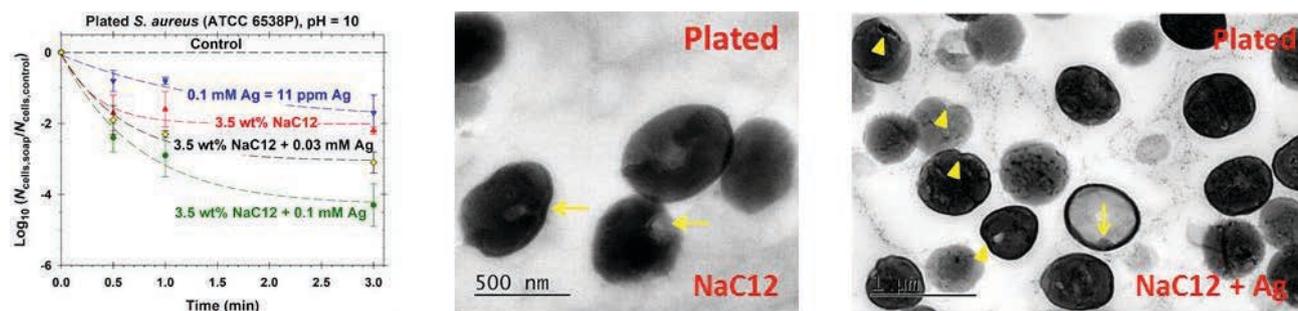


Figure 1. Biocidal effect of sodium laurate (NaC12) and/or Ag on plated *S. aureus* – surviving cells and TEM images.

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Effect of melatonin on the structural and thermal properties of pure and cholesterol containing lipid membranes

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Melatonin is a hormone present in the organisms of all living beings from algae to humans in levels varying during the daily cycle. It is a powerful antioxidant, produced in the human brain having a special role in DNA preservation and protective role against Alzheimer's disease. It is also famous as "The Youth Hormone" due to its function to maintain and regulate the sleep to wake cycle. While the interaction of cholesterol with membranes has been extensively studied, the effect of melatonin on the structural and physicochemical properties of lipid membranes is not yet completely clear. In-depth research on the joint effect of melatonin and cholesterol on lipid membranes are of great importance because both molecules are known to have connection to amyloid toxicity associated with Alzheimer's disease.

The main goal of our study is to investigate the effect of melatonin on the thermal and conformational structural characteristics of pure and cholesterol containing 1-stearoyl-2-oleoyl-sn-glycero-3-phosphocholine (SOPC) phospholipid in a wide range of melatonin concentration. For that purpose, we use the methods differential calorimetric analysis, Raman and FTIR spectroscopy.

In the present work we investigate the influence of melatonin incorporated in the pure and cholesterol containing phospholipid membrane on the phase transition temperatures and enthalpies of the complex system and discuss the possible physical mechanism driving the energetic and conformational states of these bio-nano-composites.

The results analysis shows a certain influence of melatonin on the structure and properties of both pure and cholesterol enriched phospholipid membranes demonstrating a fluidizing effect of melatonin on the SOPC membrane that counteracts the condensing effect of cholesterol.

Keywords: membrane, melatonin, cholesterol, phase behavior, enthalpy, Raman and infrared spectroscopy

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The effect of internal architecture on the assembly of soft particles at fluid interfaces

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Monolayers of soft colloidal particles confined at fluid interfaces are at the core of a broad range of technological processes, from the stabilization of responsive foams and emulsions, to the assembly of functional materials. [1] However, establishing the relation between their internal architecture, which is controlled during synthesis, and their structural and mechanical properties upon interfacial confinement, which define the monolayer's properties, remains an elusive task.

Here, we propose a comprehensive study elucidating this relation for a system of microgels with tunable architecture. [2] We synthesize core-shell microgels, whose soft core can be chemically degraded in a controlled fashion, yielding particles ranging from analogues of standard batch-synthesized to completely hollow microgels. Combined experimental and numerical studies show that our hollow particles have a thinner and more deformable shell compared to previous works, leading to a temperature-responsive collapse of the internal cavity and a complete flattening after adsorption at a fluid interface. Mechanical characterization shows that a critical degree of core removal is required to obtain soft disk-like particles at an oil-water interface, which present a distinct response to compression. In particular, at high compression, the absence of a core enables the particles to deform in the direction orthogonal to the interface and be continuously compressed without altering the monolayer structure. These findings show how fine, single-particle architectural control during synthesis determines the interfacial behavior of microgels, enabling new design strategies for tailored materials.

Going a step beyond in controlling the assembly of microgels at fluid interfaces, we show that varying the composition of the system (*e.g.*, oil polarity and fluid interfacial tension) greatly affects the structural reorganization of adsorbed microgels. This can be advantageously used to control the mechanical and structural response of the resulting monolayers. [3]

Keywords: pNIPAM microgels, liquid interface, self-assembly, polymer networks, Atomic Force Microscopy, colloidal particles

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A comparison between the structures of reconstituted salivary pellicles and oral mucin (MUC5B) films

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Salivary pellicles are thin proteinaceous films which form from the selective adsorption of saliva onto the oral surfaces, providing protection against both mechanical and chemical insults [1]. They have been shown to be excellent lubricants and provide significantly low friction coefficients [2] and present a high resistance to wear [3] despite their wettability. This phenomenon has become the focus of many studies, however despite the in depth knowledge of the composition of the pellicle, the structure is still not fully understood.

The pellicle is generally speculated to be a two layer structure, with the outer layer mainly composed of MUC5b mucins. It has been hypothesized that mucin films lubricate by means of a hydration lubrication mechanism similar to that exhibited by polyelectrolyte brushes [4]. However, this has not yet been proved and the fact is that neither how mucins integrate in salivary pellicles nor the mechanisms underlying pellicle lubrication are fully understood.

Therefore, we present a comparison between the responses to change in ionic strength of both salivary pellicles and oral mucins (MUC5B) films, as this response (swelling/coiling) is a common approach for structural investigations of polymer brushes and similar systems [5]. Our investigations reveal that, whereas both systems swell when the ionic strength is lowered, in the case of mucin films this is followed by a gradual coiling not observed in the case of salivary pellicles. This suggests that the outermost layer of salivary pellicles is not only composed of mucins, in agreement with previous studies indicating that the lubrication performance of mucin films is improved by addition of other low molecular weight components [6].

Keywords: mucin, salivary pellicle, MUC5b, ionic strength, steric forces

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Effect of temperature on rheology and slip of polymer solutions

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A basic assumption of fluid mechanics is the no-slip boundary condition which assumes that the velocity of a liquid at the solid wall is zero. For many liquids, this hypothesis is relevant because the friction between the liquid and the wall is so high that the liquid molecules right at the interface are – on average – barely flowing. However, for highly viscous liquids, this is not true anymore, and the velocity of the fluid on the wall depends on the balance between the viscosity of the fluid and the friction between the liquid and the wall (**Figure 1**) [1]. Both quantities depend on temperature but how the temperature affects the amount of slip is still an open question: numerical simulations report non-monotonic slippage with respect to temperature [2-3] while experimental measurements have noticed a constant or decreasing slip with temperature [4-5].

Polymer solutions can exhibit a very high slippage, even if the solvent itself does not slip, which makes them a tool of choice to understand the underlying mechanisms of slip. In addition, if the rheology of polymer solutions is well understood at high temperatures, very rich behaviors emerge when the solution is cooled down at a temperature close to the glass transition.

Therefore, we have chosen to study polystyrene solutions in phthalate solvents. Our work is two-fold: first we conduct rheology experiments to understand the peculiar effect of temperature on the flow of polymer solutions. Second, we use a state-of-the-art photobleaching technique to measure the slip of polystyrene solutions as a function of temperature.

Keywords: polymers ; slip ; friction ; interface

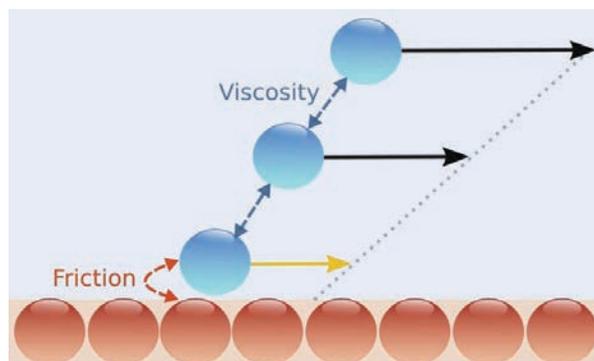


Figure 1. Slip at the solid/liquid interface. The amount of slip (yellow arrow) depends on the balance between viscosity, which tends to entrain the liquid at the interface, and friction, which tends to stop it.

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EP10.10

Metallic Liquid Gating Membranes

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A membrane is a selective barrier permitting separation of certain components in fluids by sieving or sorption diffusion mechanisms, applicable over a wide range of particle sizes and molecular weights, from macromolecular materials to monovalent ions. It has been estimated that filtering and treating water, both for human consumption and to clean industrial and municipal wastewater, account for about 13% of all electricity consumed in the US, releasing approximately 290 million metric tons of CO₂ emissions into the atmosphere annually (~5% of all US CO₂ emissions).

The liquid gating membrane (LGM) system, which uses a stabilized liquid as a reversible and reconfigurable gate, has recently been developed as an alternative to conventional hydrophobic membranes. In a liquid gating system, the infused liquid fills and seals micropores in the closed state and forms non-fouling, liquid-lined pores in the open state. Although this system has potential applications in a broad range of fields, to fulfill the needs of specific applications, especially under low- and high-pressure/temperature conditions, it would be beneficial to develop alternative fabrication methodologies and more robust membrane materials.

The development of LGM systems with tunable multiphase selectivity and antifouling properties is limited by the mechanical stability of the membrane materials. The mechanical integrity of most polymeric membranes can be compromised by deformation under harsh operating conditions (elevated temperatures, corrosive environments, foulants, etc.), ultimately leading to their failure.

Here, a facile electrochemical approach to the fabrication of multifunctional metal-based liquid gating membrane systems was developed. The membrane porosity, pore size, and membrane surface roughness can be tuned from micro- to nanometer scale, enabling function under a variety of operating conditions. The prepared LGMs demonstrate controllable gas–liquid selectivity, superior resistance to corrosive conditions and fouling chemicals, and significant reduction of the transmembrane pressure required for the separation process, resulting in lower energy consumption. The stability of the gating liquid is confirmed experimentally through sustained fouling resistance and further supported by the interfacial energy calculations. The mechanically robust metal-based membrane systems reported in this study significantly extend the operating range of LGMs, prompting their applications in water treatment processes such as wastewater treatment, degassing, and multiphase separation.

Keywords: lubricant-infused slippery surfaces, polydimethylsiloxane, corrosion resistance, anti-biofouling, blood-repellent coating

Adsorption model and phase transitions of fluorinated surfactants at the water|alkane interface

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The monolayers of diblock perfluoroalkylated alcohols exhibit phase transitions at the water|oil interface, at near room temperatures, for tail lengths as small as 8 carbon atoms. Equations of state are developed for these phases. The cohesive behaviour of the surfactants is attributed to van der Waals forces between the fluorinated blocks. The liquid monolayer is modelled as a delocalised fluid with a short-range attractive potential, using the sticky disc adsorption model of Ivanov et al. [1, 2]. The condensed phase is described as a crystalline structure with the same attractive potential between the adsorbed molecules, using a new model based on defective van der Waals crystals. The models are compared to literature data for a range of temperatures (15..30 oC) and alcohol chain lengths [3–6]. The adsorption parameters have been related to the molecular characteristics of the system with high accuracy. The adsorption constant corresponds to the predicted one within 30%. An invariant phase diagram has been constructed based on the law of corresponding states.

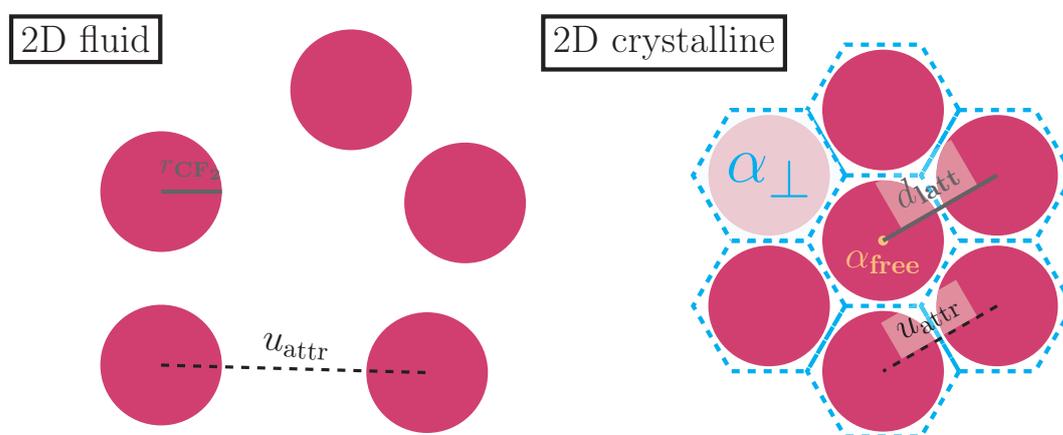


Figure 1: Schematic top-view representation of: (left) delocalised fluid monolayer of hard discs (radius r_{CF2}) interacting with potential u_{attr} ; (right) hexagonal 2D crystal (lattice parameter d_{latt}) with cell area α_{\perp} and free area α_{free}

Keywords: Fluorosurfactant, Surface phase transition, van der Waals crystal, Cohesive pressure

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Protective role of flavonoids incorporated into DOPC liposomes upon initiated lipid peroxidation

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Structural properties of lipid membranes, such as integrity, elasticity, and fluidity are critical for cellular activities. One of the main components of biological membrane are unsaturated lipids, which are particularly susceptible to peroxidation by reactive oxygen species due to highly reactive hydrogen atom on the methylene bridge. The peroxidation of unsaturated lipids, in our case 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), induces structural reorganization of the membrane [1]. Flavonoids, polyphenolic biomolecules with antioxidative activity, show great potential for the protection of the lipid membrane.

Interactions of flavonoids with membranes exposed to the oxidative stress have been investigated with the respect to their influence on the membrane structure, elasticity, and functionality. Multiple methods have been used to investigate the interaction of flavonoids with model cell membranes. The calculation of the percentage inhibition was carried out using infrared spectroscopy (ATR technique) by monitoring the change in the carbonyl stretching band [2]. Mass spectrometry was used to identify some products of lipid peroxidation reaction and to gain insight into the mechanism which takes place. In addition, atomic force microscopy (AFM) measurements were performed to gain more insight into protection of the membrane during the reaction.

The aim of this study is to use complementary methods to elucidate the mechanism and the products of the lipid peroxidation reaction, as well as to study protective role of flavonoids which were incorporated into model lipid membranes in different molar ratios.

Keywords: antioxidative activity, flavonoids, lipid peroxidation

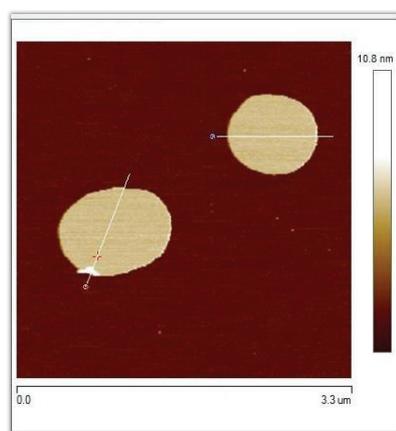


Figure 1. AFM topography of DOPC liposomes.

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Fine control of nanoparticle monolayer structure at the air/water interface

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The formation of colloidal particles monolayers at the liquid interface is the focus of numerous studies. The interface acts as a scaffold for the assembly of colloidal systems, in which the dimensional confinement and the asymmetric environment allow to create nanostructured interfaces whose properties are related to the characteristics of the particles and to the inter-particle interactions acting at the interface. [1] [2]

We have recently shown how the structure of model surfactant-decorated nanoparticle monolayers can be tuned by controlling the nanoparticle/surfactant ratio *in bulk*. [3] In particular, the increase in the surfactant concentration affects the interparticle distance which decreases up to a threshold concentration value. Above this threshold concentration we observe an increase of the inter-particle distance, caused by the adsorption of isolated surfactant molecules. Moreover, the inter-particle interactions were quantitatively investigated through synchrotron-based grazing incidence small angle x-ray scattering (GISAXS) measurements performed during the monolayer compression.[3]

In the present work, we have further studied the monolayer nanostructure of 0.1% wt silica NPs with trimethylammonium bromide-based surfactants, as a function of the hydrophobic chain length and concentration. We have found that the shorter is the surfactant chain length, the wider is the adjustability range of the inter-particle distance (Figure 1a). Furthermore, the compression-induced inter-particle distances acting among NPs, studied by GISAXS (Figure 1b), show two different trends depending on the surfactant chain length, as well as on electrostatic and steric factors.

