

Water-In-Diesel Fuel Nanoemulsions: Preparation, Stability and Physical Properties

[M.R. Noor El-Din](#)^{1*}, Sabrnal H. El-Hamouly², H. M. Mohamed¹, Marwa R. Mishrif¹ and Ahmad M. Ragab¹

¹*Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El- Zomor St., Nasr City, Cairo, 11727, Egypt.*

²*Chemistry Department, Faculty of Science, Menoufia University, Menoufia, Egypt*

***mrned04@yahoo.com**

Abstract

In this work, water-in-diesel fuel nanoemulsions were prepared with mixed nonionic surfactants. Several mixtures of sorbitan monooleate and polyoxyethylene (20) sorbitan monooleate, with different Hydrophilic-Lipophilic Balance (HLB) values (9.6, 9.8, 10, 10.2 and 10.4) were prepared to achieve the optimal HLB value. Three mixed surfactant concentrations were prepared at 6, 8 and 10% to identify the optimum concentration. Five emulsions with different water contents: 5, 6, 7, 8 and 9% (wt/wt) were prepared using high energy method at the optimum conditions (HLB=10 and mixed surfactant concentration=10%). The effect of HLB value, mixed surfactant concentration and water content on the droplet size has been studied. The interfacial tension and thermodynamic properties of the individual and the blended emulsifiers were investigated. Droplet size of the prepared nanoemulsions was determined by dynamic light scattering and the nanoemulsion stability was assessed by measuring the variation of the droplet size as a function of time. From the obtained results, it was found that the mean droplet sizes was formed between 49.55 and 104.4 nm depending on HLB value, surfactant concentration and water content of the blended emulsifiers. The physical properties, kinematic viscosity and density, of the prepared nanoemulsions and the effect of different temperatures on these properties were measured.

Key words: Emulsification; Ostwald ripening; Water-in-diesel fuel nanoemulsions; Interfacial tension; Kinematic viscosity; Density.

Polymer-surfactant complexes for microencapsulation of active ingredients

S.B. Aidarova^{a*}, A.A. Sharipova^{a,b}, D. Grigoriev^b and R. Miller^b
^a *International Postgraduate institute "Excellence PolyTech" of Kazakh National
Technical University, Almaty, Kazakhstan*
^b *Max-Planck Institute of Colloids and Interfaces, Potsdam, Germany*

zvezda.s.a@gmail.com

Microencapsulation is a versatile technique to enclose various active ingredients in tiny envelopes (microcapsules) which can be used for the broadest purposes such as protection, targeted and/or controlled release or micro confined reactions between materials encapsulated. The preparation of microcapsules of desired characteristics depends on various factors such as size and nature of the core substance, the properties of the wall material, techniques and parameters of encapsulation. The layer-by-layer technique is the most popular and frequently studied method for the encapsulation of sensitive reagents. However this technique has different challenges which connected to many polyelectrolyte layers with many steps of washing procedure, to giving the certain initial surface charge to the template and etc.

In this work a novel approach to encapsulation of Vitamin E was developed. The droplets of an o/w emulsion stabilized by polyelectrolyte-surfactant complexes were used as initial carriers for the active agent and simultaneously as liquid templates for the microcapsules build up using the layer-by-layer polyelectrolyte deposition. It is noteworthy that the polyelectrolyte-surfactant complex served not only as an electrosteric emulsion stabilizer but also as a charged precursor for the subsequent shell assembly. Comprehensive characterization of initial and final capsules on each preparation stage was carried out by CLSM, Cryo-SEM, size distribution and Zeta-potential measurements.

Gradual slowing down of the Vitamin E release was observed in each stage of capsules shell formation. The final microcapsules showed a sustained release of Vitamin E within at least 80 hours.

The microencapsulation approach developed is straightforward and economic and could be used for the encapsulation of bioactive ingredients for cosmetic and food applications.

Preparation of Water-In-Diesel Fuel Nanoemulsions and Study Its Stability and Physical Properties

[M.R. Noor El-Din](#)^{1*}, Marwa R. Mishrif¹, R. E. Morsi¹, E. A. El-Sharaky¹, A.M. Rashad¹,
D.I.Osman¹, and Rania.T.M.Ghanem¹.

¹*Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El- Zomor St., Nasr City, Cairo, 11727,
Egypt.*

***mrned04@yahoo.com**

Abstract

In this work, water-in-diesel fuel nanoemulsions were prepared with mixed nonionic surfactants. Several mixtures of sorbitan monooleate and polyoxyethylene sorbitan trioleate, with Hydrophilic-Lipophilic Balance (HLB) value (10). Four mixed surfactant concentrations were prepared at 4, 6, 8 and 10% to identify the optimum concentration. Six emulsions with different water contents: 5, 6, 7, 8, 9 and 10% (wt/wt) were prepared using addition low energy method at HLB=10 and different mixed surfactant concentration. The effect of mixed surfactant concentration and water content on the droplet size has been studied. Droplet size of the prepared nanoemulsions was determined by dynamic light scattering and the nanoemulsion stability was assessed by measuring the variation of the droplet size as a function of time. From the obtained results, it was found that the mean droplet sizes were formed between 28.48 and 268.8 nm depending on surfactant concentration and water content. The physical properties as kinematic viscosity, pour point, freezing point and density of the prepared nanoemulsions were measured.

Key words: Emulsification; Ostwald ripening; Water-in-diesel fuel nanoemulsions; Interfacial tension; Kinematic viscosity; Density.

surface properties and antimicrobial activity of new synthesized quaternary ammonium surfactants based on diphenyl methane.

T.M. Kassem, A.S. Mohamed, D.E. Mohamed and F.M. Abdel hafiz
Egyptian Petroleum Research Institute Cairo, Egypt

Presenting author's email : tawfikkassem2015@gmail.com

In the present work, a series of novel conventional diphenyl methane derivatives have been obtained in high purity by chloromethylation of diphenyl methane to give mono chloromethylated diphenyl methane, followed by esterification of the fatty acids (octanoic, decanoic and dodecanoic) by methyl diethanol amine to give their corresponding esters. The final step was quaternization of the chloromethylated product with esters to give conventional cationic surfactants. The chemical structures of the prepared compounds were confirmed by FTIR and ¹H-NMR. The results are in good accordance with the expected structure for each compound. Surface activity of these compounds have been thoroughly studied and their surface properties including surface and interfacial tension, emulsification power, critical micelle concentration, effectiveness, efficiency, maximum surface excess and minimum surface area were determined. The thermodynamic parameters including standard free energy change (ΔG°) of both adsorption and micellization were calculated at 25°C. The prepared surfactants showed significant surface activity. Also, all the prepared surfactants were evaluated as biocides against different bacterial and fungal species as well as against sulfate reducing bacteria (SRB). The synthesized cationic surfactants showed significant biocidal activity against Gram +ve, Gram -ve bacteria and different fungal species. Also the results indicated that, all the synthesized cationic surfactants have significant antimicrobial activity against sulfate reducing bacteria (SRB).

REFERENCES

- 1- Cheng Y. F., Yuen C. W. M., Kan C. W and Hu J. Y., J. Applied Polymer Science, 104, (2007), 803.
- 2- Okoliegbe I. N., Agarry O. O., Scholarly J. of Biotechnology 1, (2012), 15.
- 3- Pileni M. P., Langmuir 17, (2001), 7476.

Experimental and computational study of light scattering by foams

R. Hans Tromp^{1,2}, and Marcel B. J. Meinders³

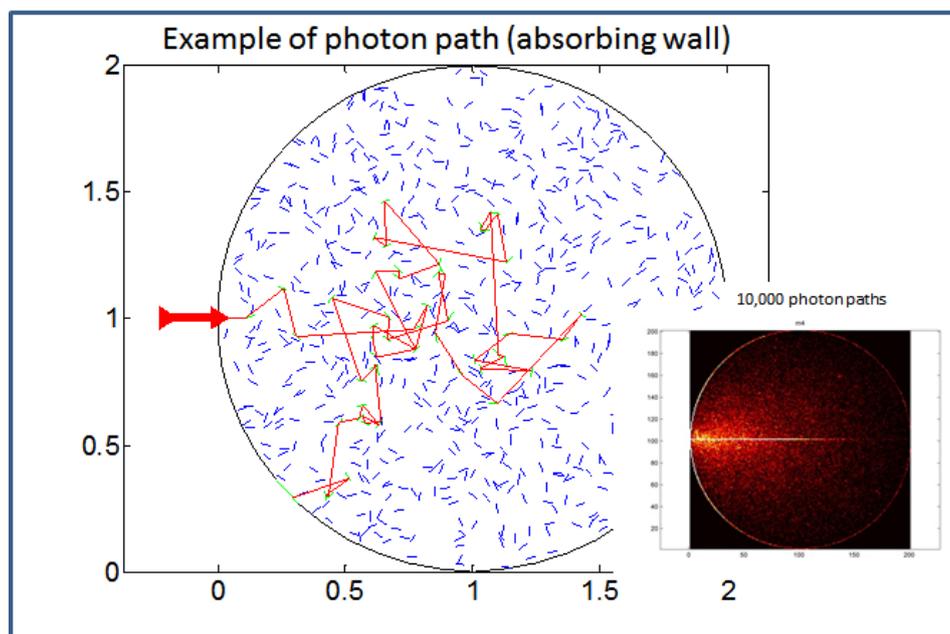
1. NIZO food research, Kernhemseweg 2, 6718 ZB Ede, The Netherlands

2. University of Utrecht, van't Hoff laboratory for Physical and Colloid Chemistry, Padualaan 8, 3584 CH Utrecht, The Netherlands

3. Wageningen UR Food & Biobased Research, Bornse Weiland 9, 6708 WG, Wageningen, The Netherlands

The interaction of foam with a light beam causes the light to be scattering by multiple light scattering. After a typical penetration distance –traditionally labelled l^* - the beam spreads in a way that can be described by classical diffusion of photons, with the appropriate boundary conditions set by the optical properties of the container wall. In this work, the static intensity and the fluctuations of light scattered and transmitted by foams in a cylindrical geometry were studied. The results were interpreted in terms of the volume fraction of air and the dynamics of the structural elements of the foam. The interpretation of the experiments was assisted by a simple 2-dimensional simulation of the pathways of photons in a system of reflecting rods with a specific ordering.

It turned out that in order to obtain structural information from light scattered by foams, it is of great use to induce a considerable degree of light absorption. This can be accomplished by adding a colorant to the liquid. The meaning of l^* in the case of foams, and the interpretation of the time autocorrelation function (diffusing wave spectroscopy) will be discussed*.



*This work was partly funded by TI Food and Nutrition, Nieuwe Kanaal 9A, 6709 PA Wageningen, The Netherlands

An improvement of electrowetting hysteresis of oil droplets on hydrophobic dielectric coatings with the addition of amphiphilic compounds

Varioptic is the leader in production and commercialization of electrowetting based optical devices.

The typical configuration used in Varioptic's electro-optical devices is the electrowetting of oil droplets surrounded by a conductive phase on a hydrophobic dielectric surface. One of the features of these devices is their very low optical hysteresis, thanks to a good understanding of electrowetting hysteresis : some early work from our research group demonstrated that low electrowetting hysteresis is obtained when the contact angle of the oil droplet on the hydrophobic dielectric is very low (lower than 15°).¹ However, the preferred formulation for the design of new liquid lenses present sometimes a poor contact angle of the oil phase on the dielectric surface (typically parylene C). In this communication, we will present specific amphiphilic compounds we added in our formulations to improve the wetting of the oil phase on hydrophobic surfaces. We will describe the results obtained with different types of amphiphilic compounds and present the optimum design of liquid formulations using these compounds. Therefore, we can now obtain very low electrowetting hysteresis with systems which have basically poor wetting properties. Afterwards, we will propose a rationale of the optimum design.

1. Maillard, M., Legrand, J. and Berge, B., "Two Liquids Wetting and Low Hysteresis Electrowetting on Dielectric Applications," *Langmuir* 25, 6162 (2009)

Nanoparticle-Laden Surfactant Mesophases Under Confinement and Shear

J. Berge^a and W. H. Briscoe^a

^a*School of Chemistry, University of Bristol, Bristol, United Kingdom*

johanna.berge@bristol.ac.uk

Mesophases self-assembled from surfactants and lipids are fascinating states of matter. When under confinement, they exhibit structures and properties different from those in the bulk, such as smectic layering,¹ confinement-induced phase transitions² and enhanced lubrication properties.³ Such confinement is ubiquitous in natural systems such as the knee joints.⁴

The interactions between surfaces mediated by lyotropic mesophases mixed with nanoparticles in a well-defined nanocavity have not been reported previously. Fundamentally, it is interesting to see how nanoparticles of different size, shape and surface chemistry would perturb these highly organized mesomorphic structures. Using a surface force apparatus (SFA), we have made direct measurement of interactions in CTAB/hexanol/water lamellar mesophase systems (d -spacing = 23 nm),⁵ and our results show significantly different surface force, but particularly friction, when 14 nm negatively charged gold nanoparticles are present in the mesophase at nanoparticle/surfactant volume ratio $\sim 10^{-3}$. Such results have fundamental implications to nanotoxicology,⁶ in particular endocytosis of nanoparticles by cells,⁷ drug delivery,⁸ and applications of nanofluids.⁹

1. Horn, R. G., *et al.*, *J. Phys. France* **1981**, 42 (1), 39.
2. Petrov, P., *et al.*, *Langmuir* **1994**, 10 (4), 988.
3. Richetti, P., *et al.*, *Europhys. Lett.* **2001**, 55 (5), 653.
4. Chen, M., *et al.*, *Science* **2009**, 323 (5922), 1698.
5. Abillon, O.; Perez, E., *J. Phys. France* **1990**, 51 (22), 2543.
6. Donaldson, K., *et al.*, *Occup. Environ. Med.* **2004**, 61 (9), 727.
7. Siegel, D. P., *Biophys. J.* **1993**, 65 (5), 2124.
8. Libster, D., *et al.*, *J. Colloid Interface Sci.* **2007**, 308 (2), 514.
9. Pilkington, G. A.; Briscoe, W. H., *Adv. Colloid Interface Sci.* **2012**, 179–182 (0), 68.