Keywords: colloids, inter-particle interaction, GISAXS

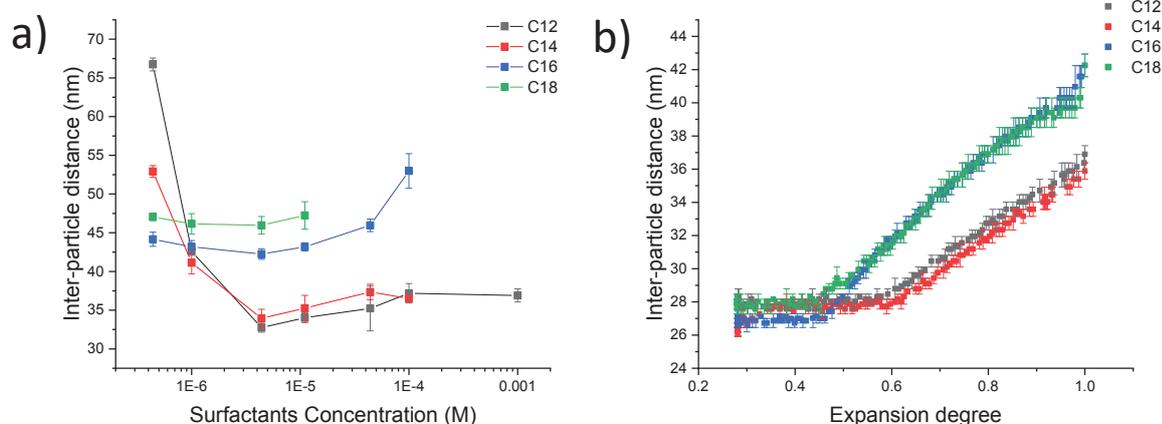


Figure 1. Inter-particle distance of 0.1% wt silica NPs decorated with various surfactants chain length vs surfactants concentration (A). Progressive reduction of the interparticle distance during compression(B). Both inter-particle distances were determined by GISAXS.

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Study of Active Janus Particles in the Presence of an Engineered Oil–Water Interface

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Micromotors are autonomously propelled artificial machines that harvest energy from their environment and transform it into motion. Because of their unique properties such as enhanced mass transfer, they have been proposed for various applications ranging from waste water remediation to sensor development. However, most of these real life applications involve complex surroundings and are dominated by various flows. Hence, considerable efforts have been made to study the behavior of micromotors in proximity of complex environments such as walls, boundaries, confinements, interfaces or flows.

Inspired from this idea we designed an oil-water interface to investigate the behavior of well-studied Pt@SiO₂ Janus micromotors in proximity of an oil surface and compare their performance to a solid surface. A special microfluidic trap was fabricated for creating such an oil-water interface. The large surface of the microfluidic trap resulted in high surface energy, which was lowered by partial wetting of the glass substrate. This partial wetting created patches of oil on the glass which we refer to as ‘oil dimples’. The oil dimples at first seem to be unfortunate, but it provided us a distinctive opportunity to directly compare the propulsion of Janus motors at both interfaces within the same setup. This also ensured similar conditions at both interfaces in terms of additive content such as surfactant and H₂O₂ concentration. When a droplet of Pt@SiO₂ particles was merged with a droplet of H₂O₂, the particle activity was witnessed by a change in orientation and propulsion. The swimming pattern and the speed values were found to be similar at the two interfaces. Interplay of various factors such as microscale friction, lubrication, surface locking by the surfactant, reaction product absorption by oil and potential Marangoni influences contributed to comparable propulsion behavior at the two interfaces.

Keywords: liquid-liquid interface, Pt@SiO₂, microfluidics

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Influence of Charge Distribution within Lipid Head Groups on the Properties of Electric Double Layer

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The lipid head groups internal degrees of freedom impact the structure of the electric double layer. We consider the most general shapes and charge distributions of lipid head groups. This lipid monolayer is in contact with an electrolyte solution composed of simple monovalent point-like ions. The system is considered by means of a generalized classical Density Functional Theory model and Monte Carlo simulations. Starting from the free energy of the system the calculus of variation was used to derive Euler-Lagrange equations which were solved numerically by Finite element method. The results show that the lipid head group structure strongly impact the surface potential profile. The strongly charged monolayer induces a non-monotonous conditional probability density and tendency of head groups more perpendicular to the surfaces. On contrary the weakly charged surface causes more constant conditional probability density. The flexibility of head groups switches the perpendicular to more parallel orientation of head groups due to possibility of intermediate positive charge to be in the vicinity of negatively charged plane of phosphate groups and terminating negative charge to be extended more in the solution. Monte Carlo simulations confirm the results of the model.

Keywords: Electrostatics, Lipid head groups, Electric double layer

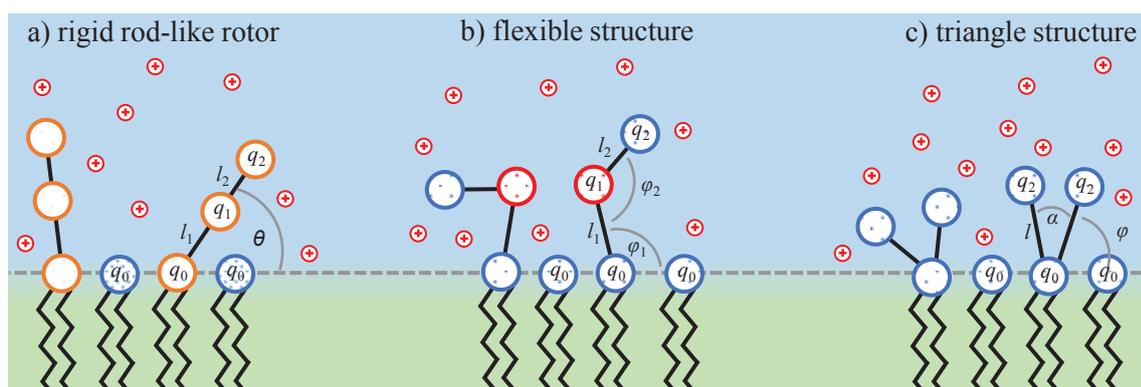


Figure 1. Schematic presentation of the lipid monolayer, where head-groups with the spatial charge distribution are in contact with the aqueous solution.

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Taking a Closer Look: A Molecular-Dynamics Investigation of Microscopic and Apparent Dynamic Contact Angles

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We use large-scale MD to explore the steady displacement of a water-like liquid bridge between two molecularly-smooth solid plates under the influence of an external force F^0 . A coarse-grained model of water reduces the computational demand and the solid-liquid affinity is varied to adjust the equilibrium contact angle θ^0 . Protocols are devised to measure the microscopic and apparent dynamic contact angles (θ_m and θ_{app}) as a function of contact-line velocity U_{cl} . We prove that for all θ^0 , θ_m is velocity-dependent and consistent with the molecular-kinetic theory of dynamic wetting (MKT). However, θ_{app} diverges from θ_m as F^0 is increased, especially at the receding meniscus. The behavior of θ_{app} follows that predicted by the Voinov hydrodynamic formula: $(\theta_{app})^3 = (\theta_m)^3 + 9Ca \cdot \ln(L/L_m)$, where Ca is the capillary number and L and L_m are suitably-chosen macroscopic and microscopic length scales. For each θ^0 , there is a critical velocity U_{crit} and contact angle θ_{crit} at which $\theta_{app} \rightarrow 0$ and the receding meniscus deposits a liquid film. Setting $\theta_{app} = 0$, $\theta_m = \theta_{crit}$ and $U_{cl} = U_{crit}$ in the Voinov equation yields the value of L/L_m . The predicted values of θ_{app} then agree well with those measured from the simulations. Since θ_m obeys the MKT, we have, therefore, demonstrated the utility of the combined model of dynamic wetting proposed by Petrov and Petrov.

Keywords: wetting, dynamics of wetting, MD simulations.

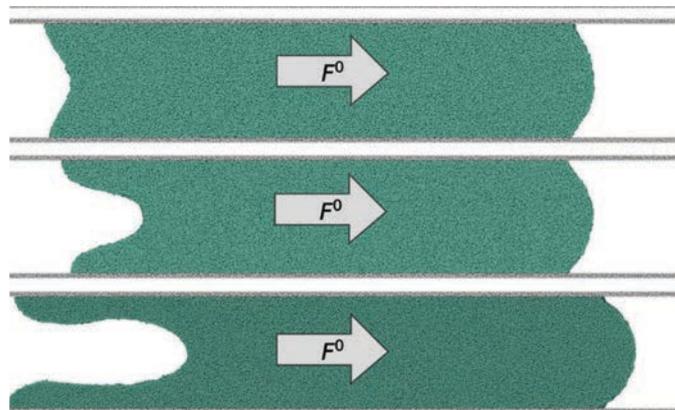


Figure : . Snapshots from simulations of the liquid bridge with solid-liquid coupling parameter $C_{SL} = 8$ under the influence of successively larger external forces F^0

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Mixed liposomes containing gram-positive bacteria lipids: Lipoteichoic acid (LTA) induced structural changes

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Lipoteichoic acid (LTA), a surface associated polymer amphiphile tethered directly to the Gram-positive bacterial cytoplasmic membrane, is a key structural and functional membrane component. Its composition in the membrane is regulated by bacteria under different physiological conditions. How such LTA compositional variations modulate the membrane structural stability and integrity is poorly understood.

Here, we have investigated structural changes in mixed liposomes mimicking the lipid composition of Gram-positive bacteria membranes, in which the concentration of *Bacillus Subtilis* LTA was varied between 0–15 mol% [1]. Small-angle neutron scattering (SANS) and dynamic light scattering (DLS) measurements indicated formation of mixed unilamellar liposomes, presumably stabilized by the negatively charged LTA polyphosphates. The liposome size increased with the LTA molar concentration up to ~6.5 mol%, accompanied by a broadened size distribution, and further increasing the LTA concentration led to a decrease in the liposome size (Figure 1). At 80 °C, SANS analyses showed the formation of larger vesicles with thinner shells. Complementary Cryo-TEM imaging confirmed these observations.

The results are discussed in light of the steric and electrostatic interactions of the bulky LTA molecules with increased chain fluidity at the higher temperature, which affect the molecular packing and interactions, and thus depend on the LTA composition in the membrane. These unprecedented experimental observations shed light on the intermolecular interactions in bacterial membranes [2].

Keywords: Lipoteichoic acid (LTA), Bacterial membranes, Liposomes, SANS, Self-Assembly

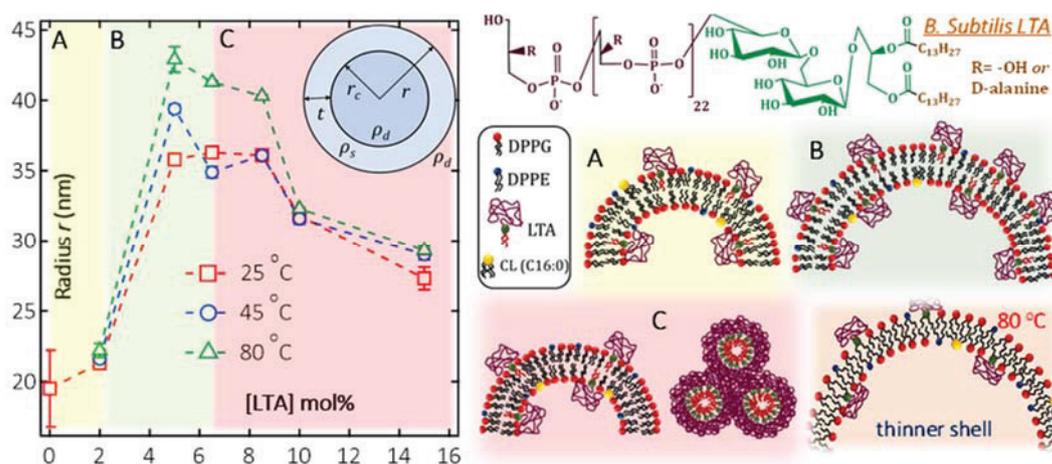


Figure 1. Left: Radius r of mixed liposomes from small-angle neutron scattering (SANS) data fitting as a function of LTA concentration in the liposomes at different temperatures; Right: LTA molecular structure and schematics of LTA-induced structural changes in the liposome membranes [1].

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A Sample Environment for Neutron Scattering Studies of Thin Films under Mechanical Confinement and Shear

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The study of mechanically confined soft matter is central to the understanding of interactions that lead to adhesion, lubrication and colloidal stability among others. These studies were originally made possible by the emergence of the Surface Force Apparatus and, especially, by the Atomic Force Microscope. However, while these techniques provide accurate interaction forces at different confinement distances, they barely provide structural information. Neutron Scattering is instead a technique that allows detailed structural studies of thin and soft surface layers, even under mechanical confinement if novel sample environments are used [1-3]. We have worked on this success and developed a novel sample environment that allows structural studies of thin soft films not only under normal mechanical confinement but also under shear. This sample environment can be used in both Neutron Reflectometry and GISANS geometries, making possible to investigate how mechanical confinement and shear originate changes in the out-of-plane and in-plane structure of soft matter thin films. Here we will present the design of this novel sample environment as well as the first obtained results.

Keywords: Confinement, Shear, Reflectivity, SANS, GISANS

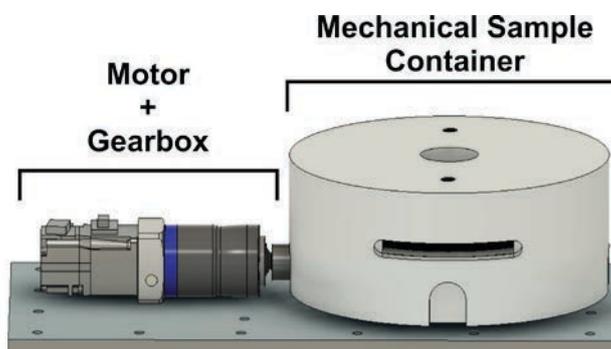


Figure 1. Sketch of the prototyped mechanical confinement and shear cell.

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Adsorption of hot water-extracted birch glucuronoxylans on hydrophobic interfaces

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Lignocellulosic side streams from the forestry industry can be valorized into functional materials. One interesting application is the dispersion of hydrophobic materials in aqueous systems, including liquids [1] and semi-solids [2, 3]. However, the typical variability in the physicochemical properties of lignocelluloses, such as residual lignin content, charged sugar residues, and solubility, undermines efforts in this area. Such variabilities are related to the raw materials and the extraction method [2]. Hence, understanding the impact of such variations at hydrophobic interfaces would allow for their stabilizing capability to be tailored for different colloidal products.

We characterized the adsorption behavior of hot water-extracted glucuronoxylans (GX) from birchwood at the liquid-liquid and liquid-solid interfaces by dynamic interfacial tension (DIT) and quartz crystal microbalance with dissipation (QCM-D), respectively. We used three types of GX: spray-dried extract (sGX), lignin-deficient ethanol-precipitated extract (eGX), and carboxymethylated derivative (CMGX). We compared them to methylcellulose (MC) and carboxymethylcellulose (CMC) as soluble polysaccharide emulsifiers, and to anionic (aCNC) and desulfated (dCNC) cellulose nanocrystals as polysaccharide-based Pickering emulsifiers. The adsorption of the emulsifiers from their 0.03% (w/v) dispersions was monitored towards a floating drop of water-saturated hexadecane (DIT) and a paraffin wax-coated gold sensor (QCM-D).

Across the different GXs, we observed a delay in the onset of rapid interfacial tension fall with increasing hydrophilic character, with sGX having the earliest decrease and CMGX being the latest. Residual lignin in CMGX appeared to enhance adsorption compared to CMC, which exhibits a similar negative charge but is lignin-free. QCM-D measurement of the amount of adsorbed GXs showed agreement with the DIT observations. Dissipation data indicated that the adsorbed GXs formed rigid layers compared to MC and aCNC. These results highlight the importance of lignin and hydrophobicity in the adsorption behavior of GXs and imply the need for further characterization of the adsorbed layers.

Keywords: birch glucuronoxylan, lignocellulose, dynamic interfacial tension, QCM-D

Acknowledgements: We thank the Academy of Finland for funding this project, Petri Kilpeläinen of the National Resources Institute Finland for providing sGX and eGX, and Sami Hietala and Sami-Pekka Hirvonen of the Department of Chemistry, University of Helsinki for the use of their optical tensiometer.

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Interface-induced hysteretic volume phase transition of microgels: simulation and experiment

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Thermo-responsive microgel particles can exhibit a drastic volume shrinkage upon increasing the solvent temperature. Recently we found that the spreading of poly(N-isopropylacrylamide)(PNiPAm) microgels at a liquid interface under the influence of surface tension hinders the temperature-induced volume phase transition¹. In addition, we observed a hysteresis behavior upon temperature cycling, i.e. a different evolution in microgel size and shape depending on whether the microgel was initially adsorbed to the interface in expanded or collapsed state. We have modeled the volume phase transition of such microgels at an air/water interface by monomer-resolved Brownian dynamics simulations and compared the observed behavior with experiments². We reproduced the experimentally observed hysteresis in the microgel dimensions upon temperature variation. Our simulations did not observe any hysteresis for microgels dispersed in the bulk liquid, suggesting that it results from the distinct interfacial morphology of the microgel adsorbed at the liquid interface². An initially collapsed microgel brought to the interface and subjected to subsequent swelling and collapsing (resp. cooling and heating) will end up in a larger size than it had in the original collapsed state^{1,2}. Further temperature cycling, however, only shows a much reduced hysteresis, in agreement with our experimental observations. We attribute the hysteretic behavior to a kinetically trapped initial collapsed configuration, which relaxes upon expanding in the swollen state. We find a similar behavior for linear PNiPAm chains adsorbed to an interface². Our combined experimental - simulation investigation provides new insights into the volume phase transition of PNiPAm materials adsorbed to liquid interfaces.

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Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface

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In this study, we explored the spontaneous capillary driven self-assembly of composite prolate shaped microgels at air-water interface. The core-shell microgels contain a polystyrene (PS) core surrounded with a cross-linked fluorescently labelled poly(N-isopropylmethylacrylamide) (PNIPMAM) shell. The aspect ratios of the composite microgels can be finely adjusted upon uniaxial stretching the particles embedded into polyvinyl alcohol films [1]. The ellipsoidal particles obtain an aspect ratio range ρ varying from 1 to 8.8, measured from confocal laser microscopy (CLSM) in their swollen conformation at 20°C. Using inverted fluorescence microscopy, we investigated their spontaneous interfacial self-assembly at the air-water interface. Comparing with spherical particle ($\rho=1$) with small assembly having weak capillary forces to an apparently random trigonal assembly for $\rho=2.1$ to highly elongated particle ($\rho=8.8$) with a side-to-side assembly into long chains transition is observed. The transition occurs between $\rho=2.6$ and 3.3 for which a trigonal and trigonal/side to side coexistence assembly are respectively identified. The influence of the composite microgel softness and anisotropy on the assembly is discussed as well its influence on the interfacial tension derived from time-resolved pending drop measurements.

Keywords: Core-shell ellipsoidal Microgels, Self-assembly, air-water interface, Fluorescence Microscopy

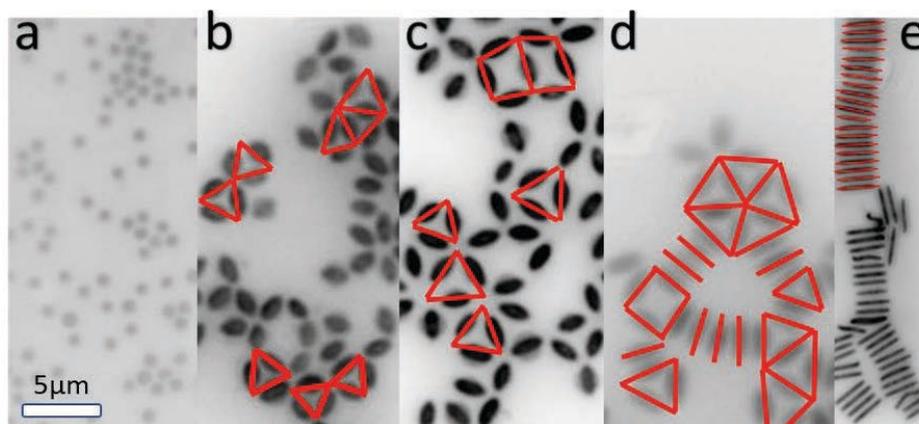


Figure 1. Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.

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Drainage and stability of solidifying hydrogel films: towards an understanding of pore opening mechanism in hydrogel foams

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Controlling the pore connectivity of polymer foams is of utmost importance for tuning foam properties (absorption, mechanics or acoustics). We are interested here in hydrogel foams, which are widely used in the biomedical field. Even though several studies discuss the connectivity of hydrogel foams produced via “liquid foam templating” [1-3] (gelation of an initially liquid foam containing a cross-linkable polymer), a clear understanding of the mechanisms underlying the rupture of solidifying hydrogel films separating neighbouring pores has yet to be elaborated.

For this purpose, we use a model system consisting of an alginate hydrogel cross-linked with calcium ions. We design reproducible experiments to study isolated, free-standing horizontal thin films undergoing cross-linking while reproducing the same pressure conditions as in a foam (Fig. 1A). To this end we develop a novel *microfluidic thin film pressure balance* (μ TFPB, Fig. 1A), which allows for precise characterisation of film drainage and of the apparition of holes in the gelling films [4]. We tweak both the pressures controlling the drainage process and the formulation to quantify film thinning and rupture (Fig. 1B). This investigation leads us to address the issue of gelation in the presence of interfaces and under *soft confinement*, since the characteristic film thickness before hole formation (10-100 nm) is smaller than the unconstrained mesh size of the hydrogel.

We show that gelation kinetics, interfacial viscoelasticity and depletion forces play a decisive role in controlling the film drainage and the final film thickness profile of the gelled films. Moreover, soft confinement for low film thicknesses hampers the cross-linking process, yielding hydrogel films with low elasticity. This allows us to fix a set of key parameters (and their interplay) for tuning the connectivity of hydrogel foams.

Keywords: Hydrogel foams, Thin films, Soft confinement, Depletion interaction

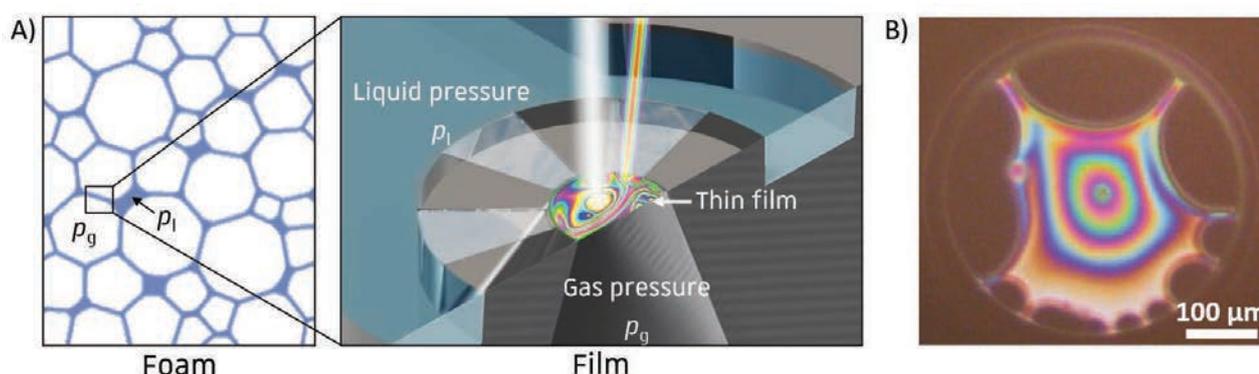


Figure 1. (A) The μ TFPB allows for the generation of thin liquid films under the same conditions as within a foam [4] (B) Example of a thin film draining in the μ TFPB. Different colours indicate different thicknesses.

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An X-ray reflectivity study of synergistic and competitive adsorption of nanoparticles and lipids at the oil-water interface

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Fundamental insights into the interplay and self-assembly of nanoparticles and surface-active agents at the liquid-liquid interface play a pivotal role to understand the ubiquitous colloidal systems present in our natural surroundings, including foods and aquatic life, and in the industry for emulsion stabilization, drug delivery or enhanced oil recovery. Moreover, well-controlled model systems for mixed interfacial adsorption of nanoparticles and surfactants allow unprecedented insights into non-ideal or contaminated particle-stabilized emulsions. Here, we investigate such a model system comprised of hydrophilic, negatively and positively charged silica nanoparticles and the oil-soluble cationic lipid octadecyl amine with in situ synchrotron-based X-ray reflectometry which is analyzed and discussed jointly with dynamic interfacial tensiometry [1]. Our results indicate that negatively charged silica nanoparticles only adsorb if the oil-water interface is covered with the positively charged lipid, indicating synergistic adsorption. Conversely, the positively charged nanoparticles readily adsorb on their own, but compete with octadecyl amine and reversibly desorb with increasing concentrations of the lipid. These results further indicate that with competitive adsorption, an electrostatic exclusion zone exists around the adsorbed particles (Figure 1). This prevents the adsorption of lipid molecules in this area leading to a decreased surface excess concentration of surfactants and unexpectedly high interfacial tension [2].

Keywords: nanoparticles, surfactants, oil/water interface, synchrotron x-ray reflectivity, interfacial self-assembly

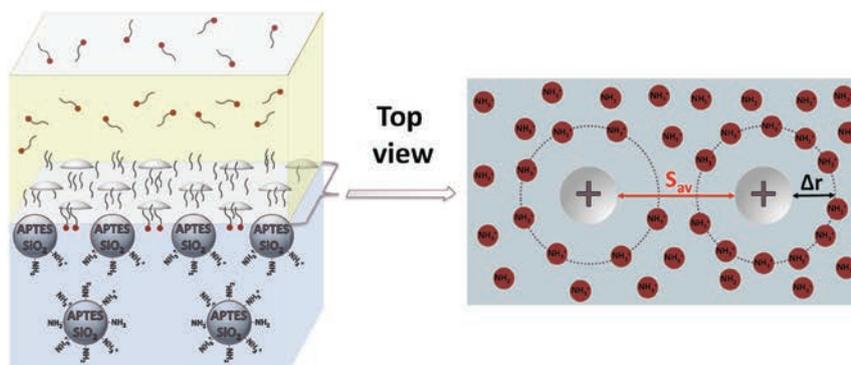


Figure 1. Adsorption is synergistic in the case of oppositely charged particles and surfactants and competitive when their charges are equivalent, forming an exclusion zone that prevents adsorption of surfactants.

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Effect of surfactant dynamics on flows inside microfluidic drops

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Flow fields inside microfluidic drops are of great importance for many applications, such as cell screening, encapsulation or using drops as microreactors. Surfactants are an often included component in such drops and can affect the internal flow fields through surfactant redistribution in adsorption layer.

The effect of surfactant redistribution over the interface is well documented for an air bubble rising in contaminated water. Surfactant being swept by the flow from the front part of the drop to the rear can result in partial or full surface retardation and dependence of bubble terminal velocity on surfactant concentration. The picture is much more complicated for a microfluidic drop moving in a rectangular microfluidic channel. In this case the surface stresses from the continuous phase are strongly non-uniform. They are always retarding from the liquid films near channel walls, but can be accelerating from the continuous phase bypassing the drop through the liquid corners.

In this study, the flow fields inside drops moving in rectangular microfluidic channel were investigated using Ghost Particle Velocimetry (GPV), a technique using the speckle patterns of white light scattered by particles smaller than the diffraction limit as tracers of liquid motion [1,2]. Using the capability of GPV, flow patterns were recorded in several cross-sections along the channel height, providing insight into 3D flow structure.

Studies based on several surfactants with the range of critical micelle concentrations (CMC) 0.06 – 90 mM and a range of concentrations for each surfactant have shown considerable dependence of the flow patterns not only on surfactant concentration, but also on CMC value, i.e. on surfactant adsorption dynamics (Fig. 1).

Keywords: microfluidics, surfactant solutions, surfactant dynamics, flow fields, Ghost Particle Velocimetry

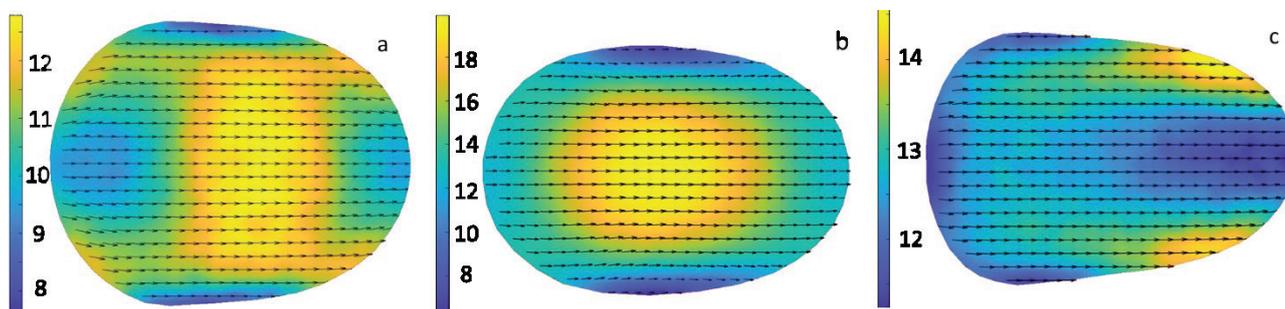


Figure 1. Flow fields inside drops moving in a rectangular microfluidic channel: a – surfactant-free drop, $L = 431 \mu\text{m}$, $V = 9.8 \text{ mm/s}$; b – drop laden with 40 mM (2 CMC) of C12TAB, $L = 432 \mu\text{m}$, $V = 12.5 \text{ mm/s}$; c – drop laden with 6 mM (10 CMC) of Triton X-100, $L = 437 \mu\text{m}$, $V = 11.3 \text{ mm/s}$. Superficial flow velocity in the channel 9.2 mm/s.

Acknowledgements: This work was funded by the EPSRC Programme Grant PREMIERE (EP/T000414/1).

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EP10.27

Frothing of asymmetric liquid mixtures

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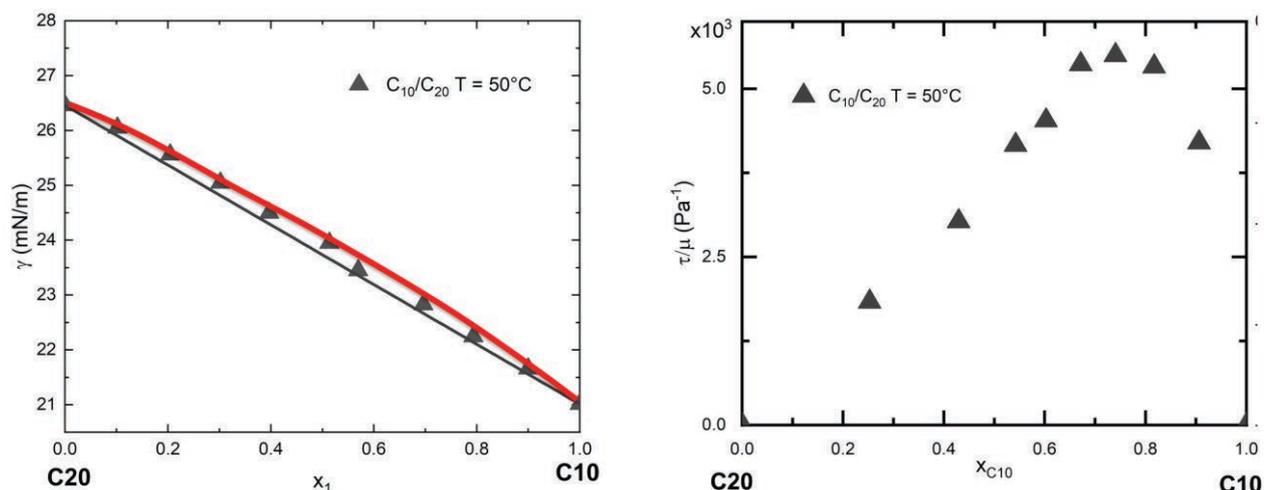
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Binary Mixtures of liquid foams, or more precisely exhibits foams (or more precisely froth) with life-time of the order of the second. As explained in [1], this is due to the different partition of the molecules in bulk and at interfaces, that leads to a thickness dependent superficial tension. Molecules of lower superficial tension are more concentrated at the interfaces than in bulk, for energetic reasons. As a consequence, the interfacial tension smaller than the average of the interfacial tension of each component. This sub-linearity is at the origin of the thickness dependent superficial tension, and thus of the life-time of the binary mixture froths. However, in the case of mixture of molecules with very different molecular surfaces, a competition between partition effects and molecular surface determine the superficial tension. Superficial tension can be super-linear simultaneously with large froth stability. We will explain these results using experiments and models of asymmetric molecules mixtures superficial properties.