The Adsorption of Lipopolysaccharide Molecules on Various Polymyxin-B (PMB) immobilized Surfaces

R. Tsay,^a W.P. Lin,^a Y.L. Liu^a

^aInstitute of Biomedical Engineering, National Yang-Ming University, Taipei, Taiwan

tsay@ym.edu.tw

Presenting minute amounts of lipopolysaccharides (LPS) in blood results in severe toxic effects; therefore, there are many researches focus on neutralizing and detoxifying the LPS. It has been known that polymyxin B (PMB) molecules can effectively detoxify LPS and has very high binding affinity with LPS. In this study, branched polyethyleneimine (PEI) was grafted on the HS-(CH₂)₁₀-COOH self-assembled monolayer (SAM) to build up a PEI based modified surface. And PMB was immobilized on the PEI based surfaces to promote the LPS binding efficiency. The film thickness was measured by ellipsometry and FTIR was applied to analyze the surface properties.

For the PEI based surface modification, experimental results showed that higher pH value of PEI solution could promote the adsorption of PEI on SAM surfaces. And the thickness of immobilized PMB follows the similar trend as PEI thickness. For the LPS binding efficiency, polycationic PEI could adsorb small amount of LPS through electrostatic interaction. The adsorption thickness of LPS changes with the thickness of PEI surfaces modified at various pH although the difference is slight. The LPS adsorption film thickness was around 0.2 nm for PEI adlayer immobilized at pH 4. Immobilization of PMB on PEI surfaces increases the surface density of primary amines and positive charges and therefore can substantially increase the LPS adsorption thickness to about 0.65 nm. By further adjusting the reaction conditions of crosslinker to immobilize PMB on PEI film could control the degree of crosslinking and keep a loose structure of PEI layer, which could push the LPS adsorption thickness up to 0.8 nm. For PEI layer immobilized at higher pH value, its thickness was much larger than a PEI film obtained at pH 4. Such PEI film further immobilized with PMB molecules can increase the adsorption film thickness of LPS to 1.59 nm.

Measurement of Surface Forces at High Pressure

D.W. Pilat^a, B. Pouligny^b, A. Best^a, K. Koynov^a, R. Berger^a, H.-J. Butt^a

^a*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

^b*Centre de recherche Paul-Pascal, Avenue Schweitzer, 33600Pessac, France*

butt@mpip-mainz.mpg.de

Today, surface force measurements are typically limited to ambient pressure, with few exceptions (Schurtenberger & Heuberger, *J. Supercritical Fluids* 2012, 71, 120). This is rather unfortunately because important colloidal systems are exposed to high pressure. Examples for high pressure environments include secondary and tertiary oil recovery or gas release in hydrothermal vents in deep sea. Here we will present a method for measuring surface forces at hydrostatic pressures between 1 and 103 bar. The method is based on optical trapping of particles (Nadal et al., *Appl. Phys. Lett.* 2001, 79, 23). A silica bead of 5 μm diameter is pushed against a transparent solid wall by a moderately focused laser-beam. In case of a repulsive surface force F_S the bead will move against the wall until an equilibrium distance d is reached. In equilibrium the force applied by the laser, F_D is equal to F_S at that distance. Using an interferometry technique, d is determined. Thus, by varying the intensity of the laser, the force-vs-distance is measured. The advantage of this method is that it can readily be used in combination with a high pressure cell as developed for optical microscopy.

Effect of lauryl gallate on wetting properties of organized thin lipid films on mica

M. Jurak

Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

malgorzata.jurak@poczta.umcs.lublin.pl

Lauryl gallate is an ester of gallic acid and has both a hydrophilic galloyl group and a hydrophobic alkyl chain. Such surfactant-like structure facilitates its penetration into the membrane interior where it interacts with the lipid components altering the membrane stability. Membrane binding ability of the lauryl gallate can be correlated with its pharmacological antibacterial, antiviral and antitumour activity. On the other hand, the membrane functionality is determined by the hydrophilic/hydrophobic balance which results from molecular interactions between lipids and water (and also other liquids). Water is the external medium of most biological systems. Therefore studies of interactions of molecules building the cell membranes with the surrounding water are of particular interest especially for practical purposes in development of biosensors, biocompatible implants or targeted drug delivery. This work provides experimental evidence of the character of interactions between lauryl gallate (LG) and components of biological membranes, i.e. 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), 2-oleoyl-1-palmitoyl-*sn*-glycero-3-phosphocholine (POPC), 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) or cholesterol (Chol), as well as interactions of these layers with liquids of different properties. The binary mixed monolayers: DPPC/LG, POPC/LG, DOPC/LG, and Chol/LG, were deposited on mica applying the Langmuir-Blodgett technique. The wetting properties of the lipid layers were determined from the contact angle measurements of three probing liquids, two of which were polar (water and formamide) and one apolar (diiodomethane). The values of measured contact angles were used for evaluation of surface free energy and its components of the studied surfaces based on the theoretical models proposed by van Oss, Good, Chaudhury (LWAB) and Chibowski (CAH). From the analysis of the contact angles and the surface free energy values, it results that stability and permeability of the binary films deposited on mica are determined by the kind of lipid and stoichiometry of the mixed monolayers.

Funds for the investigations carried out by young researchers No. BS-03-0000-D011 are highly appreciated.

**Properties of polymer-supported films of biological substances
prepared by the Langmuir-Blodgett technique**

M. Jurak,* A.E. Wiącek, K. Terpiłowski, M. Worzakowska
Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

*malgorzata.jurak@poczta.umcs.lublin.pl

Polymers are widely recognized in the fields of drug technology, pharmacy and medicine. They are responsible for the transport of therapeutic substances in the organism and their gradual release at target sites. To increase the polymer biocompatibility and adhesion, its surface can be modified with low-temperature plasma. Additionally, covering the polymer surface by a film of natural biological substances and/or substances of pharmaceutical importance can make such systems as promising carriers of drug to diseased sites in the body. Our studies were aimed at determination of (oxygen, argon, nitrogen) plasma effect on changes of surface properties of the polymer polyetheretherketone (PEEK), in two aspects: specific mechanical properties and their adhesive properties. Mechanical, viscoelastic and thermal properties of PEEK were determined both before and after using plasma. Original polymer plates and those after modification with plasma were coated with biological substances, i.e. phospholipid, lauryl gallate or mixed layers, by means of the Langmuir-Blodgett (L-B) method which was found to be useful to prepare highly organized two-dimensional (2D) films. Lipid layers were studied with regard to their affinity for biological membranes while lauryl gallate layers – potential activity towards tumours, bacteria and viruses. Wettability of both unmodified and modified surfaces of the polymer, as well as those covered with films of biological substances was investigated by measurements of advancing and receding contact angles of water, formamide and diiodomethane. Then, the values of the measured contact angles were used for determination of surface free energy and its components of the studied surfaces based on the theoretical models. The results demonstrate that the appropriate plasma choice and deposited film composition influence on wettability and thermodynamic parameters of the studied systems. This is of relevance for a rational development of targeted drug-carrier systems.

Support from Maria Curie Initial Training Network “Complex Wetting Phenomena” (Project number 607861) is highly appreciated.

Lubrication Properties of Alkylphenyl Ether Lubricants Studied by Resonance Shear Measurement

Junichi Watanabe¹⁾, Masashi Mizukami¹⁾ and Kazue Kurihara^{1,2)*}

¹⁾Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
2-1-1, Katahira, Aoba-ku, Sendai, 980-8577, Japan

²⁾WPI-Advanced Institute for Material Research, Tohoku University
2-1-1, Katahira, Aoba-ku, Sendai, 980-8577, Japan

*Corresponding author: kurihara@tagen.tohoku.ac.jp

Lubricants are often used in a confined narrow space between solid surfaces under a high pressure, especially, in the boundary lubrication region of the Stribeck curve. However, the properties of nano-confined lubricants have not been investigated. In order to study the nano-confined liquids, the resonance shear measurement (RSM), which we developed, is a powerful tool. In this study, the tribological properties of four phenyl ether lubricants, monoalkyldiphenyl ether (MADE), dialkyldiphenyl ether (DADE), m-phenoxyphenoxy m-biphenyl (m-4P2E), and m-bis(m-phenoxyphenoxy) benzene (m-5P4E), confined between mica surfaces have been investigated using RSM. The RSM study revealed that the viscous parameter (b_2) of these lubricants significantly increased when they were confined in narrow space. In a gap smaller than ca. 2–3 nm, the b_2 values were in the order of MADE > DADE > m-4P2E \approx m-5P4E, while their bulk viscosities were in the order of m-5P4E > m-4P2E > DADE > MADE. Further, the MADE, which has the lowest bulk viscosity, was relatively easily squeezed out from the gap compared to others. Thus, the direct characterization of confined lubricants is imperative for designing efficient lubricants, especially for boundary lubrication. It was also indicated that the high friction in the boundary lubrication, which has been considered to be due to the partial direct contact of the solid surfaces, could be due to the significantly high viscosity of the lubricants confined in a nano-space gap. We will discuss the friction force estimated using the parameters determined by analyzing the resonance curves.

Reference

J. Watanabe, M. Mizukami and K. Kurihara, "Resonance Shear Measurement of Confined Alkylphenyl Ether Lubricants," *Tribol. Lett.*, 56 (2014) 501.

Importance of the formulation pathway on the growth of LbL multilayer films

J. Giermanska,^a S. Sekar,^a I. Ly,^a J.-P. Chapel,^a

^aCentre de Recherche Paul Pascal (CRPP), UPR CNRS 8641, Université Bordeaux, Pessac, France

giermanska@crpp-bordeaux.cnrs.fr

One of the most important objectives in the fabrication of LbL multilayers is a reproducible fine control of the morphology and the thickness of the growing film. A feature rarely investigated and put forward in the literature and intimately related to the formulation pathway. In this work, we show on a system of oppositely charged polyelectrolytes that failure to control the processing condition might strongly influence the film growth. The growth of the fully organic poly(acrylic) PAA / poly(diallyldimethylammonium) PDDAC multilayer system is indeed inhibited in the presence of salt at pH=7 where only electrostatic forces are at play (we confirm the result of Alfonso and al. ⁽¹⁾ for different salt contents). Lowering the pH to 4 or replacing the PAA chains by PAA covered ceria nanoparticles triggers the appearance of secondary forces (hydrophobic, H-bonding) allowing then the multilayer formation. The final characteristics of the film will depend however on the aggregation state of the building-blocks and the pathway followed to acidify the solution. Finally, if one of the constituents presents some hydrophobicity, the numerous crossing of the air/water interface during the LbL process can generate large morphological inhomogeneities; a feature not seen inside the cell of a QCM set-up where the LbL growth is entirely monitored under solution. Another striking example of the strong influence of the processing pathway....

(1) Alonso, T.; Irigoyen, J.; Iturri, J. J.; Larena, I. L.; Moya, S. E. *Soft Matter* **2013**, *9*, 1920–1928.

Measurements of liquid content in 2D overflowing foams with positron emission tomography (PET)

K. Cole^{a,*}, P. Brito-Parada^b, J.J. Cilliers^b, S. Neethling^b, A. Buffler^a
^a Department of Physics, University of Cape Town, South Africa.
^b Department of Earth Science and Engineering, Imperial College London, UK.

katie.cole@uct.ac.za

Liquid content is an important factor in determining the structure and stability of aqueous foams. Measurements of the liquid content of aqueous foams are necessary to validate numerical models of foam behaviour, and have been made possible by the application of medical imaging techniques to foam research. Recently positron emission tomography (PET) was used to directly measure the liquid content inside flowing 2D foam (Cole et al., 2015). The foaming liquid is labelled with a solution of a “PET radioisotope” such as ⁶⁸Ga which is allowed to disperse throughout the foam to steady state. Positrons from the ⁶⁸Ga tracer ions annihilate with local electrons to produce pairs of back-to-back 0.511 MeV gamma rays which can be detected in coincidence by the PET scanner to define a line along which the annihilation occurred. With multiple lines, a three dimensional map can be derived of the distribution of the ⁶⁸Ga tracer ions, which is directly proportional to the density of fluid present, allowing 3D images of the liquid content at different positions in the foam to be calculated. The images were recorded with spatial and temporal resolutions of 1 mm and 1 second, enabling the imaging of foams flowing at speeds similar to those found in industrial mineral flotation froths. The liquid content in an overflowing 2D foam column was compared to measurements of the bubble size distribution, the velocity flow field and the air recovery, determined from high speed photography.