Left : Superficial tension of eicosane/decane mixtures. The superficial tension is superlinear.
 Right : Froth life-time divided by viscosity of eicosane/decane mixtures. Despite the superlinearity of the superficial tension, the life-time is important. This originates from the role of asymmetry in the partition of eicosane/decane at the interface.

Keywords: Foamability; Thin liquid films; Surface tension

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Levelling of an axisymmetric bare freestanding thin liquid film real-time investigation

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Freestanding thin liquid films are of great interest in many fields. Most of the time, when two fluids are separated by a thin film we are talking about emulsions and foams. These kind of systems are very challenging due to their geometry which is characterized by hundreds nanometers to tens microns in case of their thickness, the diameters space over hundreds of microns to millimeters and the curvature radii can be microns to meters. Therefore, these films are very complex to study as it is necessary to characterize them at nanometric, micrometric and macroscopic scale. Moreover, it is difficult to observe their temporal evolution [1-3].

In this work we evaluate the levelling of an axisymmetric bare freestanding thin liquid film by using a custom setup that merges Digital Holographic (DH) and white light measurements and allow us to perform real-time characterization of these systems [1-3].

A commercial iris of 16 leaves was actuated by a stepper motor and a drop of liquid was placed in the center of the closed iris, then the iris was opened to form the axisymmetric bare freestanding thin liquid film. The opening parameters were set from a computer connected to the stepper motor. The fluid used was a silicone oil of 60'000cSt. Numerical simulations of the phenomenon are in qualitative agreement with the experiments results.

Keywords: capillary levelling, freestanding thin film, numerical simulations, digital holography

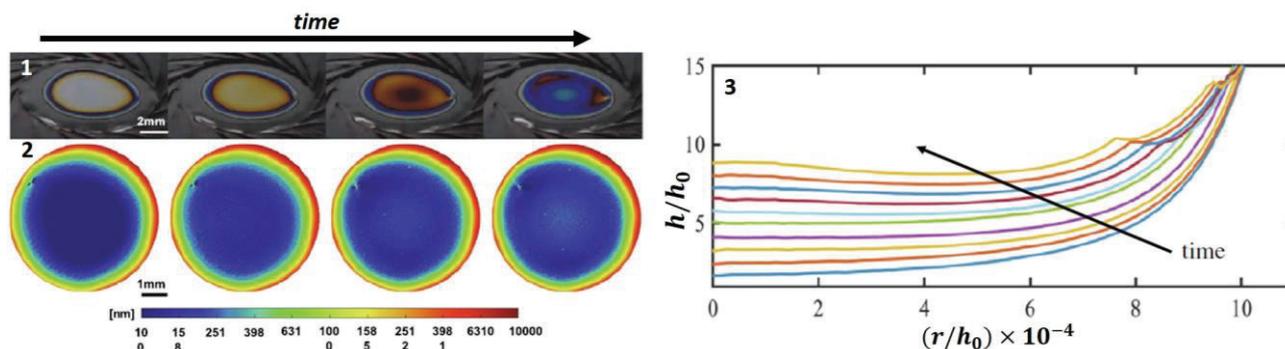


Figure 1. (1) Thin liquid film obtained on the optical iris and recorded on a webcam to observe the white light interferometry fringes (2) high resolution thickness map of the same film obtained by digital holography (3) thickness profiles over time obtained by merging the two techniques

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EP10.29

Remote Control of Aqueous Interfaces and Foam Stability using Photo-Switchable Polyelectrolyte-Surfactant Mixtures

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New photo-switchable surfactants [1,2] that can undergo E/Z photo-isomerization and change their surface structure and activity as a function of light irradiation are used to expand the properties of oppositely charged polymer/surfactant (P/S) mixtures.

We demonstrate that prevailing hydrophobic intermolecular interactions can be tuned remotely between poly(sodium styrene sulfonate) (PSS) and arylazopyrazole tetraethylammonium bromide (AAP-TB) surfactants but also for other mixtures such as PDADMAC/AAP and lead to remarkable and drastic property changes of the P/S mixtures.

In particular, we report on bulk and interfacial properties of PSS/AAP-TB mixtures as a function of mixing ratio and light irradiation. In the bulk, PSS/AAP-TB complexes are formed with varying electrophoretic mobility and particle size. Irradiation with green light drives the AAP-TB surfactants in their predominant E form and leads to negligible mobilities as well as large aggregates at selected mixing ratios. Subsequent to UV irradiation even large aggregates from P/S complexes can be redispersed where an optically turbid solution becomes fully transparent in the visible spectrum. This is associated by a strong increase in the net charging state of PSS/AAP-TB complexes in the bulk, but also the apparent charging state at the air-water interface changes drastically as confirmed by sum-frequency generation (SFG) spectroscopy.

In fact, the P/S molar ratio where complexes with zero net charge at the polyelectrolyte chain are formed is about one order of magnitude smaller when the surfactants are in their Z compared to their E form. Clearly, E/Z photo-isomerization can be used to fine tune polymer-surfactant binding and to change bulk as well as interfacial properties in an unprecedented way.

In addition, we make use of the molecular changes of PSS/AAP-TB mixtures and drive through structure-property relations macroscopic foam properties from molecular structure changes. In particular, we demonstrate that control of foam stability globally but also locally with light irradiation is possible.

Keywords: Photoswitches, Surfactants, Polyelectrolytes, Foam, Interfaces

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Antifungal activity of newly synthesized C10- and C12-vinylimidazolium based ionic liquids and their polymers

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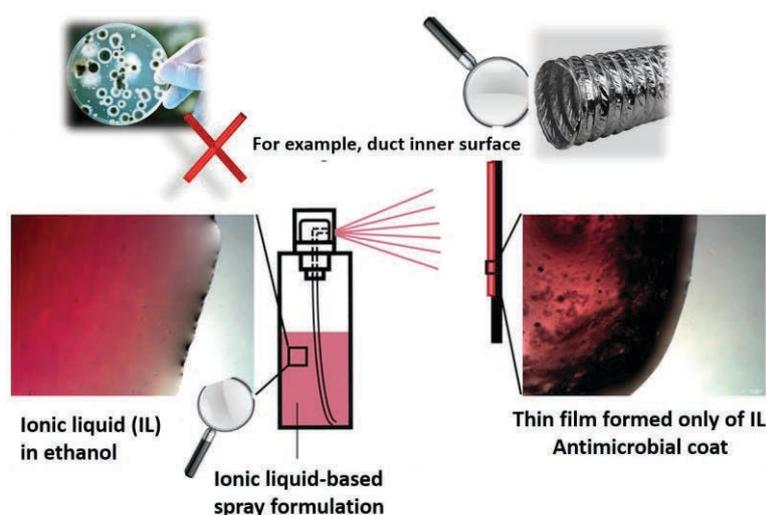
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The study aimed to prove how changes in lipophilicity of surfactants and their various structural modification (existence of the saturated and unsaturated alkyl chain, the elongation of alkyl chain on imidazolium cation of ionic liquid) influence toxicity towards investigated fungi. The purpose of the present study was to examine the effectiveness of newly synthesized ionic liquids (ILs) and salts on *Aspergillus niger*, *Aspergillus flavus*, *Penicillium italicum*, *Mucor mucedo* and *Trichophyton mentagrophytes*. The strategy of IL synthesis was a structural modification of ionic liquids through changing the substituent elongation on imidazolium cations and replacing the saturated ethyl-chain with vinyl- one. Further, the 1-alkyl-3-vinylimidazolium bromide ILs are polymerized in order to investigate the polymers effect on fungi. The findings clearly suggest that the length of alkyl chain on the cation is the most determining factor for IL toxicity. All these results demonstrate the high level of the interdependency of lipophilicity and toxicity for investigated ILs towards the investigated fungi.

Keywords: ionic liquids, polymers, surfactants, antifungal and antibacterial activity



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EP10.31

Surface Potential and Interfacial Water Order at the Amorphous TiO₂ Nanoparticle/Aqueous Interface

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Colloidal semiconductor nanoparticles exhibit unique size-dependent properties compared to their bulk counterparts, which can be particularly beneficial for catalytic applications. To develop highly efficient, environmentally-friendly photocatalytic devices it is essential to understand the surface chemical reactivity of nanoscale semiconductor materials and the microscopic structure of the nanoparticle-liquid interface.

Here we use polarimetric angle-resolved second harmonic scattering to determine surface potential values as well as interfacial water orientation of ~100 nm diameter amorphous TiO₂ nanoparticles dispersed in aqueous solutions, without any initial assumption on the distribution of interfacial charges. We find three regions of different behavior with increasing NaCl concentration. At very low ionic strengths (0-10 μM), the Na⁺ ions are preferentially adsorbed at the TiO₂ surface as inner sphere complexes. At low ionic strengths (10-100 μM), a distribution of counterions equivalent to a diffuse layer is observed, while at higher ionic strengths (>100 μM), an additional layer of hydrated condensed ions is formed. We find a similar behavior for TiO₂ nanoparticles in solutions of different basic pH. Compared to identically-sized SiO₂ nanoparticles, the TiO₂ interface has a higher affinity for Na⁺ ions, which we further confirm with molecular dynamics simulations. With its ability to monitor ion adsorption at the surface with micromolar sensitivity and changes in the surface potential, AR-SHS is a powerful tool to investigate interfacial properties in a variety of (photo) catalytic applications.

Keywords: Solid-Liquid Interfaces, Nanoparticles, Surface Potential

EP10.32

Correlation between lipophilicity of new B3 based salts and selected *Fusarium graminearum* growth rate

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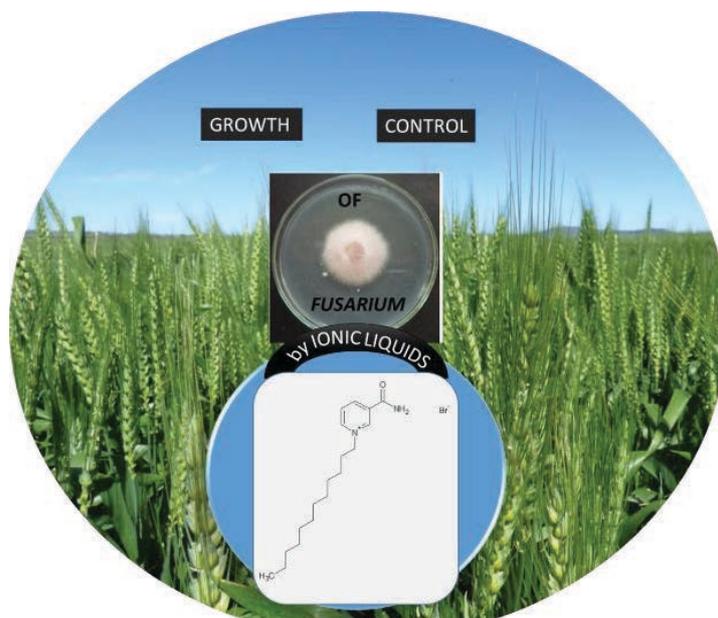
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The study aimed to prove how changes in lipophilicity of surfactants and their various structural modification (existence of the aliphatic or aromatic polar group, the introduction of oxygen and sulfur) influence toxicity towards investigated plants. The calculated lipophilic parameter (AlogP) shown to be a useful parameter for predicting potential toxicity of the compound. The purpose of the present study was to examine the effectiveness of newly synthesized ionic liquids (ILs) and salts on *Fusarium graminearum*, *Sclerotinia sclerotiorum* and *Botrytis cinerea*. The strategy of IL synthesis was a structural modification of ionic liquids through changing the polarity of imidazolium and pycoliniumcations and replacing halide anions with well known antifungal anions (cinnamate, caffeate and mandelate). The findings clearly suggest that the length of alkyl chain on the cation is the most determining factor for IL toxicity. In order to examine how IL structure affects their toxicity towards *Fusarium graminearum*, *Sclerotinia sclerotiorum* and *Botrytis cinerea*, lipophilic descriptor AlogP is calculated from density functional theory and correlated with growth rate. All these results demonstrate the high level of the interdependency of lipophilicity and toxicity for investigated ILs towards the *Fusarium* genus.

Keywords: C12 surfactants, toxicity, MD simulation, *Fusarium* genus



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Hydrophobically functionalized chitosan as a stabilizer for Pickering O/W emulsions

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In recent years chitosan (CHIT) drew great attention as an emulsion stabilizer. Due to many advantages of CHIT, such as being bio-sourced, biocompatible and biodegradable, its utilization in the preparation of Pickering emulsion allows replacing synthetic or inorganic stabilizers. However, despite many positive aspects of CHIT, it is not always the most suitable amphiphilic agent for preparing the O/W emulsions. In other words, CHIT, as a polysaccharide with a prominent hydrophilic character, requires modifications, e.g., grafting of hydrophobic moieties, in order to improve its interfacial properties [1-4].

The aim of the current work was to synthesize hydrophobically modified chitosan (30 % hydrophobization of both amino or hydroxyl groups). Functionalization was done by grafting side alkyl chains (*n*-octyl, *n*-dodecyl and *n*-hexadecyl derivatives) via secondary amide or ester linker to the chitosan backbone (abbreviated as R-X-CHIT, where R=*n*-C₈H₁₇, *n*-C₁₁H₂₃, *n*-C₁₅H₃₁; X= -C(O)O-, -C(O)N-) by the Steglich's amidation or esterification.

Secondly, various O/W Pickering emulsions (70:30 water:oil phase), stabilized by R-X-CHIT particles, were fabricated by rotor-stator, high-pressure or ultrasound homogenization. Dodecane was used as an oil phase, while the aqueous phase (sodium chloride solution, 10⁻⁴ – 10⁻¹ M) contained a dispersion of R-X-CHIT at a concentration range of 0.2 – 1.5 wt%. As a reference, a standard emulsion stabilized by Tween20 (1 wt%) or AOT (dioctyl sulfosuccinate, 4.5 wt%) instead of R-X-CHITs was used. Physicochemical properties studies of R-X-CHITs stabilized Pickering emulsions included measurements of the creaming indices, emulsion stability by laser scanning turbidimetry, microstructure observation by optical microscopy (droplet size of approx. 100 μm) and determination of the interfacial structure by dynamic interfacial tension measurements.

The obtained findings gave us the key information about the R-X-CHITs structure and its impact on the formation and stability of O/W emulsions.

Keywords: functionalized chitosan; polyelectrolyte; Pickering emulsion; physicochemical studies

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EP11.1

Development of nanoemulsions containing Vitamin D₃ for fortification of sheep milk

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The modern food industry is facing an increasing demand for healthier food options. To meet this need, innovative products containing bioactive substances that offer significant health benefits, the so-called functional foods, are constantly being developed [1]. Nanoemulsions have been proposed as good candidates for the encapsulation of sensitive desirable substances, such as vitamin D [2].

The aim of the present study was the replacement of the fat of milk products with vegetable oils. Fortification of sheep milk with Vitamin D₃ (cholecalciferol) using nanoemulsions was also studied. More specifically, oil-in-water (O/W) nanoemulsions using Tween 40, Tween 60 or emulsifiers used in dairy products were formulated. Vegetable oils such as soybean oil, sunflower oil and olive oil were used as the oil phase. For the development of the aforementioned systems a high-pressure homogenizer was used in accordance with the conditions dictated from the industrial partner. Following, Dynamic Light Scattering (DLS) technique was performed in the presence and absence of the bioactive substance, providing information on the size of the dispersed phase and the homogeneity and stability of the systems.

It was found that (O/W) nanoemulsions in the presence of Vitamin D₃ were successfully formulated for at least 15 days. More specifically, the system containing olive oil or soybean oil, Tween 40 and Vitamin D₃ remained stable for 50 days with a droplet size at around 360 nm. Overall, the proposed fortified nanoemulsions could act as good candidates for fat replacement in dairy products such as sheep milk or cheese.

Keywords: Sheep Milk, Functional Foods, Nanoemulsion, Vitamin D₃, Dynamic Light Scattering

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EP11.2

In-vitro gastrointestinal fate of milk proteins as influenced by a novel galactomannan isolated from alfalfa (*Medicago sativa* L.) seeds

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Milk proteins have found vast applications as ingredients for the food and feed sector. Besides, they can be employed as functional biopolymers in structurally and interfacially engineered colloids for controlled or sustained delivery of food bioactives [1]. Although, the interfacial activity, gelling and self-assembly properties of milk proteins have been well exploited in the design of novel encapsulation systems, their inherent ability to undergo extensive proteolytic attack during the early pre-absorptive digestion stages limit on some occasions their tangibility as wall materials. In addition, the use of non-digestible polysaccharides as co-encapsulants may provide benefits associated with their soluble dietary fiber role [2].

In the present work, a novel galactomannan (M/G \approx 1) isolated from alfalfa seeds [3] was tested for its ability to interact with milk proteins (sodium caseinate and whey protein isolate) under in-vitro simulated oro-gastrointestinal conditions. Model milk protein (10% wt) – alfalfa galactomannan (0.1 to 1% wt) aqueous solutions underwent in-vitro digestion according to the INFOGEST protocol and each of the obtained phases i.e., oral, gastric and intestine were characterized by means of oscillatory rheology, particle analysis (DLS-SLS), confocal laser scanning microscopy, OPA spectrophotometric assay and SDS-PAGE. According to our findings, the presence of alfalfa galactomannan induced a concentration-dependent increase in the in-vitro digestibility of the milk proteins, with the highest rates of free aminoacids release to be attained in the systems containing 1% of alfalfa gum. This was mainly attributed to the ability of alfalfa gum to control the acid-induced protein aggregation reciprocally to its concentration. In addition, it was assumed that extent of the segregative phase separation phenomena, and the impact of the alfalfa gum on the macroviscosity of the gastric and intestine phase constitutes an additional modulating parameter.

Keywords: Whey protein isolate, sodium caseinate; galactomannan; protein digestibility; colloidal changes

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EP11.3

Food-Approved, NADES-Based Surfactant-Free Microemulsions for Solubilization and Extraction of Curcumin

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Natural Deep Eutectic Solvents (NADES) are a new class of non-aqueous solvents. They are eutectic mixtures of naturally occurring, often hydrophilic hydrogen bond donors and acceptors, which exhibit a low melting point as compared to their single components. Through their desirable solvent characteristics, like low melting point and volatility, combined with high stability, solving capability, and biocompatibility, they can be considered an attractive, green alternative to common solvents. Since many molecules are conceivable to form these kinds of solvents, they can be specifically designed for food formulations. It is possible to form NADES only consisting of food-approved compounds, like choline-based or amino acid-based ones [1].

By mixing choline chloride-based NADES with a short-chained fat like triacetin with ethanol as the solubilizer, a completely food-agreed surfactant-free microemulsion (SFME) with a superior solubility of curcumin (2 to 5-fold increase) compared to previously studied water-based SFMEs can be generated [2]. An easy and fast room temperature extraction procedure was applied, extracting up to ~ 80 % of the total curcuminoid content of ground rhizomes of *Curcuma Longa* L. The high solubility of curcumin in the solvent systems allowed multiple extractions of fresh rhizomes in the same solvent until saturation [3]. While using the same amount of solvent, even more concentrated curcuminoid tinctures could be achieved when using the ternary NADES systems as compared to the aqueous SFMEs.

The tinctures obtained through extraction can be used for the coloration of foodstuffs and alcoholic beverages like gin and tonic (cf. Fig. 1).

Keywords: Natural deep eutectic solvents, surfactant-free microemulsions, extraction, food



Figure 1. Curcumin-colored gin and tonic.

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EP11.4

Nutrition potential of zinc– β -lactoglobulin complexes

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Micronutrients are an integral part of the immune system, and the body needs optimal levels of these nutrients for effective immune function. Micronutrient deficiencies can negatively affect the immune system and predispose to infections [1].

Whey proteins tend to interact with metal ions (e.g., zinc), affecting various areas related to human quality of life [2]. They may present opportunities for applications in food and nutraceuticals (protein as a zinc carrier). Still, they may also lead to analytical challenges related to their testing and performance in processing, storage, and food interactions. The predominant whey protein is β -lactoglobulin (β LG), a small globular protein consisting of 162 amino acid residues, accounting for 50% of the total whey protein content. It is a source of essential and branched-chain amino acids [3].

Zinc is an important trace element necessary for bone formation; a deficiency causes a risk of osteoporosis. In addition, it plays a key role in regulating immune homeostasis. Therefore, characterization of the interactions of zinc ions with β -lactoglobulin is crucial for the development of a process for the possible industrial-scale synthesis of a zinc-protein complex as a potential and inexpensive biologically active dietary supplement [4].

The present work focuses on the immobilization of zinc ions by β LG to understand the mechanism and nature of binding. Kinetic and isothermal sorption experiments were performed. In addition, spectrometric, spectroscopic, microscopic, thermal and X-ray diffraction measurements were carried out to investigate the obtained Zn- β LG complex. The stability of the prepared Zn- β LG complexes was also investigated in artificial physiological fluids: gastric and intestinal.

Keywords: whey protein, interactions of metal-protein, zinc ions, artificial physiological fluids

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Interfacial adsorption mechanism of Acacia gum: the effect of aroma hydrophobicity

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Beverage emulsions are thermodynamically unstable systems formed by an oil phase dispersed in an aqueous phase. The oil phase is generally composed by aroma molecules that belong to almost all classes of organic compounds and therefore, differ according to their molecular weight, anisotropy, and thermodynamic compatibility with water. It is well known emulsion stability can be increased by tuning the dispersing-phase parameters such as by the addition of an emulsifier as Acacia gum (AG) [1]. AG is defined as a dried exudate obtained from the stems and branches of *Acacia* trees. It consists mainly of high-molecular weight polysaccharide blocks bounded to a polypeptide chain [2]. This polysaccharide-protein duality gives an amphiphilic dimension to the gum which confers interesting interfacial and emulsifying properties.

It has also been demonstrated dispersed-phase parameters can affect emulsion stability [3], [4], [5]. However, there is room for further investigations, specifically on the aroma compounds hydrophobicity influence.

The aim of this work is to provide a better understanding of the effect of aroma hydrophobicity on the AG adsorption mechanism. The interfacial properties between AG and several aroma compounds have been studied using a drop tensiometer. Results shown different types of adsorption behavior regarding the aroma compound hydrophobicity. Based on the idea that interfacial tension is a physical manifestation of interfacial water activity, we calculated the latter using an equation based on the surface pressure [6]. For highly hydrophobic compounds, such as terpenes, interfacial water activity was around 0.6 while for hydrophilic compounds, such as alcohols, interfacial water activity tended to 1. The study of this parameter allowed to demonstrate that the interactions of the aroma compound with water, have an impact on the structural organization of water in the interphase and by consequence on the adsorption mechanism of Acacia gum.

Keywords: interphase, hydrophobicity, Acacia gum, water activity

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EP11.6

Arabinan side chains have a key influence on the emulsifying properties of sugar beet pectins

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Due to their functional properties, pectins are promising additives for the food and beverage industry. Sugar beet pectins (SBP) can be obtained from plant-based industrial by-products, thus providing a vegan, regional and sustainable alternative to established emulsifiers such as whey proteins or gum arabic. However, the relationship between structural composition and the emulsion stabilizing effect of pectins is still not fully understood; thus, systematic optimization of pectin extraction for pectins with improved emulsifying properties cannot be carried out. We assessed the underlying relationship between molecular structure and emulsifying properties. For this, relevant structural parameters of sugar beet pectins were linked to their emulsification result. Therefore, structurally different SBPs were extracted by using varying extraction conditions. Then, pectin stabilized emulsions were prepared using a high-pressure homogenizer and resulting droplet sizes were measured. The droplet sizes of the emulsions were used to correlate molecular characteristics with emulsifying properties.

The results showed that protein content, degree of methylation, degree of acetylation, mean molecular weights, and trans-ferulic acid contents are parameters that affect the emulsifying properties to some degree. However, they cannot fully explain the differences observed among all pectins. Instead, a linear correlation between the proportion of neutral sugar side chains (especially those rich in arabinose) and droplet sizes was observed.

Based on these results, we conclude that particularly branched arabinan side chains have a key influence on the emulsifying properties of SBP. We conclude that preservation of the native pectin structure during extraction leads to improved pectin-based stabilization of emulsions. Here, the arabinose content may serve as a suitable indicator for estimating the emulsifying properties of SBP. With this knowledge it is possible to optimize industrial pectin extraction and to apply improved pectins in the food industry.

Keywords: sugar beet pectins; extraction; molecular structure; emulsifying properties

EP11.7

Interfacial properties of phenolic antioxidants versus emulsion oxidative stability

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The antioxidant activity of surface active antioxidants in competitive adsorption with emulsifiers in emulsion systems has not been fully understood. The present work examines the effect of interfacial activity of selected phenolic antioxidants on their antioxidant activity in protecting the oxidation of polyunsaturated fatty acid triacylglycerols. Competitive adsorption of the antioxidants against non-ionic food grade emulsifiers is examined at different antioxidant concentrations and at emulsifier concentrations. In addition the antioxidant activity of the different phases of the emulsion is examined as well. Finally, the primary and secondary oxidation products of the lipid phase are determined.

Keywords: phenolic antioxidants, interfacial activity, competitive adsorption, emulsions

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EP11.9

Effect of ethanol on the stability of sodium caseinate stabilised emulsion

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Proteins are commonly used as emulsifying agent in food applications, although they are highly affected by their environment. One of the parameters known to influence their properties is the presence of ethanol. Cream liqueurs are emulsion-based beverages containing both, proteins and ethanol. The optimisation of their manufacturing process is a vital part in ensuring good long-term stability of such emulsion systems and in enhancing their shelf life. Especially the point of ethanol addition is believed to highly affect the physicochemical properties of the resulting products.

For this study, model cream liqueurs were created by combining sodium caseinate, aqueous ethanol solutions and sunflower oil which was freed from naturally present surface-active components. A microfluidizer was used for emulsion processing and two different points of ethanol addition in the processing route were investigated. The stability of emulsions at ethanol levels up to 50 wt.% was assessed over time.

An increasing level of ethanol was expected to result in a reduced protein functionality and, therefore, emulsion processing in the absence of this solvent was likely to lead to more stable oil-in-water emulsions. However, the results revealed that the point of ethanol addition only had an impact if the ethanol concentration was higher than 25 wt.%. For those higher alcohol levels the addition after the processing step resulted in systems which were more stable towards coalescence and gravitational destabilisation. The industrial significance of these findings could be extended by the application of additional ingredients, such as sugar and flavouring agents, as well as by the utilisation of a commercially relevant fat phase for emulsion preparation.

Keywords: cream liqueur, sodium caseinate, ethanol, oil-in-water emulsion, microfluidizer

EP12.1

Four modes of electrical conductivity observed in w/o ternary microemulsions

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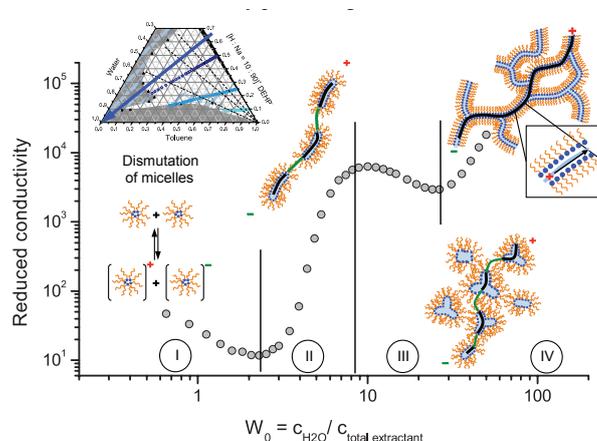
Water in oil microemulsions are at the core of all liquid-liquid extraction. Liquid-liquid extraction is currently the only known method to recycle magnets that are present in wind-mills. Rendering wind renewable means recycling the enormous amount of material used during the 20 year life-time of energy producing devices. The conductivity of water-in-oil microemulsions has been the subject of intense since fifty years, triggered by the initial puzzling observations by H. F. Eicke in the seventies (ECIS 1889 in Basel) , showing that no micelle exists in the absence of water. Thus the pseudo-phase approach introduced by Charles Tanford in the eighties for lipids and detergents.

At low water/surfactant ratio, typically below four the conductivity is extremely low, but increases or decreases depending on concentration. A higher water content, dynamic as well as static percolation behavior were suggested to explain the behavior of the most studied system (AOT/water/NaCl/isooctane). In intermediate water/surfactant ratio, an “anti-percolation” is observed upon dilution by water. This decrease of conductivity several decades to a moderate increase of water could only be explained by curvature constraints induced by partial dissociation of the head-groups and surface-to-volume constraints. Finally, less than ten years ago, the elusive dismutation regime when anionic and cationic w/o micelles coexist has evidenced by David Weitz and coworkers (ECIS 2013 in Sofia). Since no general phase prism of AOT based microemulsion was available, the generality of these various sometimes counter-intuitive behavior was questionable.

In the case of non-ionic microemulsions, the curvature is controlled by temperature, in the case of HDE-HP? The equivalent to an AOT with a phosphate head-group, the ratio of proton to sodium (hence the pH) is controlling the curvature. The HDEHP belongs to the class of flexible microemulsions, since the two hydrophobic chains are branched¹.

The knowledge of all stable single-phase zones in the phase prism allows not only the classical dilution lines with water and oil, but also to establish conductivity behavior while keeping all parameters constants, varying only the proton to sodium ratio , i.e. the spontaneous curvature². Confronting conductivity behavior observed along these different liens allows to identify and understand the condition of appearance of the four regimes of conductivity³ that were previously suspected but nether accessed in the same ternary phase diagram.

Figure 1.: The four regimes of conductivity identified for HDEHP extractant shown as function of the water to extractant mole ratio and sketch of the corresponding nanostructures (I) dismutation, (II) dynamic percolation, (III) curvaturefrustrated intermediate and (IV) static percolation. To obtain a clear identification between mechanism, one third of the H⁺ counter-cations need to be replaced by Na⁺, as shown via the dark blue arrow on the figure.



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Fabrication of Anti-Wetting Coatings for Cold Environments

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The formation and following accretion of different forms of ice poses serious safety and operational challenges in wind farms and airplanes, high voltage power lines, telecommunication systems, condenser surfaces, offshore platforms, locks and dams. Intense efforts are therefore dedicated to the development of passive ice protection systems (IPS) able to control or prevent ice formation. In particular, anti-wetting materials applied on the target surface have been explored as potential icephobic surfaces [1], with the Slippery, Liquid-Infused Porous Surfaces approach (SLIPS) being one of the most innovative and intriguing possible solutions to inhibit the ice accretion or weaken the ice adhesion strength without any power supply [2].

We present the design of anti-wetting hybrid coatings for cold environments (Figure 1A) that comprise an inorganic, porous layer based on ceramic (Al_2O_3 , SiO_2) nanoparticles obtained via sol-gel, while the organic layer consists of fluoroalkylsilane molecules. For SLIPS, either a fluorinated or a fluorine-free oil was infused in the porous hybrid coatings [3]. Through Icing Wind Tunnel located in a cold climate chamber, we assess the ability of the fabricated coatings to reduce the ice accretion on aluminum substrates in both glaze and rime icing regimes. The reduction of ice adhesion was instead determined with the Double Lap Shear Test. The dynamic behavior of droplets was also evaluated via goniometric contact angle hysteresis calculation, at both room and sub-zero temperatures (Figure 1B).

The remarkable icephobic behavior of SLIPS coatings developed highlights their potential as candidate for passive IPS especially in those application fields in which dynamic water repellency at subzero temperature is crucial (e.g. aeronautics). Moreover, in order to achieve a durable water repellency even when exposed at subzero temperature, SLIPS design proved the ability to recover functional performance after oil depletion phenomena.