Cole, K., Brito-Parada, P.R., Morrison, A., Govender, I., Buffler, A., Hadler, K., Cilliers, J.J. (2015). *Chem. Eng. Res. Des.*, 94, 721-725.

This work was supported by the Claude Leon Foundation Postdoctoral Fellowship in South Africa.

Influence of interfacial tension on emulsification process

S. Aidarova¹, A. Tleuova¹, D. Grigoriev², M. Schenderlein², and R. Miller²

*²Kazakh National Technical University named after K.I. Satpayev,
050013, Almaty, Kazakhstan*

*¹Max-Planck Institute of Colloids and Interfaces, D-14424, Golm/Potsdam, Germany
zvezda.s.a@gmail.com*

Structure of such materials as composite ones influences on their advanced functional characteristics on micro- or even nanolevel. Obtaining of micro- or nanocontainers filled with corresponding active agents is one of the most established approaches to give to these materials several specific functionalities.

Using emulsions is a unique method for the preparation of such containers. One of the ways which could be used for this purpose is spontaneously formed Pickering oil-in-water (O/W) emulsions.

The nature of this process and parameters which can influence and govern it are not understood fully.

Within the framework of investigation, we tried to research the dynamic and equilibrium interfacial tension in the corresponding systems. For this purpose we used profile analysis tensiometer (PAT). In order to investigate the importance of thermodynamic factors in the emulsion formation oil / water interface was studied first of all and then with different oil/nanoparticle weight ratios. To show the influence of thermodynamic factors on the emulsions stability the emulsions were additionally characterized by droplet size distribution (by DLS).

Spreading of Catanionic Surfactant Mixtures on Pulmonary Mucus Layer

G. Dilli Alp, N. Aydoğan

Hacettepe University, Department of Chemical Engineering, Ankara, Turkey

anihal@hacettepe.edu.tr

Lungs –with their large surface areas and advantageous properties are favorable for drug delivery applications. Pulmonary mucus layer covers the airway surface and acts as a barrier against therapeutic agents especially in case of chronic lung diseases. Therefore it gets harder to spread the formulation on the airway. Recently, aerosolized formulations dissolved in saline are used for treatment. However formulations cannot efficiently spread because saline solutions have high surface tension and spreading is directly related to the surface tension difference between the spreading solution and subphase. Adding surfactant to the formulations increases the surface tension difference and triggers Marangoni Forces to enhance the spreading behavior [1]. Although spreading experiments have been conducted with different types of surfactants on mucus-mimicking subphases, still an effective formulation could not be maintained. On the other hand, catanionic (cationic+anionic) surfactant mixtures are useful for drug delivery applications with their advantageous interfacial and structural properties.

In this study, catanionic surfactant mixtures composed of different surfactants mixed at various mole ratios are prepared and their spreading behavior on both mucin and cystic fibrosis mucus model are investigated. Characterizations of catanionic mixtures are implemented with surface tension measurements and light scattering analysis. Spreading experiments are utilized via tracking the movements of tracer particles and analyzing their spreading characteristics with mathematical methods. The results are also supported with the contact angle measurements. A synergistic interaction is obtained between the components of the mixtures and this interaction has enhanced the spreading of the droplet. As it is vital to transport the sufficient amount of drug to the targeted region, this study takes an important step by means of drug delivery.

[1] Koch et al., *Molecular Pharmaceutics*, 2011.

Development of model lipid membranes to elucidate the role of stratum corneum intercellular lipid lamellar structures in the skin barrier function.

S. Yonenaga^a, H. Nakazawa^a, T. Uchida^b, S. Kato^a

^a School of Science & Technology, Kwansai Gakuin University, Sanda, Japan

^b R&D –Development Research- Skin Care Products Research, Kao Corporation, Odawara, Japan

sy0802@kwansai.ac.jp

The stratum corneum (SC), the outermost layer of the human skin, is composed of protein-rich corneocytes embedded in intercellular lipid lamellae. The lipid lamellae consist of several kinds of ceramides (Cer), free fatty acids (FFA) and cholesterol (Chol) in an approximately equimolar ratio and play a key role as a barrier against penetration of harmful agents, drugs and so on. Artificial lipid membranes mimicking the SC lipid organization are quite useful in the systematic study of the relationship between the membrane structures and the barrier function because of easy handling of their composition. The goal of this study is to establish a simple method for preparation of the model lipid membranes and to make clear the structure-function relationship.

Recent studies have revealed that the spray method is applicable to the reconstitution of homogeneous lipid membranes from lipids extracted from the SC [1][2]. By modifying the spray method, we prepared model lipid membranes from commercially available Cer, Chol and FFA on a filter paper and analyzed their structural organization by X-ray diffraction and thin-section electron microscopy.

Lipid lamellar structures filled in the filter pores were observed in the thin-section. X-ray diffraction experiments revealed that the lipid organization in the model lipid membrane is significantly affected by the chain length of FFA and the molar ratio of Chol. We will discuss the conditions for preparing the model lipid membrane having structures similar to the SC intercellular lipid lamellae.

References:

[1] M. W. de Jager et al. (2006) *Biochim. Biophys. Acta* 1758, 636-644.

[2] M. Oguri et al. (2014) *Biochim. Biophys. Acta* 1838, 1851-1861.

Film Formation Process of Polystyrene Latexes Depending on Particle Size

Şaziye Uğur^{a*} and M. Selin Sunay^b

Istanbul Technical University, Department of Physics, 34469 Maslak-Istanbul, Turkey

Piri Reis University, Faculty of Science and Letter, 34940, Tuzla-Istanbul, Turkey

*saziye@itu.edu.tr

The effect of particle size on film forming process of pyrene (P) labeled polystyrene (PS) latexes was studied by means of steady state fluorescence (SSF) and UV-Vis techniques. Different latex dispersions of same polymer content but different particle size ranging between 203nm and 900nm were synthesized for this purpose and the latex films were prepared from these latexes dispersions by casting method at room temperature. Then films were annealed above the glass transition temperature, T_g of PS at a temperature range of 100-280 °C for 10 min. Transmitted light (I_{tr}), scattered light (I_{sc}) and fluorescence (I_p) intensities were measured after each annealing step to monitor the stages of film formation. Minimum film formation (T_0), void closure (T_v) and healing (T_h) temperatures were determined. Void closure and interdiffusion stages were modeled and related activation energies were measured. It was found that T_0 , T_v and T_h were shifted to lower temperature range and also energy values decreased with decreasing particle size. These results showed that as the particle size decreases the film formation of PS particles occur at lower temperature and require less energy due to the highly confined state of polymer chains. The polymer chains contain more free volume and less interactions between segments in small particles leading to higher conformational energy and less interaction of polymer chains. This leads to small latex particles to complete the film formation at lower temperatures with less energy due to their larger surface energy.

A Study on the Method of Short-Time Approximation – Criteria for Applicability

Alvin Casandraa, Boris A. Noskovb, Libero Liggieric, and Shi-Yow Lina

^a *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan;* ^b *Department of Colloid Chemistry, St. Petersburg State University, Petersburg, Russia;* ^c *CNR - Istituto per l'Energetica e le Interfasi IENI - UOS Genova, Genova, Italy*

sylin@mail.ntust.edu.tw

Despite its widespread use in the determination of adsorption mechanisms and the estimation of surfactant diffusivity, the short-time approximation method, used for linearly fitting experimental dynamic surface tension data, should be validly applied only over a very specific range of time intervals or surface pressures. Therefore, the definition of general criteria for the applicability of this method and for error evaluation in diffusivity estimations is fundamental. In this work, a theoretical numerical simulation of the short-time approximation method was conducted, and general benchmarks for its accurate utilization were investigated. Specifically, for systems assuming planar gas–liquid surfaces, diffusion-controlled kinetics and a Langmuir adsorption isotherm, simple rules were developed in terms of limiting surface pressure and dimensionless time (t^*_{\max}) as a function of dimensionless surfactant concentration (C_0/a). For values greater than the limiting (maximal) conditions, the dynamic surface tension curve deviates from the short-time approximation straight line, and thus, the corresponding linear fitting could lead to significant errors in evaluating the diffusivity. The simple criteria proposed in this study thus precisely define the range of applicability for the short-time approximation method.

Adsorption of the intrinsically disordered saliva protein histatin 5 to silica surfaces

K. Hyltegren,^a T. Nylander,^b M. Skepö^a

^a*Theoretical Chemistry, Lund University, Lund, Sweden*

^b*Physical Chemistry, Lund University, Lund, Sweden*

kristin.hyltegren@teokem.lu.se

Histatin 5 is a short, cationic protein consisting of 24 amino acid residues. It is produced by the human salivary glands. At physiological conditions, histatin 5 has no well-defined secondary or tertiary structure, which classifies it as an intrinsically disordered protein.

Histatin 5 kills the fungus *Candida albicans* by targeting its mitochondria. The first step of this process is adsorption to the cell membrane. Histatin 5 also takes part in forming a protective film (pellicle) on the tooth surface. Thus, the adsorption of histatin 5 to surfaces in the mouth is important for our oral health.

Using ellipsometry, we have studied the effects of buffer pH, NaCl concentration and urea content on the amount of histatin 5 that adsorbs to a hydrophilic silica surface. The charges of the protein and the surface differ depending on pH, NaCl screens the electrostatics and urea disturbs hydrophobic interactions and hydrogen bonding. Thus, we can see which interactions that are important.

We find that under alkaline conditions (corresponding to a highly negative surface), the adsorbed amount of histatin 5 decreases with increased salt content. At neutral pH, there is no effect of NaCl for concentrations up to 200 mM. Addition of urea has been found to decrease the adsorbed amount for some conditions but needs to be investigated further.

We have also made coarse-grained Monte Carlo simulations of the adsorption of histatin 5 under conditions like those of the experiments. Preliminary results for free energies, conformations etc. will be shown.

By comparing with the experimental results for histatin 5, we try to improve our modelling of intrinsically disordered proteins and achieve a better understanding of their properties. We also hope that our results will lead to an increased understanding of the function of saliva, and help developing new and better salivary replacements.

Study of Interactions Between Lipid Membranes by SAXS : The role of Composition

R. Leite Rubim,^{a,b} B. B. Gerbelli,^b K. Bougis,^{a,b} C. L. Pinto de Oliveira,^b
L. Navailles,^a F. Nallet,^a and E. Andreoli de Oliveira.^b

^aCentre de recherche Paul-Pascal – CNRS, Université de Bordeaux, Pessac, France

^bGFCx, Instituto de Física, Universidade de São Paulo, São Paulo, Brazil

rleiterubim@gmail.com

Lipid membranes are present in many structures of living cells, such as the plasma membrane, the Golgi complex and other organelles. Changes in the composition of the membranes can modify their mechanical properties and structure, like the rigidity, which plays a key role in their three dimensional spatial organization.

In this work, we carried out a study of structural and elastic properties of membranes stacked in lamellar phases, focusing onto the relevant interactions that lead to stabilization of these periodic structures. The composition of the membrane, as well as hydration, were varied systematically. The lamellar phase is composed by lecithin, in which is incorporated in different proportions a co-surfactant consisting of a mixture of ethoxylated fatty acids,

To study the interactions between membranes, the lamellar phase was placed under a known osmotic pressure Π , applied by a polymer solution. The structural parameters characterizing the lamellar phase, in particular the stacking parameter d , were determined by Small Angle X-ray Scattering (SAXS) experiments. The experimental results provide equations of state $\Pi(d)$ and those are fitted considering an effective interaction potential between the bilayers, allowing the determination of quantitative parameters characterizing the different attractive and repulsive contributions.

For membranes containing up to 50% of co-surfactant, we observe that the lamellar period is shifted to higher values upon incorporation of ethoxylated fatty acids for a constant pressure, indicating that repulsive forces are enhanced. Increasing the amount of co-surfactant, we observe a change on this behaviour. Results show that interactions are sensitive to the incorporation of ethoxylated fatty acids, suggesting some changes in the membrane flexibility. These findings reveal the great potential of this methodology for studies of membranes of biological interest.

ACKNOWLEDGMENTS

This work was supported by FAPESP, process number 2011/16149-8.

REFERENCES

- Gerbelli et al, *Langmuir* (2013) 29 (45), 13717
Oliveira et al, *J. Appl. Cryst.* (2012) 45, 1278

Surface topography and free energy of modified Ti-6Al-4V alloy

Y. Yan, A. Szczes, K. Terpilowski, E. Chibowski, M. Jurak

*Maria Curie-Sklodowska University, Faculty of Chemistry, Department of Physical Chemistry-
Interfacial Phenomena, 20-031 Lublin, Poland*

email: yingdi.yan@umcs.pl

Because of increase of life expectancy, the number of elderly people is growing along with the demands on medical implants that are seen as safe and long-enduring solutions for physical problems. Nowadays, problems related to orthopedic and oral disorders affect millions of patients per year [1,2]. Titanium and its alloys have become a promising therapy due to their good mechanical properties, corrosion resistance and reliable biocompatibility. However, because of their inherent surface bio-inertness, they hinder the long-term survival of implants. Consequently, a variety of efforts on the surface improvement have been made for decades [3].

Phospholipids, being the main components of biological membranes, play a key role in the controlling of ions and molecules transportation between the inside and outside cellular environments [4]. Phospholipids are promising candidates for titanium surface modification because of their intrinsic biocompatibility.

It has been well-documented that geometry, surface topography and surface wettability are crucial for the short- and long- term success of the implanted material. In our work, four samples of Ti-6Al-4V titanium surface were prepared; i) untreated, ii) mirror-polished, iii) plasma treated, and iv) with dipalmitoylphosphatidylcholine (DPPC) deposited. The surface topography was investigated by Atomic Force Microscopy (AFM) and surface profilometer. The wetting of surface was evaluated via the surface free energy determined from the contact angles of water, formamide and diiodomethane, using two different approaches to the interfacial interactions, namely; van Oss et al. (LWAB), and the contact angle hysteresis (CAH) [5].

References:

1. Zethraeus, N., et al., *Osteoporos Int*, 2007. **18**(1): p. 9-23.
2. Golub, M., et al., *Biointerphases*, 2013. **8**:21.
3. Kazemzadeh-Narbat, M., et al., *Biomaterials*, 2013. **34**(24): p. 5969-5977.
4. Richter, R.P., R. Berat, and A.R. Brisson, *Langmuir*, 2006. **22**(8): p. 3497-505.
5. Chibowski, E. *Advances in Colloid and Interface Science*, 2003. **103**(2): p. 149-172.

Acknowledgements: Financial support of this project from Marie Curie Action FP7-PEOPLE-2013, Initial Training Network: "Complex Wetting Phenomena" (Project No: 607861) is highly appreciated.

Study of coarsening and coalescence for dry foams in 2D

A. Hutin^a, A. Cagna^a, C. Honorez^{a,b} & W. Drenckhan^b.

^aTECLIS, Longessaigne, France

^bLPS, Orsay, France

anthony.hutin@teclis-instruments.com

Just after its generation a liquid foam undergoes three important ageing processes: drainage, coarsening and coalescence. It is very complicated to study simultaneously these three phenomena since they are tightly coupled. An elegant solution to this problem is to use 2D foams which consist of a monolayer of bubbles trapped between two plates (figure 1). These have the advantage of providing direct access to visualization, hence providing the information on which process occurs during the foam life (1, 2). For example, coarsening is simple to observe: Von Neuman demonstrated that the time evolution of 2D bubbles depends only on the number of their sides: the evolution of the area A as a function of time of a bubble of n sides is $dA/dt \propto (n - 6)$. It means that bubbles with $n > 6$ grow, bubbles with $n < 6$ shrink and the area of hexagonal bubbles ($n = 6$) is constant. The coalescence is related to the disappearance of the bubbles, if a bubble disappears even though its area is not equal to zero so the foam is coalescing. However, the coarsening is also occurring during the coalesce phenomenon. These two processes may be simultaneous, so it is necessary to separate them to have a better understanding of foam life.

We used a 2D cell ("Hele Shaw" configuration) adapted on a Foamscan to generate and study the coarsening and the coalescence of liquid foams obtained with different surfactant concentrations and different liquid fractions. The foam height was measured and analyzed through the Foamscan software and the geometrical and topological aspects of the bubbles were studied by the dedicated CSA software. The analysis allows to investigate the influence of the physical parameters and the formulation of foams on the competition between coarsening and coalescence.

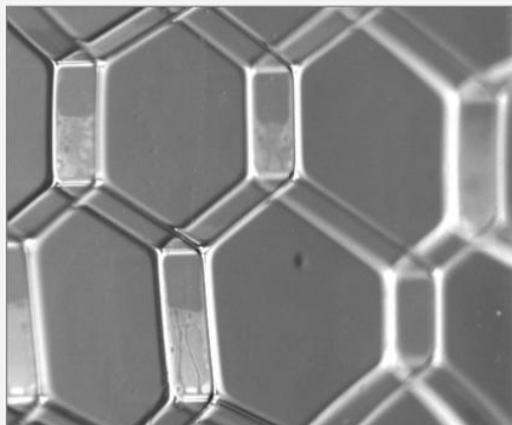


Figure 1: Monolayer of bubbles trapped between two glass plates

1. Saint-Jalmes A. *Soft Matter*. 2006;2(10):836-49.
2. Saulnier L, et al. *Colloids and Surfaces A: Physicochemical & Engineering Aspects*. 2015(0).

A Study on the Adsorption Kinetics of Ionic Surfactants

Alvin Casandra and Lin Shi-Yow

*Chemical Engineering Department, National Taiwan University of Science and Technology,
Taipei, 106 Taiwan*

sylin@mail.ntust.edu.tw

The adsorption kinetics of ionic surfactants (SDS, AOT, DDA and decanoic acid) onto a clean air-water interface was studied. A video-enhanced pendant bubble tensiometry was employed for the measurement of the equation of state and the dynamic/equilibrium surface tensions. Relaxation profiles of surface tension for the surfactant molecules absorbing onto a freshly created air-water interface were obtained for surfactant solutions with or without NaCl at different bulk concentrations. The relaxations of surface tension were also theoretically simulated with the ionic Langmuir (zero molecular interaction) and Frumkin (with molecular interaction between the adsorbed surfactant molecules) models. From the comparison between the equilibrium/dynamic surface tension data and the theoretical tension curves one can obtain the following information: (1) the controlling mechanism of the adsorption process from bulk phase to air-water interface (diffusion control, kinetic control or mixed diffusive-kinetic control); (2) the diffusivity of surfactant molecules; (3) the adsorption/desorption rate constants if the process is not diffusion-controlled; and (4) the salt effect on the adsorption surfactant kinetics adsorption.

Structure and Degradation Behaviour of Poly(L-lactide) Treated with High-Pressure Carbon Dioxide

S. Asai, D. Miura, S. Akasaka
Tokyo Institute of Technology, Tokyo, Japan

asai.s.aa@m.titech.ac.jp

Poly(L-lactide) (PLLA) is a bio-based and biodegradable polymer and starts to be used in various fields of industry as an environmentally friendly material. PLLA is a semi-crystalline polymer and possesses crystal polymorphism (α , α' , β , γ , and δ) [1, 2]. In addition, we found the formation of disordered α (α'') form by high-pressure CO₂ treatment [3].

In this study, the crystalline higher-order structure, mechanical properties, and degradation behaviour of PLLA films treated with high-pressure CO₂ were examined. The PLLA films treated with CO₂ at the temperatures of 10°C and below showed good mechanical properties and transparency. These characteristics of the CO₂-treated PLLA films are due to the fine structure comprised of many small crystallites which are dispersed well in an amorphous phase without forming spherulites. Furthermore, the α'' form crystallites were found to be destroyed during the process of film elongation indicating that α'' form is more fragile than α form.

The alkaline hydrolysis degradation rate of various PLLA films were investigated. The degradation rates of PLLA films treated with high-pressure CO₂ at the temperature range from -20°C to 10°C were slower than those of cold-crystallized and amorphous PLLA films. This is also due to the fine crystalline structure without spherulites.

References

- [1] K. Wasanasuk, K. Tashiro, M. Hanesaka, T. Ohhara, K. Kurihara, R. Kuroki, T. Tamada, T. Ozeki, T. Kanamoto, *Macromolecules*, 2011, 44, 6441.
- [2] K. Wasanasuk, K. Tashiro, *Polymer*, 2011, 52, 6097.
- [3] H. Marubayashi, S. Akaishi, S. Akasaka, S. Asai, M. Sumita, *Macromolecules*, 2008, 41, 9192.

Characterisation of Sulphonated Methyl Esters in the Bulk and at the Air-Water Interface

J.T. Petkov^{a,*}, K.D. Danov^b, P.A. Kralchevsky^b, R.D. Stanimirova^b, E.S. Basheva^b,
P.V. Petkov^b

^a *KLK-OLEO, Mutiara Damansara, 47810 Petaling Jaya, Selangor Dalur Ehsan, Malaysia*

^b *Department of Chemical & Pharmaceutical Engineering, Sofia University, Sofia, Bulgaria*

*Presenting author's email: jordan.petkov@klkoleo.com.my

Sulphonated methyl esters (SME) have been growing for the last ten years and currently stand at more than ten percent of the total linear alkyl-benzene sulphonates (LAS) production. It is an environmentally friendly alternative of LAS and irrespective of the current crude oil pricing situation is considered as a viable replacement of LAS. Despite their wide usage, mainly in cleaning formulations, their physical characteristics published in the literature often differ, sometimes up to order of magnitude. The lack of clarity on their physical properties has been one of the limitations for increasing the scope of their applications. To address this issue, we investigated the SME homologous series (C12, C14, C16, C18) with regard to their surface tension (Fig. 1), adsorption properties; critical micellization concentration; micelle aggregation number and ionization degree, and the effect of added salt [1]. Data on the foaminess of SME solutions and foam stability will be also reported.

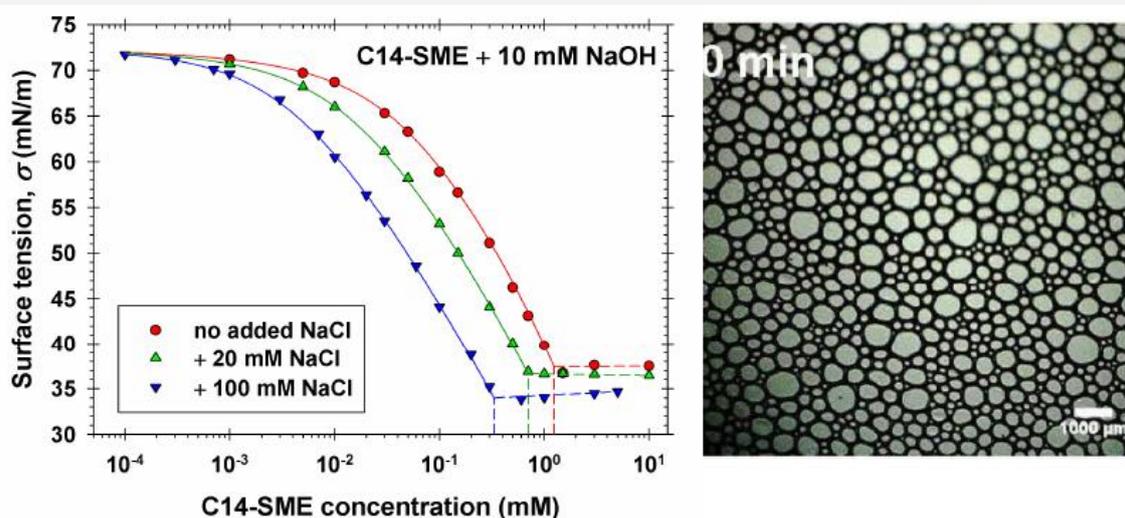


Fig. 1. Surface tension of C14-SME solutions (left) and the produced foam (right).

Literature:

1. K.D. Danov, R.D. Stanimirova, P.A. Kralchevsky, E.S. Basheva, J.T. Petkov, Sulphonated methyl esters in aqueous solutions: Interfacial and micellar properties – manuscript in preparation.

Counterion Distribution and Surface Charge Density in Adsorbed Films Studied through Total Reflection XAFS

Y. Imai,^a H. Matsubara,^b T. Takiue,^a M. Aratono^b

^a Faculty of Arts and Sciences, Kyushu University, Fukuoka 819-0395, Japan

^b Department of Chemistry, Faculty of Sciences, Kyushu University, Fukuoka 812-8581, Japan

y-imai@artsci.kyushu-u.ac.jp

To investigate the relation between counterion distribution and surface charge density, total reflection X-ray absorption fine structure (TR-XAFS) was applied to the surface adsorbed films on the dodecyltrimethylammonium bromide (DTAB), hexadecyltrimethylammonium bromide (HTAB), and 1-decyl-3-methylimidazolium bromide (DeMIMBr) single surfactant aqueous solutions.

X-ray absorption spectra of Br⁻ counterions in the surface region were analyzed. The surface density of surfactant ions (Γ_s) was obtained as the surface charge density, from the K-edge absorption jump values of XAFS spectra for Br⁻ at different concentrations. Through EXAFS analysis, the ratio of the Br⁻ ions bound to the hydrophilic heads of surfactant ions (bound-Br) to the fully hydrated Br⁻ ions distributed in the diffuse double layer (free-Br) was estimated.

For each surfactant, the ratio of bound-Br (α) was increased almost linearly with increasing Γ_s as shown in Fig. 1. The α values for DTAB and HTAB were close to each other at given Γ_s , indicating that the difference in chain length is not so influential on counterion distribution. The value for DeMIMBr was smaller than those for DTAB and HTAB, and then the charges of imidazolium groups were less neutralized by Br⁻ counterions than trimethylammonium ones in the adsorbed films. This is possibly attributable to the difference of the hydration states of the different kinds of headgroups.