Keywords: coatings/surfaces with reduced ice adhesion; anti-icing coatings and surfaces; bio-inspired coatings for anti-icing applications; nanostructured surfaces against icing.

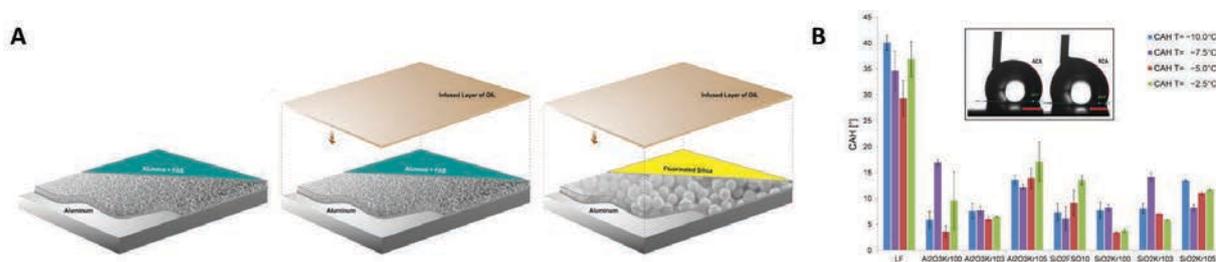


Figure 1. A) Coating design scheme, B) below-zero Contact Angle Hysteresis (CAH) grouped by coating type

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Preparation of Organic and Inorganic Hybrid Thermoelectric Materials Using PEDOT:PSS-Protected Ag Nanoplates

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Keywords: Ag nanoplates, Carbon Nanotubes, PEDOT:PSS, Thermoelectric material

Thermoelectric technology is used to convert heat energy to electric energy and vice versa, which is an interesting technology to recover electric energy from waste heat [1,2]. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has recently attracted increasing attention as a p-type organic thermoelectric material. The thermoelectric conversion efficiency is defined as the dimensionless figure of merit, i.e. the ZT value: $ZT = (S^2\sigma/\kappa) T$, where S , σ , κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Thermoelectric materials with a high ZT and power factor, $PF (=S^2\sigma)$ are desirable, yet there remains a trade-off between the σ and S . We believe that use of organic–inorganic composite materials is one of the effective routes to improve the thermoelectric properties and consider PEDOT:PSS to be a suitable matrix. Previously, we reported the thermoelectric properties of the composite thin films of PEDOT:PSS containing several types of metal nanoparticles as the inorganic component. In this study, we focused on a ternary hybrid system consisting of PEDOT:PSS, carbon nanotubes (CNTs), and Ag nanoplates.

The PEDOT:PSS-protected Ag nanoplates were synthesized by a hydrogen peroxide method. The nominal molar ratio, PEDOT:PSS / silver(I) nitrate was 0.7. A solution of AgNO_3 (0.025 mmol, 4.25 mg) in 24.5 mL PEDOT:PSS (0.0175 mmol in monomer unit), sodium citrate (96.8 mg 0.375mmol), 30wt% hydrogen peroxide (0.06 mL) and H_2O 25 mL was stirred under a N_2 atmosphere at room temperature. An aqueous solution of 0.1M sodium borohydride aq. (0.25 mL, 0.025 mmol) was then rapidly injected into the solution, and the mixture was stirred for 30 min. The PEDOT:PSS/CNT hybrid films containing various weight ratios of PEDOT:PSS-protected Ag nanoplates were prepared by the drop-cast method. 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.

The average diameter of PEDOT:PSS-protected Ag nanoplates was 28.9 nm. The Seebeck coefficient in the presence of the PEDOT:PSS-protected Ag nanoplates was almost unchanged. The electrical conductivity of the PEDOT:PSS/CNT films increased from 441 to 554 S cm^{-1} in the presence of the PEDOT:PSS-protected Ag nanoplates. The highest power factor, 63.1 $\mu\text{W m}^{-1} \text{K}^{-2}$, was observed for the 0.01 wt.% PEDOT:PSS-protected Ag nanoplates; the carrier flow within the film was accelerated by adding a small amount of the conductive PEDOT:PSS-protected Ag nanoplates, as shown in Figure 1. The electrical conductivity of the films containing the metal nanomaterials with the conductive layer increased with increasing metal concentration, i.e., the power factor improved.

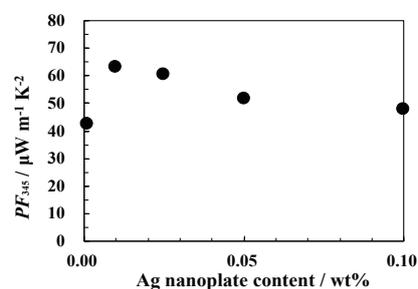


Figure 1. Thermoelectric power factor of PEDOT:PSS/CNT hybrid film containing various weight ratios of Ag nanoplates.

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EP13.1

Synthesis of Molecularly Imprinted Polymers for fenamiphos extraction

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Fenamiphos is an organophosphorus insecticide used in several stages of plant growth [1]. It is known for its high toxicity [2] and it is a persistent pollutant which can be found in rivers and soil. So it is necessary to control its concentration. But due to the complexity of the matrix containing fenamiphos, it is directly impossible to quantify it by means of chromatographic techniques such as HPLC.

- In this work, our purpose is to synthesize a polymer that contains specific cavities for adsorption fenamiphos molecules to be used later as adsorbent in the SPE technique. The molecularly imprinted polymers (MIP) were synthesized using surface molecular imprinting technique with silica covered with 3-mercaptopropyl groups as a support. Three types of molecularly imprinted polymers were prepared on the modified silica surface based on three types of monomers (methacrylic acid, 2-(methacryloyloxy)ethyltrimethyl ammonium chloride, 4-vinylpyridine).

- The characteristics of these MIPs were investigated by Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis.

- The recognition properties of the prepared materials were evaluated by the adsorption process using HPLC-DAD in order to select which functional monomer establishes the strongest interactions with the fenamiphos molecules.

- A modeling of adsorption isotherms of fenamiphos onto the prepared materials was realized and a thermodynamic study was applied to the chosen MIP by varying the temperature (35°C, 45°C, 55°C).

Keywords: Imprinted polymer, Fenamiphos, HPLC, Adsorption

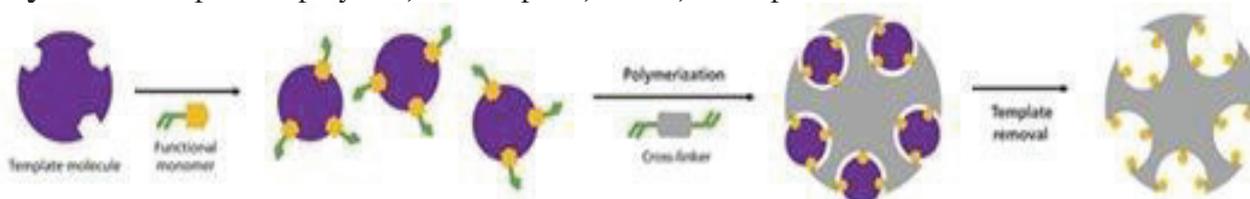


Figure 1. Synthesis of molecularly imprinted polymers

Acknowledgements This work was supported by the “PHC Utique” program for French-Tunisian cooperation (project number 19G1204).

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EP13.2

Design of molecularly imprinted material for the extraction of Histamine

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Introduction: Molecularly imprinted polymer materials (MIPs) are solid materials having "cavities" with well-positioned functional groups that act as selective molecular recognition sites for adsorption of target molecules, histamine in the present case. MIPs may be used for a wide variety of applications, such as analytical chemistry, chemical sensors, catalysis, and in particular drug delivery and specific capture of biological molecules. The present communication aims at a general introduction to the way MIPs are designed, and a discussion of a particular case dealing with the application to SPME devices (solid phase molecular extraction) used for pre-concentration of samples collected in complex matrices (environment, food, biological media) in order to make their subsequent analysis easier. Histamine is a cytokin involved in immune response. It is responsible for itch. Histamine poisoning has become very common in recent years due to its presence in many foods, more specifically in foodstuff containing bluefish. Ingestion of this substance at low doses, exceeding 50 ppm, can induce severe skin, respiratory, and gastrointestinal inflammation. The search for these toxic substances present in trace amounts in food based on fishery products is facing problems related to the treatment of the sample before analysis. Even though high performance analytical devices have good precision and sensitivity, the reliability of analyses crucially depends on the method of pre-treatment of the sample.

Method: The main objective is to develop a new method to optimize the extraction of histamine using solid supports based on molecularly imprinted polymer immobilized on a silica materials coated with a thin layer of MIP. MIPs manufacture requires a careful selection of a functional monomer that strongly interacts with the target. The functional monomer and the target molecule associated as complex species are copolymerized with a large amount of cross-linker so as to yield a solid polymer material that keeps the template molecule in its rigid network. Extraction of the target leaves a molecular imprint that keeps the memory of the shape of the target. Molecular imprints are sites for selective recognition of the target during utilization.

Results: The preparation of MIP allowing a selective separation of histamine requires a preliminary study leading to the choice of the functional monomer and the adequate cross-linker which establishes a suitable interaction with the target molecule. The materials were characterized by Elemental Analysis, TGA, IR, Zeta potential ...). The selective adsorption of histamine is demonstrated by a comparison of imprinted and non-imprinted materials.

Conclusions: The performance of these materials for histamine separation were verified by measurements of adsorption to these materials using LC-MS. As a prospect to this work, adaptation of the materials towards optimization of their performances in various situations such as pre-concentration devices where fast adsorption is required, capture in the environment, application to analysis and capture in biological systems and finally controlled drug release.

Keywords: MIP, Histamine, LC-MS, Polymers, Radical polymerization.

Acknowledgements: This work was supported by the "PHC Utique" program for French-Tunisian cooperation (project number 19G1204).

Molecular imprinted polymer using nitroxide-mediated controlled radical polymerization for selective and efficient extraction of UV filter degradation products in aqueous solution

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Molecular imprinted polymers (MIPs) were prepared for selective and efficient extraction of 3,5-dichlorohydroxyacetophenone (DCHA), a degradation product of octylmethoxycinnamate (OMC) detected in the aquatic environment. Controlled radical polymerization (CRP) was used to immobilize thin layer of polymer onto the silica surface in order to select the most suitable materials for SPE application. Firstly, modified silica with varying graft densities of methacrylate groups was used as supports. Secondly, the methacrylic acid monomer (MAA) was copolymerized with a small amount of styrene (S), DCHA as a Template molecule and ethylene glycol dimethacrylate EGDMA as a cross-linker in the presence of N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide (Styryl/DEPN) as a control agent. Adsorption kinetics and adsorption isotherms data of imprinted and non-imprinted (MIPs and NIPs) polymers were compared for all prepared materials. In all cases, the capacity to uptake DCHA of MIPs is greater than of NIPs. Interestingly, the MIP prepared by nitroxide-mediated polymerization exhibited higher selective DCHA site than that resulted by a free radical polymerization (FRP). The isotherm model shows that Volmer isotherm was suitable for the adsorption of SiO₂(PS-co-PMAA)@NIP-CRP and Langmuir–Volmer isotherm is the best fit model for SiO₂(PS-co-PMAA)@MIP-CRP. Thermodynamic behaviors of DCHA adsorption onto imprinted and non-imprinted materials were studied in detail and the thermodynamic parameters displayed a spontaneous and exothermic process.

Keywords Controlled radical polymerization; Imprinted materials; Pre-polymerization interactions; Selective adsorption; 3,5-Dichlorohydroxyacetophenone.

Acknowledgements This work was supported by the “PHC Utique” program for French-Tunisian cooperation (project number 19G1204).

Structure and orientation behaviour of spider silk films

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Recombinantly produced spider silk proteins eADF4(Cx) with x = 1-16 modules based on the fibroin 4 of the European garden cross spider *Araneus diadematus* (ADF4) have been established almost 2 decades ago.^[1] Responsible for the outstanding mechanical^[2] and biomedically relevant^[3] properties of such spider silk proteins are their special multiblockcopolymer-like structure including hydrophilic amorphous and hydrophobic crystalline blocks. Aiming at a better understanding of folding processes in spider silks, herein we report experimental work on thin films of eADF4(Cx) proteins, examining the influence of methanol and water treatment on the secondary structure and orientation within these proteins.

Thin films of eADF4(Cx) (≈ 40 nm) were cast from hexafluoroisopropanol solutions on silicon substrates (Si), which were post-treated with methanol vapor for 24 h (pt) and afterwards treated with MilliQ water (5 min). eADF4(Cx) films were characterized as-cast, during pt and after water treatment using dichroic attenuated total reflection (ATR-) FTIR spectroscopy, circular dichroism (CD), and scanning force microscopy (SFM).^[4]

As-cast, FTIR reveals low β -sheet ($< 10\%$) and high random coil content ($> 65\%$) using Amide I band analysis, whereas films after pt reveal higher β -sheet content (28 – 43 %) and lower random coil content ($< 50\%$).^[4-5] Post-treated films are stable against water and no further changes in secondary structure and orientation can be observed. CD measurements confirm observations of an increased β -sheet content for eADF4(Cx) proteins after pt.^[4] By dichroic ATR-FTIR spectroscopy, dichroic ratios R^{ATR} up to 1.58 for the Amide I component at 1697 cm^{-1} assigned to antiparallel β -sheet structures are found, suggesting an *out-of-plane* orientation of the antiparallel β -sheets of the crystalline blocks embedded in the random coil phase of the amorphous blocks (Fig. 1).^[4]

Keywords: FTIR spectroscopy, spider silk, orientation, secondary structure

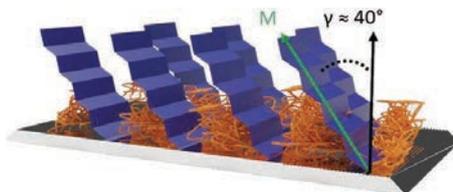


Figure 1. Out-of-plane oriented antiparallel β -sheets (blue) embedded in an amorphous matrix (orange) in eADF4(Cx) protein films after MeOH post-treatment.^[4]

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EP13.5

Classified as Confidential PMMA colloidal particles as model to study the electrokinetic surface response to diabetic environments

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The use of model particles to study physical surface changes due to adsorption processes is a starting point to understand more complex colloidal systems. This is the case of studies that try to understand the physicochemical changes that the surface of bacteria undergoes when they are in the presence of compounds that promote their pathogenicity. Pathogenicity is defined as the ability of these bacteria to adhere to a host surface, proliferate and ultimately form an infection. One of the environments that causes a higher incidence of infections is associated with metabolic alterations in diabetic patients [1].

Different surface properties can be studied, but this work will focus on the study of a key surface property to promote-avoid bacterial infections such as the electrical interaction potential or zeta potential. The research will be carried out with PMMA model particles and will analyze the changes in the zeta potential at 25°C and 37°C when the surfaces are exposed to molecules present in diabetic serum such as glucose and ketone bodies (acetone, acetoacetate and hydroxybutyric acid).

The surface of PMMA in contact with glucose, acetone and ketone bodies mixture is more negative at 25°C than at 37°C. Changes in the zeta potential depend on the type of diabetic component: glucose, acetoacetate and acetone tend to increase the negative value of the zeta potential, especially at 25°C, while the presence of hydroxybutyric acid reverses this trend: the absolute value of the zeta potential is drastically reduced. This is also the case when the mixture of components is studied. The discussion of results will take into account the changes that the addition of these components causes in the conductivity of the medium and will attempt to separate the possible effect of pH and molecule-surface interactions on the electrokinetic potential.

Keywords: PMMA, Zeta Potential, Diabetes, Glucose, Ketone bodies

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Physicochemical and adsorption characteristics of S,S'-thiodi-4,1-phenylenebis(thiomethacrylate)-co-divinylbenzene microspheres as materials for the removal of aromatic compounds

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Water is an essential compound for life of many organisms (people, animals or plants), however the industry development and globalization make the problem of water pollution getting worse [1]. One of the problematic substances are the organic compounds which the molecules are built of aromatic rings. The benzene derivatives are usually hazardous substances which are difficult to decompose in water. For this reason, the selective sorbents for water remediation from aromatic compounds are intensively looking for [2-3].