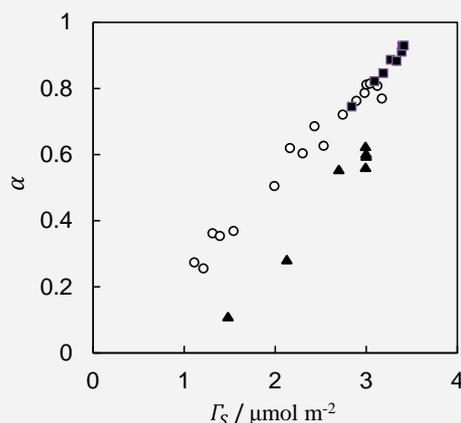


Figure 1. The ratio of bound-Br vs. the surface density of surfactant ion for DTAB (open circle) HTAB (filled square), and DeMIMBr (filled triangle) systems.

Microscopic segregation of hydrophilic ions in critical binary aqueous solvents

M. Witala,^a R. Nervo,^b O. Konovalov,^b K. Nygård^a

^a Department of Chemistry and Molecular Biology, University of Gothenburg, Sweden

^b European Synchrotron Radiation Facility, Grenoble, France

monika.witala@chem.gu.se

Recently anomalous interactions between colloidal particles immersed in binary aqueous liquid mixtures containing hydrophilic salt have been observed [1], where one of the proposed mechanisms is due to asymmetric ion solvation. However, such unequal partitioning of ions is yet to be observed directly in experiments. In order to address this phenomenon, we have probed the interfacial ion distributions in a salt-containing critical binary aqueous solvent. The critical mixture is composed of water and 2,6-dimethylpyridine with potassium chloride as hydrophilic salt and we have studied it using grazing-incidence x-ray fluorescence from the liquid-vapour interface. Our data provide the first direct experimental evidence of microscopic segregation of hydrophilic ions in critical water-oil mixtures. However, the experimental results are only in qualitative agreement with state-of-the-art theory, indicating the need for a more sophisticated microscopic model including preferential cation and anion solvation.

[1] U. Nellen et al., *Salt-induced changes of colloidal interactions in critical mixtures*, *Soft Matter* **7**, 5360 (2011).

Novel NIPAm-based-microgels with aromatic comonomers for cross-linked transferable surface coatings

J. Bookhold¹ and T. Hellweg¹

¹University Bielefeld, Bielefeld, Germany

johannes.bookhold@uni-bielefeld.de

Stimuli-responsive surfaces are in the focus of interest for a multitude of applications such as sensors[1], anti-fouling coatings[2] and cell culture substrates. For the latter, coatings of the thermoresponsive polymer Poly-(*N*-isopropylacrylamide) pNIPAm have been found to allow reversible switching of cell adhesion upon heating and cooling.[3-5] In all of these works the microgel layer had to be prepared on the substrate intended for use. Hence, the dimensions and material properties of the substrate can strongly influence the adsorption of the microgel particles. The aim of this contribution is the preparation of free standing membranes from cross-linkable microgels. The approach is based on the deposition of microgels, containing aromatic moieties, by spin-coating the particles on a sacrificial-polyelectrolyte layer.

During this work three new monomers, *N*-(1-Phenylethyl)acrylamide, *N*-(2,3-dihydro-1H-indene-1-yl)acrylamide and *N*-Benzhydrylacrylamide, for copolymerization with NIPAm have been synthesized. In a precipitation reaction using a solvent mixture copolymer particles from NIPAm and the aromatic comonomers were obtained, with different comonomer concentration, 2.5 mol-%, 5 mol-% and 10 mol-%. To confirm the incorporation of the aromatic component into the microgel structure the purified particles were analyzed with NMR-spectroscopy (Nuclear magnetic resonance spectroscopy). The microgels itself were characterized using PCS (Photon correlation spectroscopy) and UV/Vis-turbidity measurement. Monolayers of the microgels were spin-coated onto a silicon-wafer covered with a polyelectrolyte. Atomic force microscopy (AFM) was used to study the surface coverage, topography and the thickness in addition to ellipsometry measurements. Both methods for the characterization of the surface were done in dried and wetted state to determine the thermoresponsive properties of the layers.

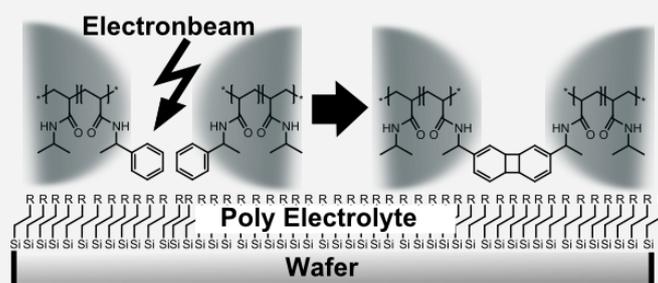


Figure 1: Schematic drawing of the principle of function for the electron-beam-cross-linking between two microgel particles adsorbed at a surface.

- [1] C. D. Sorrell, *Adv. Funct. Mater.*, **2011**, *21*, 425.
- [2] J. L. Dalsin et al., *Materials Today*, **2005**, *8*, 38.
- [3] J. Yang et al, *Controlled Release*, **2006**, *116*, 193.
- [4] S. Schmidt et al., *Adv. Func. Mater.*, **2010**, *20*, 3235.
- [5] A. Burmistrova et al. *J. Mater. Chem.*, **2010**, *17*, 3502.

Modelling Foam Displacement with the Pressure-Driven Growth Model for a Heterogeneous Reservoir

E. Mas-Hernández,^a P. Grassia,^b N. Shokri^a

^aUniversity of Manchester, Manchester, UK

^bUniversity of Strathclyde, Glasgow, UK

elizabeth.mashernandez@manchester.ac.uk

Foams are used in underground oil reservoirs for improving the displacement efficiency in production processes. An injection technique consists of introducing surfactant followed by gas to form the foam in situ within the reservoir.

A foam model known as pressure-driven growth has been used successfully to study the foam displacement within a homogeneous reservoir [1, 2], following the motion of discrete points that represent the shape of the foam front (a wet foam region between an aqueous surfactant phase in front and a gas phase further back). Convex curves are obtained for the evolving front shape in this case.

Contrary to a homogeneous reservoir, a heterogeneous formation has a spatial variation in permeability. The pressure-driven growth model has previously been used to describe the foam displacement when permeability is anisotropic (vertical and horizontal permeability differ) [3].

Here we use a suitable modification of the same model to study the foam displacement when permeability varies across the reservoir depth, which causes the formation of concave regions in the foam front. These concavities can be mathematically awkward to handle requiring special treatment.

References

1. D. Shan and W. R. Rossen. Optimal Injection Strategies for Foam IOR. *SPE Journal*, 9(2):132-150, 2004.
2. P. Grassia, E. Mas-Hernández, N. Shokri, S. J. Cox, G. Mishuris, and W. R. Rossen. Analysis of a Model for Foam Improved Oil Recovery. *J. Fluid Mech.*, 751:346-405, 2014.
3. R. M. de Velde Harsenhorst, A. S. Dharma, A. Adrianov, and W. R. Rossen. Extension and Verification of a Simple Model for Vertical Sweep in Foam Surfactant-Alternating-Gas Displacements. *SPE Reservoir Evaluation & Engineering*, 17(3):373-383, 2014.

Dry heat whey protein-pectin conjugates largely improve the heat stability of protein stabilized O/W emulsions

A.D. Setiowati, S. Saeedi, P. Van der Meeren
Ghent University, Particle & Interfacial Technology Group, Gent, Belgium

Paul.VanderMeeren@Ugent.be

Whey Protein Isolate (WPI) is known to have excellent emulsifying properties. However, WPI is also known to be very susceptible to denaturation during thermal processing, which is a very common unit operation in industry. As a further consequence of this heat induced denaturation, heating of whey protein stabilized emulsions may lead to undesired effects, such as the transformation from a liquid emulsion to a highly viscous fluid or a gel.

Previous research has shown that combining the amphiphilic properties of whey proteins and the hydrophilic properties of polysaccharides, such as Low Methoxyl (LM) Pectin can help improving the functional properties and heat stability of whey proteins. This can be achieved through conjugation of protein and polysaccharide, e.g. by dry heat treatment of mixtures at controlled relative humidity. The effectiveness of this process, considering a 2:1 ratio of WPI to LM Pectin, was proven by both SDS-PAGE and diffusion NMR. Subsequently, oil in water emulsions (10% w/w) were prepared which were either stabilized by 0.5 % conjugates of WPI and LM Pectin (with ratio of 2:1), by 0.5% WPI, or by 0.5% of a mixture of WPI and LM Pectin. These emulsions were prepared by microfluidisation at a driving air pressure of 4 bar, at a pH value of 6.5 and 5, and with a NaCl concentration of 30 mM. Whereas WPI tended to have lower emulsifying properties at pH 5, i.e. around its isoelectric point, electrophoretic mobility measurements indicated that conjugation shifted the protein's isoelectric point to a lower pH value, which caused the conjugates to be able to maintain their functionality at the native protein's isoelectric point. Particle size distribution results, obtained by laser diffraction, indeed showed that the conjugates displayed much better emulsifying properties at pH 5.

In a last step, the heat stability of these emulsions was evaluated. WPI stabilized emulsions displayed a poor stability towards heat irrespective of pH and ionic strength at temperatures above 80°C. On the other hand, emulsions stabilized by conjugates of WPI and LM Pectin exhibited excellent heat stability. Upon heating at 80°C up to 20 minutes, oil droplet size measurements showed that there was almost no change in the particle size distribution of the conjugate-stabilized emulsions after heating. Viscosity measurements showed a similar trend: whereas the consistency of emulsions stabilized by WPI ranged from a highly viscous to a gel-like structure after heating, heat treated emulsions stabilized by conjugates did not show any change in consistency and had flow behavior index values close to that of a Newtonian fluid ($n=1$). This pronounced heat stabilizing effect of LM Pectin, however, was not observed in emulsions stabilized by a simple mixture of WPI and LM Pectin (i.e. without dry heat treatment).

Overall, our experiments indicated that conjugation of WPI and LM Pectin by dry heat treatment could largely improve the functional properties of the protein, whereby not only the pH sensitivity, but also the heat-sensitivity of WPI-stabilized emulsions could be significantly improved.

T. Brunet^a, A. Merlin^b, B. Mascaro^a, K. Zimny^b, J. Leng^c, O. Poncelet^a, C. Aristégui^a,
O. Mondain-Monval^b

^a *University of Bordeaux, Institute of Mechanics & Engineering-CNRS-INPB, Talence, France*

^b *University of Bordeaux, Centre de Recherche Paul Pascal-CNRS, Pessac, France*

^c *University of Bordeaux, Laboratory of the Future-CNRS-Solvay, Pessac, France*

mondain@crpp-bordeaux.cnrs.fr

In 1968, Veselago theoretically explored the physics of electro-magnetic (em) propagation in materials having both their dielectric permittivity ε and magnetic permeability μ negative. His theoretical work remained speculative until it was shown that simultaneous negative effective values of ε and μ can be achieved in propagating media containing a sufficient concentration of physical entities that are able to resonate with the incoming em field, thus leading to negative values of the effective optical refractive index close to the resonance frequencies of the resonators. The synthesis and characterization of such materials – called “locally resonant metamaterials” – have motivated intensive worldwide research due to the large number of potential applications of em metamaterials (super lenses, cloaking materials, sub-wavelength optical microscopy, filters, antenna, wave guides etc...). Realizing that several of these promising applications could be transposed to acoustics, researchers begun to work on the design and synthesis of materials which would exhibit negative values of the effective density ρ_{eff} and/or of the effective compressibility κ_{eff} . Such acoustic metamaterials indeed open the route to many applications such as planar perfect acoustic lenses, acoustic cloaking devices, sub-wavelength acoustic microscopy, frequency-selective acoustic isolators and attenuators, waveguides ...

Up to now, these achievements were obtained through the use of essentially micro-mechanical techniques, which resulted in the build-up of solid, most of the time 1 or 2D materials active in the audible frequency range due to the typical structuration scale of the material (typically 1 mm).

We present the synthesis and acoustic characterization of the first fluid 3D acoustic metamaterial obtained through the use of soft matter techniques (emulsion templating and microfluidics). The material is constituted of porous polymer beads suspended in a water-based gel. We show that our material possess a negative refractive index in a frequency range that can be tuned by playing with the resonators sizes and volume fraction (Brunet et al., *Nature Materials* 2015). Potential applications will be discussed.

Features of the formation of thin films based on magnetic nanoparticles

S.B. Aidarova¹, G.K. Alimbekova¹, F.S. Baysimakova¹

¹*International Postgraduate institute “Excellence Polytech” of Kazakh National Technical University after K.I.Satpaev, Satpaev Street 22, Almaty, Kazakhstan
zvezda.s.a@gmail.com*

Nanoparticles, particles with core diameters of 1-100 nm possessing unique chemical and physical properties arising from their nanoscale dimensions continue to be of significant current interest for their potential applications in catalysis, quantum computers, optical, electronic, or magnetic devices, chemical sensors, ferrofluids for cell separations, as components in industrial lithography or in photochemical devices such as flat-panel displays. In each of these applications the size and size distribution of the nanoparticles are a primary concern [1].

Transmission electron microscopy (TEM) is almost always the first method used to determine the size and size distribution of nanoparticle samples [2-3].

The aim of this work was to study the features of the formation of thin films based on magnetic nanoparticles via the study of thin magnetic films using transmission microscopy.

TEM-images were obtained with a transmission electron microscope Philips CM 10 at 100 kV accelerating voltage. Samples were applied to Formvar-coated copper grids. Magnetic nanoparticle size distribution were determined using UTHSCSA Image Tool.

The resulting magnetic nanoparticles have a size ranging from 3 nm to 12 nm and have a sufficiently narrow size distribution monodispersity. Proportion of particles with sizes of 3 nm to 9 nm is about 68%, less than 4 nm 20% and more than 9 nm, about 12%, which suggests the possibility of getting close to monodisperse nanoparticles.

Monodisperse nanoparticles is an important factor for obtaining homogeneous, well-organized structures that provide structural and mechanical properties of thin films.

References:

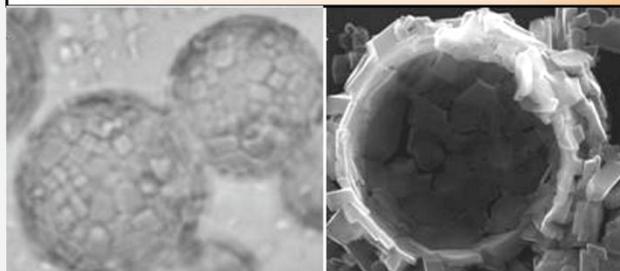
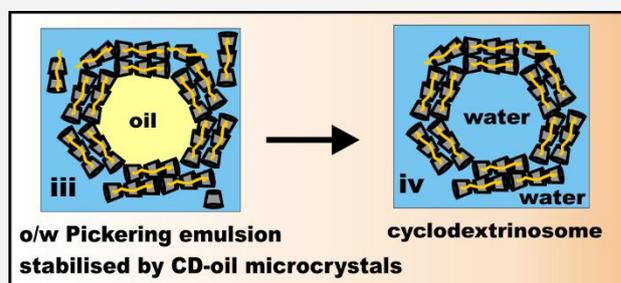
1. G. H. Woehrle, J. E. Hutchison, S. Ozkar, R.G. Finke Analysis of Nanoparticle Transmission Electron Microscopy Data Using a Public- Domain Image-Processing Program, *Image Turk J Chem* 30 (2006), 1-13.
2. B.V. Miller and R.W. Lines, *CRC Crit. Rev. Anal. Chem.* 20, 75-116 (1988).
3. T.N. Baker, *Microstructure of High Temperature Materials* 5, 161-189 (2001).

Self-assembly of cyclodextrins at the oil-water interface: surfactant-free emulsions and cyclodextrinosomes

B.G. Mathapa,^a and V.N. Paunov^a

^a Department of Chemistry, University of Hull, Hull, HU67RX, United Kingdom
V.N.Paunov@hull.ac.uk

We explored the self-assembly of cyclodextrins (CDs) at the oil-water interface through the formation of inclusion complexes (ICs) with the oil and further assemble into microcrystals at the oil-water interface. We demonstrate the spontaneous formation of a dense layer of adsorbed CD-tetradecane IC microcrystals at the tetradecane-water interface whose morphology and size are dependent on the type of CD and oil used. At large oil volume fractions, this phenomenon led to the formation of a Pickering type of oil-in-water emulsion stabilised by adsorbed CD-oil microcrystals while at low oil volume fractions it completely solubilises the oil in the form of IC microcrystals. We also report the preparation of o/w emulsions stabilised by microcrystals of cyclodextrin-oil inclusion complexes. The inclusion complexes are formed by threading cyclodextrins from the aqueous phase on n-tetradecane or silicone oil molecules from the emulsion drop surface which grow further into microrods and micro-platelets depending on the type of cyclodextrin. These microcrystals remain attached at the surface of the emulsion drops and form densely packed layers. The novelty in this emulsion stabilisation mechanism is that molecularly dissolved cyclodextrin from the continuous aqueous phase is assembled into colloid particles directly onto the emulsion drop surface, i.e. molecular adsorption leads to effective Pickering stabilisation. The β -CD stabilised



tetradecane-in-water emulsions were so stable that we used them as templates for preparation of cyclodextrinosomes after the removal of the core oil. We also report the preparation of CD-stabilized emulsions with a range of other oils and studied the effect of the salt concentration in the aqueous phase, the type of CD and the oil volume fraction on the type of emulsion formed. The CD-stabilized emulsions and cyclodextrinosomes can find applications in a range of surfactant-free formulations in cosmetics, home and personal care, and in

pharmaceutical formulations as drug delivery vehicles.

Nanocapsules for biomedical applications using an interfacial RAFT miniemulsion process

L.M. Forero^{a,b}, J. Babin^{a,b}, A. Boudier^c, C. Gaucher^c, A. Durand^{a,b}, J-L Six^{a,b}, C. Nouvel^{a,b}

^aUniversité de Lorraine, Laboratoire de Chimie Physique Macromoléculaire LCPM, FRE 3564, Nancy F-54000, France

^bCNRS

^cUniversité de Lorraine, Cithefor EA 3452, Nancy F-54001, France

laura.forero-ramirez@univ-lorraine.fr

This talk will depict the fabrication of a new platform of dextran-covered nanocapsules (NCs) with controlled morphology in term of coverage and shell structure, for drug delivery applications, particularly in cancer therapy. To assure their biocompatibility and biodegradability, Miglyol 810 (a neutral triglyceride widely used in biochemistry), poly(methyl methacrylate) (PMMA) and dextran (a natural polysaccharide) were chosen as materials constituting the hydrophobic oily core, the inner polymeric shell and the hydrophilic coverage of NCs, respectively. To achieve such NCs, Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization¹ of methyl methacrylate was performed in miniemulsion from a transurf dextran derivative (Figure 1). This transurf stabilizes the miniemulsion and acts as macro-RAFT agent during the polymerization allowing the controlled growth of polymeric chains. As a result, grafted copolymers were produced at the interface and the resulting NCs are constituted of an inner oily core and an inner-shell made of the PMMA grafts linked to the dextran outershell. Dextran coverage should ensure colloidal stability as well as protection of the NCs from the uptake by the macrophages of the mononuclear phagocytose system, prolonging their blood circulation time. In addition, the introduction of click functionality onto dextran will also enable easy post-modification of the final NCs by ligand molecules allowing a specific targeting of cancer cells.

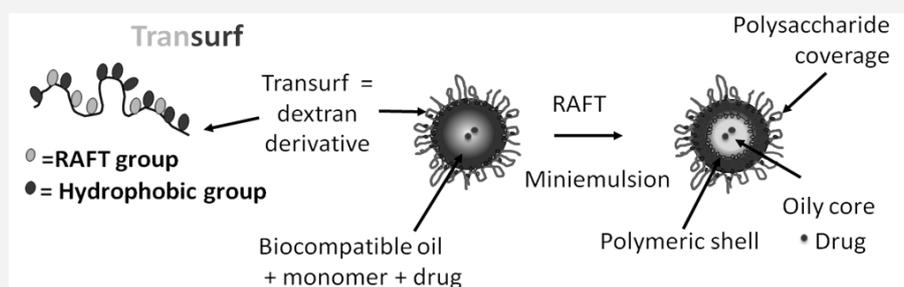


Figure 1: Nanocapsules produced by RAFT miniemulsion polymerization from a dextran-based transurf.

This communication will cover studies on miniemulsion stability and NCs synthesis. The release studies of a fluorescent molecule encapsulated inside nanocarriers as well as the preliminary evaluation of NCs stealthiness will be presented.

1. Keddie, D., Moad G., *Macromolecules*, 45: 5321-5342, 2012.

Short ranged repulsion within the first two layers of structural oscillation forces

Sebastian Schoen and Regine von Klitzing

Oscillatory structural forces are a genuine feature observed for simple and complex fluids in the vicinity of smooth wall. The origin of these forces is related to the characteristic quality of molecules or nanoparticles to form well-ordered layers in the vicinity of a confining wall. These forces can be described by the following function as proposed by Israelachvili:

$$f(x) = -A \cdot e^{-\frac{x}{\xi}} \cdot \cos\left(\frac{2\pi(x-\Delta x)}{\lambda}\right),$$

with f the force as a function of x , the separation. The Amplitude A describes the strength of the particle interaction, the decay length ξ is a measure of how fast the order decays and the wavelength λ is directly related to the inter-particle distance.

Structural oscillation forces are long ranged compared to the common DLVO forces and can be used in a variety of applications e.g. oil removal, separation of bidisperse particle suspensions or increase of colloidal suspensions. For all these applications it is important to accurately predict the strength of the oscillatory forces at very small separations.

Deviations have been observed between experimental data and the common fit function, an additional repulsive term is introduced to accommodate for these deviation which allows accurate fitting of experimental data down to very small separations and removes systematic deviations in A , λ and ξ depending on the starting point of the fit.

The short ranged repulsive energy described by the new term is investigated under different conditions such as particle concentrations, measurement speed and additives.

Influences of charges on the properties of polyelectrolyte multilayers

M. Schönhoff^a, D. Bütergerds^a, A. Ostendorf^a and C. Cramer^a

*^aInstitute of Physical Chemistry, University of Muenster,
Corrensstr. 28/30, 48149 Münster, Germany*

schoenhoff@uni-muenster.de

Polyelectrolyte multilayers (PEM) are formed by the Layer-by-Layer method resulting in defined ultrathin layers in the nanometer range. Employing weak polyelectrolytes, the charge density along the chain has a major influence on the growth law, e.g. pH-dependent growth regimes with exponential or linear growth, respectively, can be identified [1]. We have studied (i) poly(diallyldimethyl-ammonium) and poly(acrylic acid) (PDADMA/PAA) as a system containing one weak as well as one strong PE component and (ii) poly(L-lysine) and hyaluronic acid (PLL/HA) as a typical biopolymer system. We show that pH-dependent regimes of linear and exponential growth exist for PDADMA/PAA, but exponential growth at all pH values for PLL/HA films. The findings are explained in terms of a pH-dependent chain interdiffusion.

Furthermore, PEM are, due to their inherently low thickness, interesting candidates for applications as electrolytes. Therefore, we have studied fundamental charge transport properties by impedance spectroscopy. Whereas earlier results showed a strong exponential dependence of the conductivity on relative humidity as a general law and protons as charge carriers [2], conductivities of LbL films containing gold nanoparticles display a distinctly different humidity dependence [3]. Here, the conductivity can be attributed to electronic charge transport via the gold particles as the dominating conduction mechanism, involving electron tunneling between particles. Furthermore, the conductivity can be reversibly tuned by humidity via control of the interparticle distances, which determine tunneling probabilities.

- [1] Bieker, P.; Schönhoff, M. *Macromolecules* 2010, 43(11), 5052-5059.
- [2] Akgöl, Y.; Cramer, C.; Hofmann, C.; Karatas, Y.; Wiemhöfer H.D.; Schönhoff, M. *Macromolecules* 2010, 43(17), 7282-7287.
- [3] Ostendorf, A.; Cramer, C.; Decher, G.; Schönhoff, M. *J. Phys. Chem. C*, in press.

Structure of aqueous phase in oil Ramsden-Pickering emulsions

M. Schmitt, R. Denoyel, M. Antoni

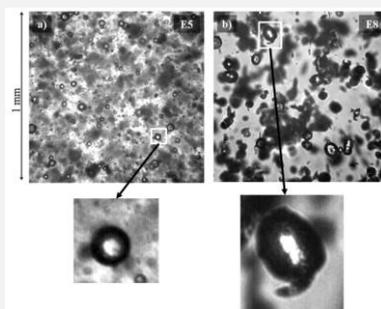
*Aix-Marseille Université, UMR/CNRS 7246 MADIREL
Centre Scientifique de St. Jérôme, 13397 – Marseille Cedex 20*

murielle.schmitt@univ-amu.fr

Recent studies have shown that aqueous suspensions of silica nanoparticles (SiO_2) modified by a surfactant (CTAB) can lead to important modifications in the structure of emulsions (see figure)[1-3]. Optical tomography and cryo-SEM investigations have demonstrated that the control parameter of the morphology was the mixing ratio $[\text{SiO}_2]/[\text{CTAB}]$.

This work aims to present the effect SPAN80 on the structure of the previous emulsions. SPAN80 is a surfactant only soluble in paraffin oil. At low concentrations, emulsions show highly deformed droplets. Increasing concentration improves emulsification. Droplets take smaller sizes due to the reduction of the interfacial tension. The unexpected result here is the fact that a spherical geometry is recovered for the droplets. The transition occurs for $[\text{SPAN80}] \approx 0.04 \text{ g/L}$.