Materials with good sorption properties have the following characteristics: well-developed surface area, well-defined pore system, presence of sorption centers, high selectivity towards adsorbates, high sorption efficiency, low synthesis costs, thermal, chemical and mechanical resistance, long lifetime [4]. On the material market is available a wide range of various monolithic sorbents: silicas, carbons, or zeolites but one-component materials have some limitations. Therefore, the new materials with better properties are the subject of search. The response for the developing market of materials are two or more phase materials which due to the synergistic effect eliminate many of the restrictions. Moreover, the design and control of synthesis procedure allow to obtain the materials with strictly defined characteristics [5].

In this work, the S,S'-thiodi-4,1-phenylenebis(thiomethacrylate)-co-divinylbenzene (DMSDS-DVB) microspheres were synthesized in the emulsion-suspension polymerization reaction with three different molar ratio compositions of phases: 3:1, 2:1 and 1:1. One of the main aim of this work was the assessment of the impact of phase molar ratio composition on the textural, structural, thermal and adsorption properties of inorganic-organic microspheres using various instrumental techniques: scanning electron microscopy (SEM), Fourier transform infrared/attenuated total reflection spectroscopy (FT-IR/ATR), nitrogen low-temperature sorption, thermal analysis coupled with quadrupole mass spectrometry (QMS) and FT-IR and UV-Vis spectroscopy. Moreover, the kinetic and equilibrium adsorption studies towards selected aromatic compounds revealed the potential applicability of the DMSDS-DVB materials as sorbent systems for the removal of water from organic compounds.

Keywords: inorganic-polymeric materials, microspheres, adsorption, water treatment

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Molecular dynamic simulation of pheromones adsorption during atmospheric transport

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Chemical communication is ubiquitous in insects and plants life but complete understanding of the paths taken by chemicals to explain the performance of these systems is not achieved. Critical gaps exist in the understanding of the physico-chemistry of these chemicals for their transport in the near-ground atmosphere. We proposed that some of them get adsorbed on aerosol surface and transported as clusters [1]. Therefore aerosols could carry chemical signals over long distances.

The kinetic of this adsorption process is sufficiently fast to occur during the atmospheric transport of the pheromones [1]. To assess this mechanism, identification of molecular candidates and model interface leading to high enough adsorption free-energy is necessary. In this talk, we will present molecular dynamics simulations that enable to evaluate and compare the adsorption on water-air interface of an iconic pheromone (bombykol) and three of its derivatives with adsorption free energy between 5 to 11 $k_B T$ (13 to 26 KJ/mol) [2]. These results help us to gain insights in the processes that might play a role in pheromonal communication of insects and illustrates the importance of physico-chemistry of interfaces in chemical ecology.

Keywords: Adsorption; pheromones; aerosols; chemical ecology; steered molecular dynamics; transport phenomena

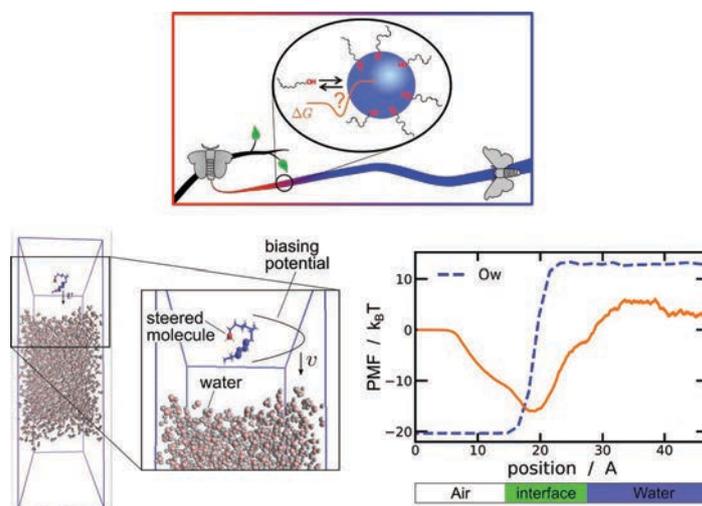


Figure 1. Steered molecular dynamics enables to evaluate the free energy of adsorption of pheromones on aqueous aerosol surface.

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Enzymatic degradation of semi-dilute polymer solutions: coupling between enzyme mobility and activity

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Biodegradable polymers (synthetic or natural) can be degraded by the action of living organisms. In most cases, biodegradation occurs through enzyme-catalysed depolymerisation, where enzymes hydrolyse bonds along the polymer chains. Lignocellulosic biomass (LC) is one of the most abundant renewable polymers that, when degraded, represents a tremendous source of interesting products. However, LC is difficult to degrade because plant cell wall polysaccharides are structurally and chemically complex molecules, forming a heterogeneous network of varying density and porosity.

During industrial degradation, enzymes are confronted with LC substrates (e.g. wheat straws) that are insoluble and partially hydrated. They penetrate and propagate in the material, while at the same time changing its properties through hydrolysis. Although fascinating, little is known about the coupling between enzyme activity and mobility in the context of dense polymeric systems. In extremely tight polymer networks, the coupling is obvious: enzymes cannot just enter the polymer mesh and consequently move by 'eroding' the polymer surface [1]. In the more general case, enzymes can enter the network, but their activity is affected by the restricted diffusion in the polymer mesh [2]. Nevertheless, studies only consider the impact of the concentration of the polymer, neglecting its structural and dynamical evolution with hydrolysis time [3]; two characteristics that must have an effect on enzyme propagation in the material.

Here we explore the coupling between enzyme mobility and activity by using a model polymer, arabinoxylan, extracted from wheat LC and a fluorescently labelled enzyme. We prepare semi-dilute polymer solutions that are concentrated at different mesh sizes. Then, the radial diffusion of the enzymes is observed using fluorescent microscopy. We present the results obtained with catalytically active and inactive enzymes. To complement these results, we present ex-situ experiments aiming at characterizing the polymer during the degradation (viscometry, SEC-MALS).

Keywords: Enzymatic mobility and activity, semi-dilute polymer solution, fluorescence microscopy, degradation of lignocellulosic biomass

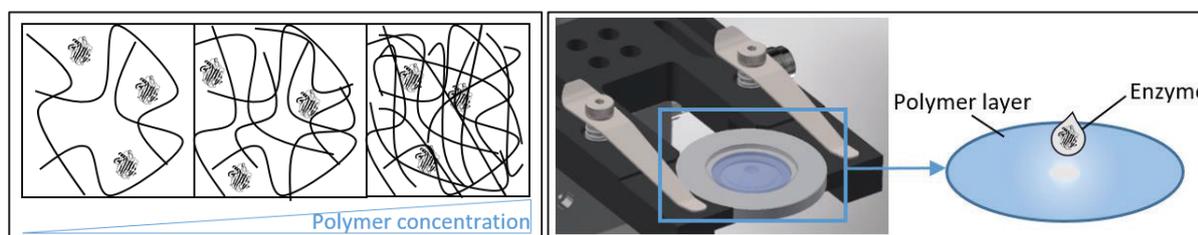


Figure 1. Left-hand side: The evolution of the mesh size and confinement with increasing polymer concentration. Right-hand side: The circular microscopy chamber containing the polymer solution. The enzyme is deposited in the middle and the chamber is sealed. The fluorescent front induced by the radial diffusion of the enzymes is then followed over time.

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Evaluation of C12 surfactants effect on growth of cucumber and wheat

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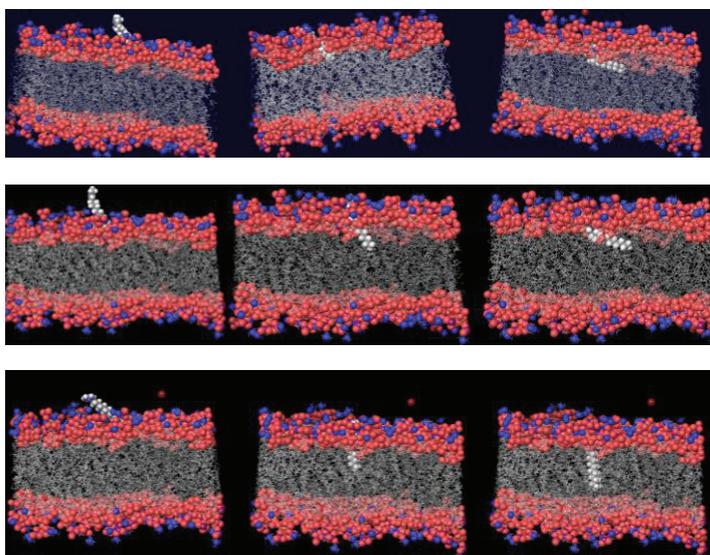
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The broad range of different surfactants is increasingly common in commercial use nowadays. This situation may lead to the contamination of the natural environment and may constitute a potential threat to all its elements, including terrestrial higher plants. We investigated the effect of 13 surfactants on germination, development and growth of wheat and cucumber, through detailed experimental and theoretical study. The study aimed to prove how changes in lipophilicity of surfactants and their various structural modification (existence of the aliphatic or aromatic polar group, the introduction of oxygen and sulfur) influence toxicity towards investigated plants. The calculated lipophilic parameter (AlogP) shown to be a useful parameter for predicting potential toxicity of the compound. The strategy of using surfactants with aliphatic polar heads instead of aromatic prove to be a promising strategy in reducing harmful effect, as well as the introduction of polar groups in the structure of cation. From all investigated compounds, surfactants with imidazolium polar head displayed the most harmful effect towards wheat and cucumber. The cucumber seeds were more sensitive to the addition of surfactants comparing to wheat. All obtained experimental results were additionally investigated using computational methods, simulating the transport of surfactant through a lipid bilayer. The surfactants with cation that best mimic the structure of bilayer have a less harmful effect on plant development.

Keywords: C12 surfactants, toxicity, MD simulation, cucumber, wheat



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EP14.1

Self-organizing biocoatings deposited on plasma PEEK polymer - preparation and characteristics

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Polyetheretherketone (PEEK) is biocompatible polymer widely used in medicine as a material for the production of human bone implants. The problem associated with regenerative process is the limited osseointegration on PEEK surface and low values of surface free energy [1]. To overcome this disadvantage, PEEK surface was activated by air plasma and coated with chitosan and Langmuir-Blodgett (LB) monolayers of drugs: cyclosporine A (CsA) and naproxen (NAP). Films created on PEEK surface were combined with phospholipid 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) and/or cholesterol (Chol). The obtained coatings with lipids should strengthen the interfacial area between the cells and the artificial material. As a consequence, the platelets adhesion, blood clot formation, and the amount of adhering bacteria can be limited [2].

Prepared systems were characterized in terms of changes of its wettability and surface free energy. The modified PEEK surfaces revealed interesting wetting properties depending on the type and composition of the films. The stability and behaviour of the film after water contact was tested applying TOF-SIMS technique. Obtained results showed the structure of hybrid coatings revealed on chemical maps as well as CsA/NAP desorption during water action.

Keywords: PEEK, wettability, surface free energy, TOF-SIMS

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EP14.2

Wetting of solids by aqueous solutions of ethanol and rhamnolipid mixture

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Wetting is an important phenomenon which results from intermolecular interactions between the solid and the liquid. Wetting and adhesion can be influenced by adding surfactants/biosurfactants to the solutions. Addition of substances that influence on the hydration of head and tail of the surfactants can affect the wetting as well. Such substances are short chain alcohols which affect surfactant adhesion, aggregation, and adsorption properties [1,2].

The aim of this study was to determine ethanol (ET) influence on rhamnolipid (RL) adhesion and wetting properties. For this purpose, the contact angle measurements were conducted using aqueous solutions of RL and ET mixture on the surfaces of polytetrafluoroethylene (PTFE), poly(methyl methacrylate) (PMMA), and quartz. Obtained results were analyzed together in regard of the surface tension components of the appropriate solids, water, ET, and RL in respect of its head and tail surface tension. Through the thermodynamic analysis, it was possible to consider adsorption of ET and RL at the solid-solution interface and to take into account the dependencies between adhesion, work of adhesion, and surface tension. Obtained results allowed to determine the critical surface tension of solid wetting for all considered solids and these values were later compared to the respective surface tensions. Basing on the calculated data, it was showed that ET molecules can replace RL molecules in the mixed interface layer and cause the increase of the contact angle. Basing on the considerations made for PTFE, it was possible to predict the contributions of RL and ET molecules adsorbed on the interface from RL and ET mixed solutions.

Keywords: wetting, adhesion, ethanol, rhamnolipid, biosurfactants

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Porous PVDF-based Membranes Coated with Superhydrophobic Nanoparticle for efficient Membrane Distillation

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Widespread water scarcity caused by population growth, climate change and water pollution has become one of the major global challenges to be addressed in order to secure adequate high quality water resources. In this context, up to now, many water treatment technologies have been proposed to address water scarcity and water purification. Among them, processes based on membrane technology such as membrane distillation (MD) have received significant scientific and technological attention. Polymeric membranes are currently the most widely used membranes for water treatment due to their enhanced structural properties and also to relatively low costs compared to inorganic membranes [1]. In this study, innovative superhydrophobic nanocomposite polymeric membranes were developed, aiming to improve the direct contact membrane distillation (DCMD) performance compared to the currently available state of the art membranes. Porous poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membranes were developed and further modified by the introduction of superhydrophobic fluorinated silica (SiF) nanoparticles [2] as top coating. The produced membranes were characterized by a variety of techniques, such as SEM, AFM, contact angle (CA), liquid entry pressure of water (LEP) and bubble point (BuP). Additionally, the anti-fouling performance of the membranes was evaluated using bovine serum albumin (BSA) as model fouling agent. It was found that, compared to the unmodified PVDF-HFP membrane, the SiF coating renders the membrane superhydrophobicity ($CA > 170^\circ$, Fig. 1A) and oleophobicity (Fig. 1B), while DCMD experiments showed 3x improvement in water flux having excellent salt rejection and enhanced anti-fouling properties (Fig. 1C). The above results indicate that the developed nanocomposite membranes exhibit improved overall performance aiming to tackle critical issues of membrane distillation process.

Keywords: Superhydrophobic nanoparticles, fluorinated silica, membrane distillation, desalination, anti-fouling.

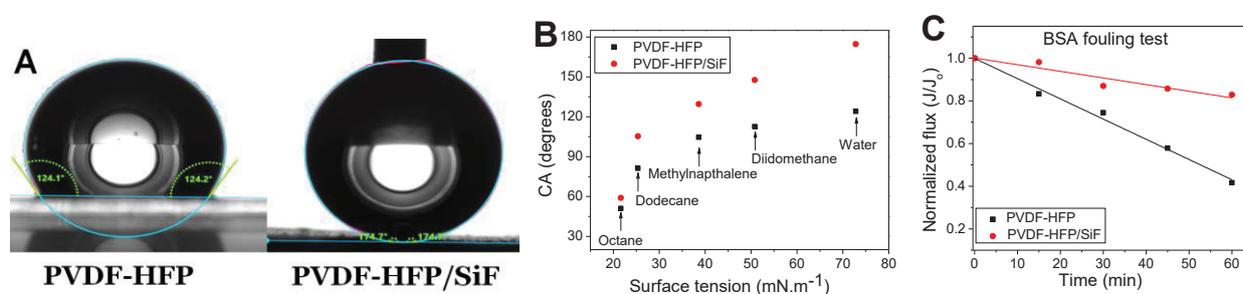


Figure 1. Water contact angles (A), contact angles as a function of surface tension (B) and anti-fouling performance (C) of PVDF-HFP vs. PVDF-HFP/SiF membranes.

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Switchable wetting of lipid vesicles on bio-inspired, non-biological polymer brushes

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Plants and animals protect themselves from environmental heavy metal ions by using proteins that have a very high affinity to heavy metal ions. Such proteins possess a common combination of side chain functionalities, carboxy- and thiol-group(s).

Inspired by biology, we have designed artificial polymers based on poly(acrylic acid) containing cysteine side chains. First, the affinity of polymers with Cd ions was assessed in solution using isothermal titration calorimetry and dynamic light scattering. Our data indicated that our bio-inspired polymer has much stronger affinity to Cd ions compared to pure poly(acrylic acid) with no -SH groups. Moreover, we found that Cd ions have a much higher affinity than Ca ions.

Next, these polymers were grafted on the planar surface. To precisely control the surface density of polymer chains with nm accuracy, polymers were modified with biotin and anchored on supported lipid membranes via neutravidin crosslinkers. [1] Analysis of the vertical Brownian motion of latex particles with microinterferometry [2] demonstrated that the binding of Cd ions drastically suppressed the height fluctuation of the particle, denoting the particle was sharply confined in the presence of Cd ions.