In the presence of SPAN80, the continuous paraffin oil phase becomes cloudy over time indicating the presence of micrometer sized objects in the emulsions. Cryo-SEM measurements show that water is transported into paraffin oil. The kinetics of this phenomenon depends on the SPAN80 concentration but not significantly on the composition of the dispersed aqueous phase. It reflects a change in the interfacial properties that favors not only the presence of spherical droplets but also self-emulsification.



Emulsion with spherical droplets (a) and non-spherical ones (b). The two bottom images are enlargements showing the shape of two droplets.

- [1] Schmitt M. et al., *Langmuir*, 25, (2009), 4266.
- [2] Limage, S., et al., *Langmuir*, 26, (2010), 16754.
- [3] Ravera, F. et al., *Colloids Surf. A*, 323, (2008), 99.

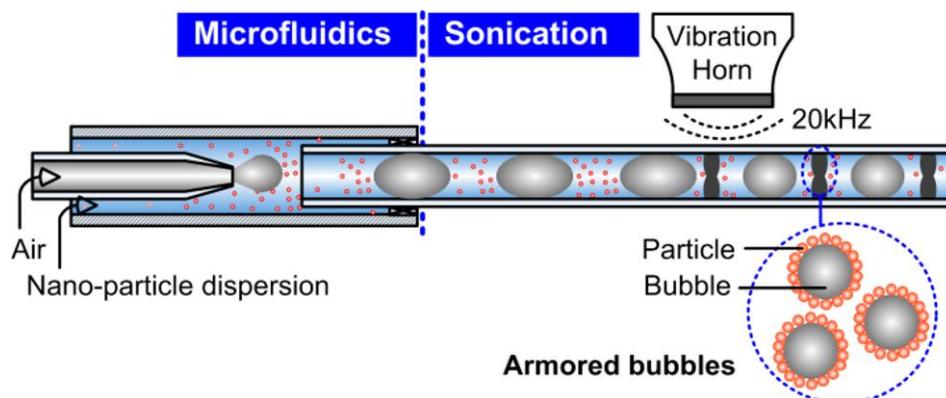
SONICATION–MICROFLUIDICS FOR FABRICATION OF NANOPARTICLE-STABILIZED MICROBUBBLES

Haosheng Chen,¹ Jiang Li,² Weizheng Zhou,³ Eddie G. Pelan,⁴ Simeon D. Stoyanov,^{4,5,6} Luben N. Arnaudov,^{4,*} and Howard A. Stone,⁷

1. *State Key Laboratory of Tribology, Tsinghua University, Beijing, 100084, China*
2. *School of Mechanical Engineering, University of Science and Technology Beijing, Beijing, 100083, China*
3. *Unilever R&D Shanghai, 66 Lin Xin Road, Shanghai 200335, China*
4. *Unilever Research & Development, 3133AT Vlaardingen, The Netherlands*
5. *Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands*
6. *Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom*
7. *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, United States*

* luben.arnaudov@unilever.com

An approach based upon sonication – microfluidics is presented to fabricate nano particle-coated micro bubbles. The gas-in-liquid slug flow formed in a micro channel is subjected to ultrasound, leading to cavitation at the gas–liquid interface (see the figure below). Therefore, micro bubbles are formed and then stabilized by the nano particles contained in the liquid. Compared to the conventional sonication method, this sonication – microfluidics continuous flow approach has unlimited gas nuclei for cavitation that yields continuous production of foam with shorter residence time. By controlling the flow rate ratios of the gas to the liquid, this method also achieves a higher production volume, smaller bubble size, and less waste of the nano particles needed to stabilize the micro bubbles.



Characterization of contact line motion during solvent evaporation, cycling breathing of triple line

Benjamin Vuillemey, Komla Ako, Yahya Rharbi

Laboratoire Rhéologie et Procédés, UMR 5520 – UJF – Grenoble INP – CNRS

Corresponding author: benjamin.vuillemey@ujf-grenoble.fr

Keywords: structured coating, convective assembly, drying, meniscus

Solvent evaporation appears as an easy way to deposit on any surface a film, which structure is directly linked to the particles contained on the suspension and its behavior with its solid and liquid environment during drying step. The coffee ring effect [1], which results in a preferential agglomeration of the particle in the drop periphery, is the most eloquent example. The deposition zone can be selected, leading to a lithography process governed by the meniscus shape [2].

Such process is difficult to assess: handling the air-liquid-substrate interface movement is a basic need to increase the technical power of that coating method. To investigate the contact line motion during drying, we focus on the meniscus which comes of a liquid flow between a sealed container and a substrate. Observations of changes regarding meniscus shape and capillary pressure, shows a cyclic phenomenon. Such breathing can be tuned in frequency and amplitude, by acting both on physical parameters of the solvents, and geometrical parameters of the device.

To increase the control of textured surfaces obtained by self-organization of particles during the evaporation process, further works will be dedicated to the selection of colloidal suspensions. Potential applications could be found in materials for optics or water repellent surfaces.

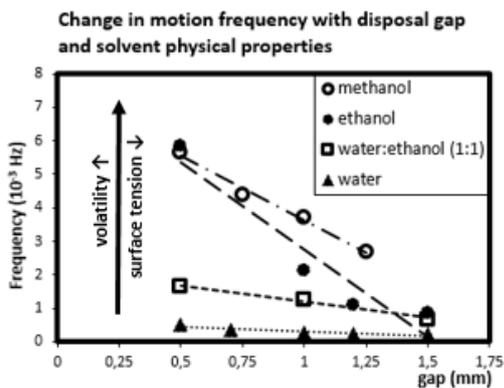


Figure 1: combined effects of solvent parameters and disposal geometry on the frequency of the contact line breathing

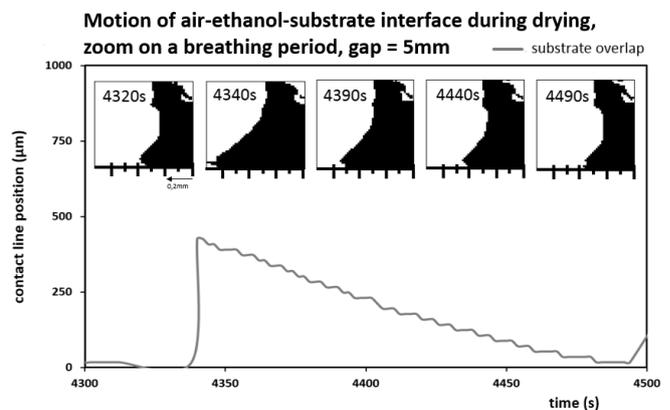


Figure 2: observed hysteresis between advancing and receding phases on a breathing cycle.

References

1. R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, T.A Witten, *Nature* **389**, 827-829 (1997).
2. L. Malaquin, T. Kraus, H. Schmid, E. Delamarche, H. Wolf, *Langmuir* **23**, 11513-11521 (2007).

First Processing of Core-shell Dispersible Solid Bitumen

P. Anaclet^a, R. Backov^b and V. Schmitt^c
Université de Bordeaux, CNRS, CRPP, UPR 8641, F-33600 Pessac, France

^a anaclet@crpp-bordeaux.cnrs.fr

^b schmitt@crpp-bordeaux.cnrs.fr

^c backov@crpp-bordeaux.cnrs.fr

Bitumen is a hydrocarbon binder resulting mainly from the direct distillation of crude oil. It is a black material exhibiting high viscosity at room temperature, mainly employed for manufacture of road surfaces.

In order to facilitate both the bitumen handling and transportation, a solution has been proposed making use of emulsions. Bitumen emulsions have a long history and exhibit many advantages. However, some drawbacks as low stability and limitation in the asphalt content have not been circumvented yet.

To overcome these issues, a process for obtaining a solid easily dispersible bituminous material is discussed. The overall synthetic path comprises preparing an emulsion of bitumen droplets stabilized by a mixture of at least two kinds of solid particles while, optionally, a continuous inorganic shell is generated around the bitumen drops before drying the native core-shell materials into powders. The solid bituminous materials can now be stored at room temperature and redispersed on demand. Final materials and whole synthetic path will be presented.

High resolution imaging to study PIT-emulsions at the solid/liquid interface

J. van Megen, A. Willmes, C. A. M. Seidel, W. von Rybinski
Heinrich Heine University, Duesseldorf, Germany

julian.megen@uni-duesseldorf.de

Emulsions are used in many everyday products and processes like cosmetics, detergency, food, pharmaceuticals and agriculture. For all these applications there are two important factors: stability of the emulsion with a defined droplet size and the ability to solubilize and release active ingredients. To meet the requirement of stable emulsions, the system must be finely dispersed with a narrow droplet size distribution.

A common process for the preparation of those long-term-stable emulsions is the phase inversion temperature (PIT) method, which utilizes the temperature dependent phase behaviour of ternary systems containing water (W), oil (O) and non-ionic amphiphiles (S) to produce O/W-emulsions with droplet sizes below 200 nm.

The functionality of emulsions regarding the transport of active ingredients is determined by interactions with solid surfaces. In order to gain new insights into the release mechanisms the emulsion structure and stability in solution and at surfaces was studied.

The phase behaviour of non-ionic surfactants in binary (S/W) and ternary (S/W/O) systems was studied to find suitable compositions for the formation of stable nanoemulsions. Lamellar liquid crystals in the external water phase were found to be one major requirement to achieve sufficient stability of the emulsion.

Atomic force microscopy (AFM) was applied to study model PIT-emulsions on different hydrophilic and hydrophobic surfaces. From high resolution imaging at ambient conditions new information about emulsion structure at the solid/liquid interface was obtained.

Influence of Physicochemical Interactions between Particles and Organic Compounds on Mineral Foams Stability

M. Auriol^a, V. Schmitt^a, R. Backov^a

^a*Centre de Recherche Paul Pascal – CNRS – Université de Bordeaux, Pessac, France*

auriol@crpp-bordeaux.cnrs.fr
schmitt@crpp-bordeaux.cnrs.fr
backov@crpp-bordeaux.cnrs.fr

Reducing energy consumption and greenhouse gas emission became a major concern in all domains and also in the construction sector. Cement based mineral foams appears to be an effective solution to these issues. Such foams can be produced by industrial processes from water, cement, organic compounds (surfactants, superplasticizers...) and other components as filler or sand¹. However, the production of these materials can be difficult because of the kinetic competition between foam stability and cement setting. Cement based mineral foams are extremely complex materials because of the number of components and all their interactions. The objective of our study is to get insight into the interactions between mineral and organic compounds and to understand their role in the stabilizing mechanisms.

Our strategy is to use a surfactant exhibiting a characteristic peak in UV-visible spectroscopy namely sodium dodecylbenzene sulfonate (SDBS) in order to determine its function and position in the complex system. We first worked on unfoamed slurries to understand the behavior of the cement suspensions in presence of surfactant and the interaction between the mineral particles and the molecules of surfactant. Then we studied the foamed materials in order to study the effect of the surfactant on the stability and the characteristic parameters of the cement based mineral foams.

¹K. Ramamurthy, E.K. Kunhanandan Nambiar, G. Indu Siva Ranjani. "A classification of studies on properties of foam concrete". *Cement & Concrete Composites* 31 (2009) 388–396

Shear and osmotic sensitivity of W/O/W-type double emulsions with a gelled internal water phase

M. Balcaen, L. Vermeir, P. Van der Meeren
Ghent University, Particle & Interfacial Technology Group, Gent, Belgium

Mathieu.Balcaen@UGent.be

Using W/O/W-type double emulsions, it is possible to produce functionalized and light O/W-type food emulsions. It has already been hypothesized that gelation of the internal water droplets might allow the application of a higher shear in the second emulsification step while maintaining a high internal water content. As such, this technique could enable the production of double emulsion droplets with a small average diameter and narrow particle size distribution.

First of all, the internal water phase of the primary W/O emulsion was gelled by thermal denaturation and subsequent aggregation of a concentrated (typically 5%) WPI solution. Low-resolution NMR T_2 -relaxometry was used to investigate whether the internal water phase was gelled. In a next step, we investigated whether gelation of the internal water phase did lead to a higher retention of internal water during the production of the double emulsions. Therefore, samples with a gelled internal water phase were compared with samples without a gelled internal water phase. As osmotic imbalances between the internal and external water phase are important to control the rheology and morphology as well as the release of encapsulated ingredients by droplet-globule coalescence, we also examined the osmotic behavior of the produced W/O/W-emulsions. To that end, the droplet size distribution of the W/O/W-double emulsions was measured over time by laser diffraction upon dilution in hypo- and hypertonic solution.

As the longitudinal, as well as the transversal relaxation time of the internal water phase in NMR-measurements decreased upon thermal treatment, it is clear that gelation indeed occurred. As a further consequence, a correction factor was necessary in order to obtain an accurate estimation of the amount of encapsulated water by PFG-NMR, because the composition of the external water phase was different from the internal water phase.

Upon gelation of the internal water phase, it was possible to produce double emulsions with an average diameter (D_{43}) of about 5 μm and a narrow particle size distribution, while maintaining a higher yield as compared to the samples with non-gelled internal water. Hereby, a faster decrease of the yield was observed when increasing the amount of microfluidization passes in case the internal water was not gelled.