Wetting of giant lipid vesicles on the surface coated with bio-inspired polymers was assessed by confocal fluorescence microscopy imaging in the absence and presence of Cd ions. The contact angle of vesicles in the absence of Cd ions was around 180°, implying that the surface is not wet by lipid vesicles (non-wetting). Intriguingly, by adding $[Cd^{2+}] = 1$ mM, a clear decrease in contact angle was observed ($\approx 140^\circ$), indicating that the vesicle underwent a transition from “non-wetting” to “partial wetting” state. Remarkably, the critical concentration for the wetting transition for Ca ions was much higher, demonstrating the ion selectivity of our bio-inspired polymer.

Keywords: bio-inspired material, wetting, switchable surface, lipid vesicles

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Fabrication of Antifouling Coating for Marine Applications

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Marine bio-fouling consists in undesirable settlement and accumulation of marine microorganism, plants and animals on submerged surface of materials and it has huge adverse influence on infrastructures. Marine bio-fouling increases the weight and roughness of ship hulls which raises the frictional resistance and causes additional fuel consumption [1]. The microorganisms contained in the sea water in contact with the surface of the hull adhere causing the growth of biofilm. Superhydrophobic surfaces have been investigated as a potential solution to avoid this phenomenon. We present the design of anti-wetting hybrid coating for antifouling environments (Figure 1a) that comprise an inorganic, porous layer based on functionalized ceramic nanoparticles (Al_2O_3 , SiO_2 , $\text{SiO}_2\text{-F}$) obtained via sol-gel, and an organic layer consisting of fluoralkylsilane molecules. Moreover, liquid-infused coatings were fabricated by infusion of fluorinated oil PFPE in the porous hybrid coating[2]. These coatings were deposited on materials like steel, aluminum and fiberglass. The reduction of the accretion of fouling was investigated by larval settlement test (*A. Amphrite*, a hard fouler[3]). In addition, release tests were carried out to evaluate the toxicity of the coating for the marine environment in accordance with the ASTM 6442 standard[4].

Keywords: i) hydrophobic coating/surface ii) antifouling surface iii) bio-inspired coating for antifouling application

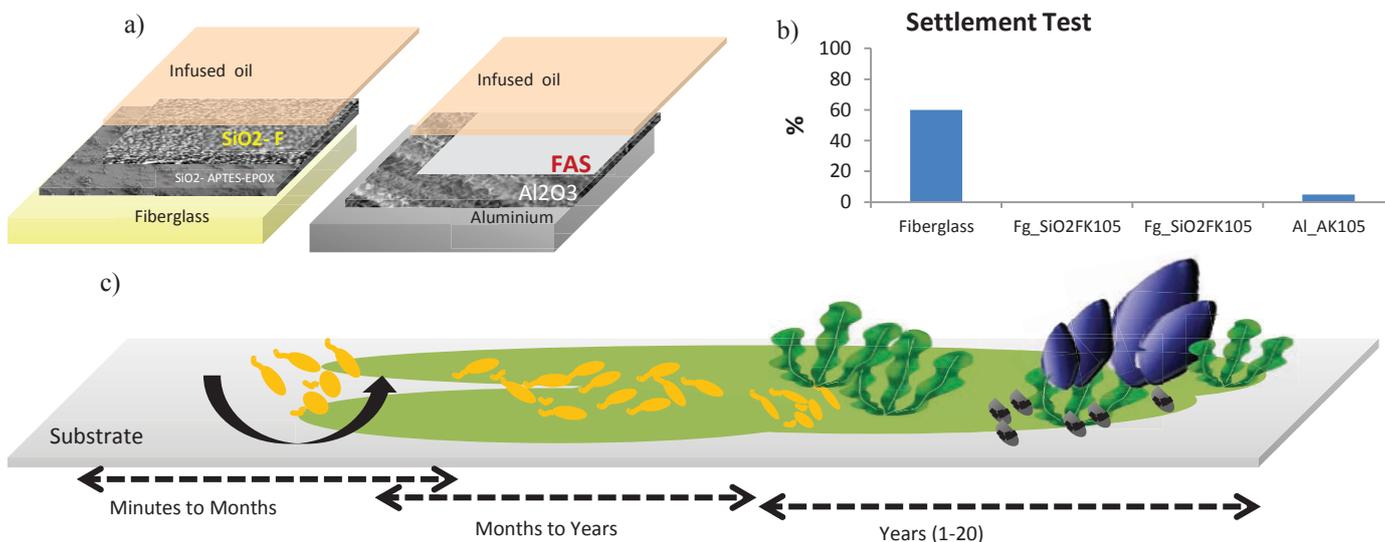


Figure 1. a) Coating design scheme b) Settlement test c) Schemating biofouling progression

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EP14.6

A Unified Approach to Disjoining Pressure in Interlayers around Lyophilic and Lyophobic Particles

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Using the unified approach within the classical density functional theory, we have calculated [1-3] the equilibrium local density profiles, the components of the pressure tensor, and the thicknesses of thin flat and spherical interlayers between a lyophilic or lyophobic solid surface and a gas or liquid phase, respectively.

These interlayers are not isotropic, and there is a disjoining pressure in them. Dependences of this pressure on the interlayer thickness have been found. In the presence of a capillary pressure inside the interlayers, the disjoining pressure counteracts it and leads to the appearance of stable long-living droplets around lyophilic solid particles and stable long-living bubbles around lyophobic particles. It has been shown that the mechanical and thermodynamic definitions of the disjoining pressure in a spherical interlayer agree with each other. In contrast to case of liquid films on lyophilic particles, the disjoining pressure in stable spherical vapor layers around a nanosized lyophobic solid particle is found to be greater than in flat vapor layers near a planar lyophobic substrate. Increasing lyophobicity provides that the disjoining pressure isotherms change from non-monotonic to monotonic functions of the vapor layer thickness.

Keywords: interlayer, lyophobic, lyophilic, disjoining pressure

Acknowledgements: This work was supported by the Russian Foundation for Basic Research (Grant 19-03-00997a).

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Condensation frosting on *Cotinus Coccigrya* leaves

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Passive anti-icing surfaces are of interest for cooling systems, aircraft and power supply infrastructure. Under real conditions leading to freezing, condensation often forms initially. Depending on the field of application, the requirements are that supercooled, impacting droplets bounce even in the presence of condensation or that condensation frosting is delayed. The first condition is subordinate to the second because once the frost is formed the impacting drops will remain adhered to the ice. The *Cotinus Coccigrya* leaf offers interesting insights to study the complex propagation dynamics of frost and to draw inspiration for the design of anti-icing surfaces. Condensation exhibits multiple and frequent coalescence-induced jumps thanks to the presence of wax nanotubules on the leaf. We studied the evolution of the droplets size and distances distributions at different surface temperature and humidity conditions and analysed the relations between the distributions, the frost propagation speed and the formation of areas of condensate depletion which slow down the advancement of the frost.

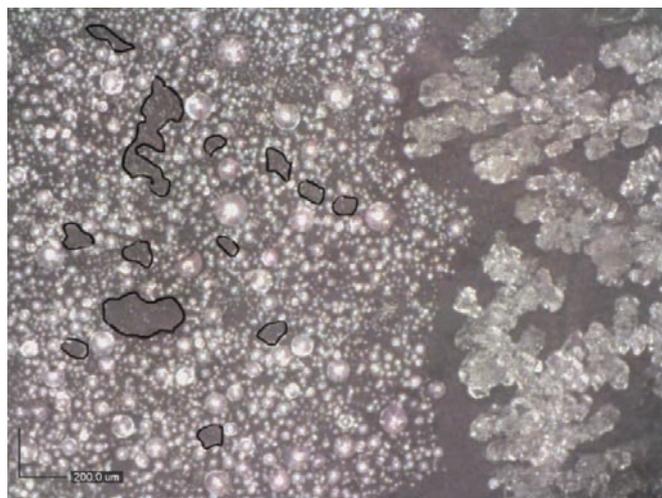


Figure 1. Condensation frosting on a *Cotinus Coccigrya* leaf ($T_{\text{leaf}} = -11^{\circ}\text{C}$, saturation ratio = 3,5). Solid black lines indicate the areas with condensate re-nucleation after multiple droplet jumping. These areas significantly contribute to the failure of ice bridges and thus slow down the frost propagation.

EP14.8

Branched ionic trimethylsilyl surfactant demonstrates superspreading properties

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Superspreading, a very fast spreading of aqueous surfactant solutions over moderately to highly hydrophobic substrates has attracted great scientific and practical interest since it was first discovered 3 decades ago [1]. The practical interest is due to applications of this phenomenon in coating, agriculture, medicine etc. The scientific challenge is to explain the mechanism of superspreading and therefore provide guidance for tailored synthesis of superspreading surfactants for specific applications. So far, only trisiloxane surfactants demonstrate distinctive superspreading properties. Therefore, some hypotheses about the mechanism are based on specific T-shaped structure of trisiloxane molecules (Fig. 1, left), and specific bi-layer aggregates formed above critical aggregation concentration. Other hypotheses suggest that Marangoni driven flow is a part of the mechanism and therefore surfactant equilibration rate is of importance for superspreading.

Here we present a new branched ionic surfactant, magnesium salt of bis (3-(trimethylsilyl)-propyl) 2-sulfosuccinate, $Mg(AOTSiC)_2$, which has very different structure compared to trisiloxane superspreaders (Fig. 1, left), but demonstrates very similar kinetics of spreading (Fig. 1, right) on a moderately hydrophobic substrate, Polyvinylidene fluoride (contact angle of water 81 °). Two surfactants also have very different values of critical aggregation concentration and equilibration rate at concentration providing the fastest spreading (Fig. 1, centre).

Keywords: aqueous surfactant solutions, hydrophobic substrate, complete wetting, superspreading

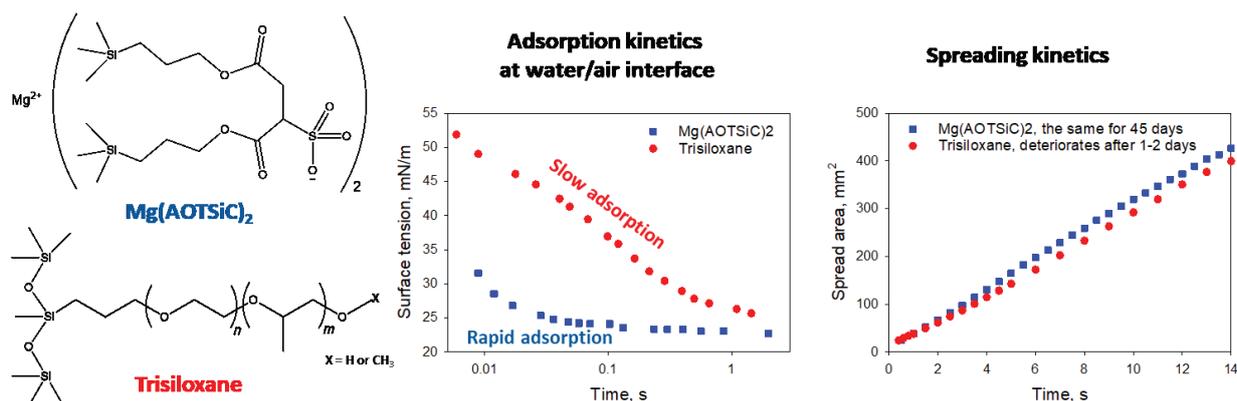


Figure 1. Comparison of branched ionic trimethylsilyl surfactant $Mg(AOTSiC)_2$ and trisiloxane superspreader: chemical structure (left), dynamic surface tension (centre), and spreading kinetics (right) [2].

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Ice Adhesion to Solids: Mechanisms, Temperature Dependence, and Ways to Control

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Ice adhesion plays a crucial role in the performance of materials under outdoor conditions, where the mitigation of snow and ice accumulation or spontaneous shedding of solid water precipitations is highly desirable. In this presentation, we will discuss the adhesion of water and ice to different surfaces and consider the mechanisms of ice adhesion to solids basing on the surface forces analysis. The role of a premelted or quasi-liquid layer in the ice adhesion [1] will be analyzed and demonstrated.

We will present a new measuring system, based on the modification of the centrifugal approach for the measurement of ice shear adhesion strength and exploiting the stroboscopic effect to detect the single ice detachment event which allows one to obtain statistically reliable values of ice adhesion strength. The application of above approach enables one to compare the values of ice adhesion strength to icephobic surfaces with different chemical compositions and study the temperature dependence of ice adhesion in a wide temperature range (Figure 1). A review of ice adhesion strength to different icephobic engineering materials will be given.

Keywords: anti-icing surfaces; work of adhesion; quasi-liquid layer; adhesion strength; superhydrophobicity; icephobic surfaces; temperature dependence; surface forces; wettability

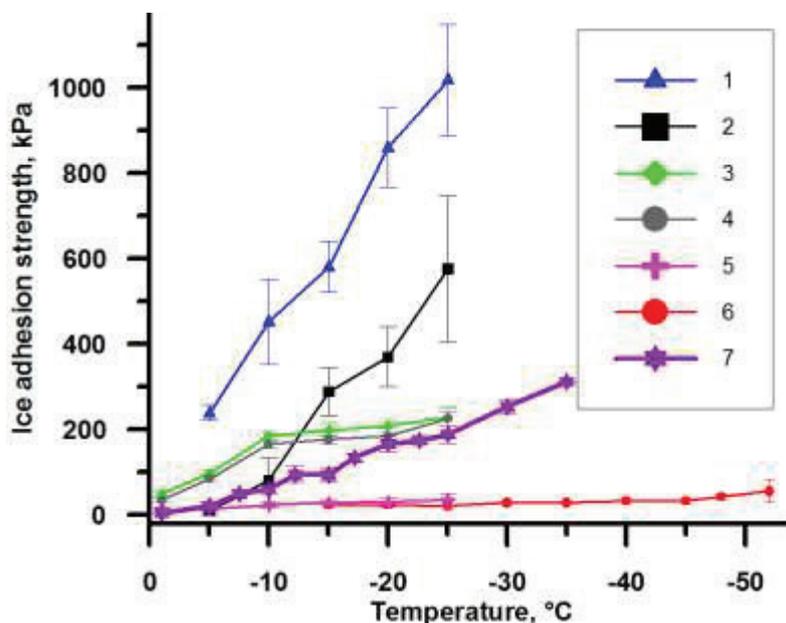


Figure 1. Temperature dependences of ice shear adhesion stress for different substrates: 1 – ultra-smooth hydrophilic silica substrates ($R_a < 0.4$ nm); 2 – silica plates coated with an adsorbed diblock copolymer layer; 3, 4, 5 – micro-nano structured aluminum surface modified by perfluorooctyltrichlorosilane, polydimethylsiloxane (PDMS), and silicon-oil-infused PDMS-modified surface, respectively; 6 – dimethylolpropionic acid–polyurethane composite coating with an aqueous lubricating layer; 7 – superhydrophobic aluminum plates fabricated in this study.

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Nanodroplets Deform Soft Substrates: Elasticity vs. Capillarity

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A liquid droplet sitting on soft substrates induces deformation of the substrates: a wetting ridge rises along the three-phase contact line and a dimple forms underneath the droplet. Whereas surface tension is usually associated with the spherical shapes of small droplets and bubbles, the tensile force at the surface of solids, known as surface stress, is responsible for surface instabilities of thin films and elastocapillary deformation of soft solids. Surface stress, as given by the Shuttleworth equation, is a coupling of elastic strain and surface free energy. However, the strain-induced increase in surface free energy is usually not considered in theoretical modeling.

In this study, we probe the three-dimensional interfacial configuration of soft substrates (with different shear moduli) deformed by nanodroplets (with different sizes). We show that the substrate deformation undergoes a transition from the substrate elasticity-dominated regime to the substrate capillarity-dominated regime with increasing a characteristic ratio γ_S/Gr (where γ_S and G are the surface tension and shear modulus of the substrate and r is the contact radius of the nanodroplet). In comparison to the theoretical models, our experimental results suggest that the Shuttleworth effect should be considered when $\gamma_S/Gr \gtrsim 1$, i.e., when the droplets are sufficiently small and/or the substrates are sufficiently soft.

Keywords: elastocapillary deformation, transition, Shuttleworth effect, nanodroplet, soft substrate,