Finally, gelation of the internal water phase, reduced swelling of the double emulsion droplets in hypotonic solution. On the other hand, internal water phase gelation could not prevent shrinking of the double emulsion droplets in hypertonic solutions.

Overall, our results indicated that internal water phase gelation, e.g. by thermal treatment of concentrated whey protein solutions, reduced the sensitivity of double emulsions towards the application of shear. As such, internal water phase gelation helps to make the formulation less susceptible to small variations in experimental conditions during production of double emulsions. Gelation of the internal water phase did not prevent swelling or shrinking of double emulsion droplets in hypo- or hypertonic solutions, respectively.

Interfacial Molecular Orientation assessed with Polarised Raman Spectroscopy

R. X. Rammeloo, C. D. Bain

Department of Chemistry, Durham University, Durham, United Kingdom

r.x.rammeloo@durham.ac.uk

We seek to quantitatively deduce interfacial molecular orientation from peak intensities in polarised Raman spectra. This requires both modelling and experimental efforts. The experimental system has been developed previously in our group and obtains surface selectivity through total internal reflection of the incident laser beam at the interface under investigation.⁽¹⁾ The evanescent wave thus generated causes Raman scattering of the molecules of interest. This system enables investigation of molecular layers at the solid-air, solid-liquid and solid-solid interfaces.

A numerical model has been constructed to provide Raman scattering intensities based on the experimental geometry used in our laboratory. Its variables include the Raman tensor of the vibrational mode under investigation, the orientation of the scattering molecule and the polarisation of the incident laser beam. We deduce molecular orientation of organic monolayers based on the symmetric and anti-symmetric stretch of the CH₂ group in aliphatic chains by fitting our modelling outcomes to experimental Raman scattering intensities.

Raman scattering is a ubiquitous phenomenon that is classically described as radiation from an induced molecular dipole upon undergoing an internal transition. This induced dipole \mathbf{p}^{Raman} can be expressed as

$$\mathbf{p}^{Raman} = \boldsymbol{\alpha}' \mathbf{E}$$

where $\boldsymbol{\alpha}'$ is the 3x3 Raman tensor specified for the transition involved and \mathbf{E} is the incident electric field that gives rise to the Raman scattering. From a fixed point of observation, the intensity of the dipole radiation is a convolution of the radiation field, the symmetry of the Raman tensor and the vectorial amplitude of the incident field. The molecular orientation can be obtained when these various contributions can be disentangled through modelling.

⁽¹⁾ David A. Woods and Colin D. Bain: Total internal reflection spectroscopy for studying soft matter. *Soft Matter*, 2014, 10, 1071-1096

Study on human corneocyte morphology by newly developed non-invasive cryosection electron microscopy.

Seren Maeda, Keisuke Nakamura, Hiromitsu Nakazawa and Satoru Kato

The primary function of the stratum corneum (SC), the outermost layer of human skin, is to protect the body from water loss. The SC consists of multiple layers of corneocytes, flattened anucleated cells filled with crosslinked soft keratin filaments, which are thought to work as water reservoirs. It has been revealed that formation of flattened, sheet-like corneocytes in the final stage of differentiation is essential for the normal barrier function of skin. The purpose of this study is to develop a simple electron microscopic method convenient for the investigation of the detailed cross-sectional morphology of corneocyte and to elucidate the relationship between skin barrier properties and cellular shape parameters such as width, thickness, and contour roughness.

Corneocytes were collected by the conventional tape-stripping method from different body sites of healthy male volunteers with informed consent. The sample sticking to the tape was sandwiched using another adhesive tape and fixed by 0.5% OsO₄ at room temperature. The non-invasively obtained sample sandwiched between two tapes was cryoultrasectioned at -80°C.

We compared the shape parameters of corneocytes from forearm, forehead, and palm and found that they significantly depended on the sample collection site. Moreover, we examined the effect of water permeation on the morphology of corneocytes by collecting them from the skin surface after exposure to water for an appropriate time. Water permeation induced increase in the number of corneocyte layers stripped off by the adhesive tape and swelling of the corneocyte. Thus, our newly developed method is widely applicable to the experiments in which the SC sample must be obtained non-invasively.

Investigation of the stabilization of pharmaceutical nanoemulsions by a globular whey protein

A. Ali^{a,b}, G. Mekhloufi^{a,b}, N. Huang^{a,b}, M. Cheron^c, I. Le Potier^{a,b}, F. Agnely^{a,b}

^a*Univ Paris-Sud, Faculté de Pharmacie, Châtenay-Malabry, France*

^b*CNRS UMR 8612, Institut Galien Paris-Sud, Châtenay-Malabry, France*

^c*Pierre et Marie Curie University, Laboratoire Jean Perrin, Paris, France*

ali.ali@upsud.fr

In the pharmaceutical field, nanoemulsions raise a growing interest as drug delivery systems. However, due to their higher specific interface area compared to macroemulsions, nanoemulsions require higher surfactant concentrations for their stabilization. Commonly used synthetic surfactants are potentially irritant and toxic, which hinders the therapeutic application especially during long-term treatment. Proteins are good candidates to replace them for stabilizing nanoemulsions. The aim of this study was to investigate the stabilization of pharmaceutical oil-in-water nanoemulsions by β -lactoglobulin (β -lg), the major whey protein. In a first step, the effect of different physicochemical and process parameters on the droplets size and the nanoemulsion stability were thoroughly investigated to determine the optimized conditions for nanoemulsion formulation. The most stable nanoemulsions were obtained when the less viscous oil (5% oil weight fraction) was dispersed in 1 wt% β -Lg solution at a homogenization pressure of 100 MPa, applied for 4 cycles. The nanoemulsions droplet size was about 200 nm with a narrow size distribution. Then, the influence of high pressure homogenization on the structure and the aggregation state of β -lg was investigated by different technics such as circular dichroism and light scattering. Protein aggregation was observed for all the tested pressures while the secondary and the tertiary structures of β -Lg were widely altered at the highest homogenization pressures. Interestingly, neither the oil/water adsorption kinetics of β -lg nor its interfacial rheological properties were significantly modified by this treatment. The protein conferred elastic properties to the interface, which is likely to prevent droplet coalescence. The next step of our study will be to assess the effectiveness of this optimized formulation as a delivery system of a hydrophobic active pharmaceutical ingredient for a topical application.

Study of Influence of Nonionic Additives on the Structural Changes of Water Droplets Confined in AOT Reverse Micelles by Viscosity Data

N. Gonashvili, T. Butkhuzi, G. Bezarashvili and M. Rukhadze
*Faculty of Exact and Natural Sciences, Ivane Javakhishvili Tbilisi State University,
3,I.Chavchavadze ave, Tbilisi, 0179, Georgia*

marina_rukhadze@yahoo.com marina.rukhadze@tsu.ge

Structure of water droplets in reverse micelles is extremely complex, therefore reverse micelles have been investigated by using of different physicochemical methods. Structure of water nanodroplets becomes more complicated in the presence of ionic and nonionic additives, especially if these additives possess kosmotropic or chaotropic nature.

The goal of the proposed work was to study the structure of AOT reverse micelles by viscometric method and to calculate different parameters on the basis of viscosity measurements, viz. volume fraction of the water droplets, their density, the concentration of micelles, aggregation number, etc. Viscosity was measured with an Ostwald viscometer. The viscosity of microemulsions was related to the volume fraction of water droplets by the equation given in literature [1]. The abovementioned parameters were calculated by the methodology described in the same work. In addition, density changes of water droplets of the reverse microemulsion under the influence of additives were estimated.

The results show that changes in density of water droplets depend on the nature of the additives: density of water droplets decreases in the presence of chaotropic urea, whereas density is increased in case of kosmotropic glucose additives. In addition, increasing of volume fraction of water droplets takes place in the presence of urea as compared with pure water. The volume fraction of the water droplets is reduced in case of glucose additives, besides the concentration of micelles in microemulsion is decreased.

The results were discussed together with the data obtained by infrared spectrometry and dynamic light scattering method.

References:

1.Takumi Kinugasa, Aki Kondo, Satsuki Nishimura, Yoshiki Miyauchi, Yasuhiro Nishii, Kunio Watanabe, Hiroshi Takeuchi. Estimation for size of reverse micelles formed by AOT and SDEHP based on viscosity measurement. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 204 (2002) 193–199.

A Comparison of Adsorption Isotherms of DPPC at Oil in Water versus Water in Oil Interfaces regarding Surface Density and Solubility

E. Hildebrandt^{1,2,3,4*}, J.-H. Sommerling^{1,2}, M.B.C. de Matos^{2,4}, D.A. Grijalva³, A. Dessy², J. Binder², D. Laufer², R.J. Kok³, H. Nirschl¹ and G. Leneweit^{2,3}

¹Karlsruhe Institute of Technology (KIT), Institute of Mechanical Process Engineering and Mechanics (MVM), 76131 Karlsruhe, Germany

²Abnoba GmbH, 75131 Pforzheim, Germany

³Carl Gustav Carus-Institute, 75223 Niefern-Öschelbronn, Germany

⁴Universiteit Utrecht, Faculty of Science, Department of Pharmaceutical Sciences, Pharmaceutics, Utrecht, The Netherlands

We studied the adsorption behavior of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) at the interface of water with the biocompatible compounds squalene or squalene as immiscible fluid phases. DPPC was dissolved in the oil phase. The dynamic interfacial tension was measured by two different droplet-settings, a boyant oil drop or a pendant water drop (Fig. 1), by profile analysis tensiometry (PAT). For the proof of the methodology water/chloroform and chloroform/water interfaces were measured additionally. DPPC was then dissolved in chloroform forming a pendant drop while the buoyant drop consisted of the water phase. From the equilibrium interfacial tension of different phospholipid concentrations the adsorption isotherms and by that the minimal area per molecule at the surface as well as the critical aggregation concentration (CAC) were extracted [1, 2] and we found differences in the results of both settings which were never reported so far. With PAT a CAC was determined in a lower range for W/O than for O/W, both for squalane and for squalene. We postulate these differences to be caused by depletion effects when the drop volume is used as the reservoir of phospholipids. Furthermore the occupied area per lipid molecule in squalane was 2-fold less than in squalene indicating a tighter packing of the emulsifying agent at that interface. Besides that we found out that interfaces with squalene consists of monolayer while at squalene/water interfaces multilayers occur.

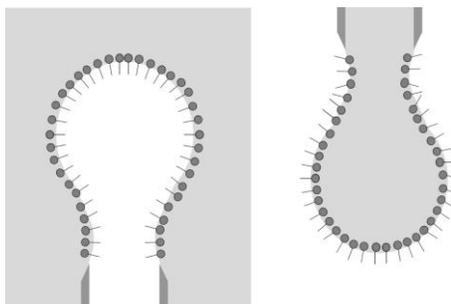


Figure 1. Schematic illustration of the two different droplet-settings. Left: oil droplet in water (O/W) and right: water droplet in oil (W/O).

References:

[1] Li, J. et al.; Colloids Surf. A; 1996, 114: 113-121

[2] Hecht, L.L. et al.; Macromol. Chem. Phys.; 2013; 214: 812-823

Acknowledgement: The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 324275 (decentAID).

[*ellen.hildebrandt@carus-institut.de](mailto:ellen.hildebrandt@carus-institut.de) Thank you for giving the opportunity to apply for the Enzo Ferroni Award during the ECIS2015 Conference. With that abstract and further presentation I would kindly like to apply for this award.

Double W/O/W Emulsions Stabilized with Gelatin/Sodium Caseinate Mixtures as Carriers of Water Soluble and Oil Soluble Vitamins

Lidija B. Petrović, Jadranka L. Fraj, Jelena R. Milinković, Jaroslav M. Katona, Sandra Dj. Bučko

Faculty of Technology Novi Sad, University of Novi Sad, Novi Sad, Serbia

lidijap@uns.ac.rs

Double emulsions are complex liquid dispersion systems known also as emulsions of emulsions. W/o/w emulsions are the most studied systems because they have the potential to become commercial products, mainly in food industry but also in cosmetics and pharmaceuticals [1, 2]. The main problem with these systems is their thermodynamic instability, while an additional problem with food related applications is selection of appropriate food-grade emulsifier and stabilizer. In order to answer the increasing demand for clean label excipients and natural ingredients, biopolymers can replace the potentially irritating synthetic surfactants. Proteins and some polysaccharides are able to adsorb at the interface leading to stabilization of emulsion. Potential interaction between used biopolymers can additionally improve emulsions stability [3].

In the present study the interactions in mixture of oppositely charged proteins, gelatin and sodium caseinate (NaCN), on w/o/w emulsions stability were investigated. In our previous studies interactions between these two proteins were investigated and complex coacervation was observed [4]. Water soluble vitamin C and oil soluble vitamin E were used as model substances.

These investigations showed the influence of interaction between proteins on emulsion stability, which, depending on the NaCN concentration, induce different type of phase separation in the system.

Reference

- [1] Garti N., Benichou A., in *Encyclopedic Handbook of Emulsions Technology*, Ed. Sjöblom J., New York: Marcel Dekker, (2001) p.177
- [2] Muschiolik G., *Current Opinion in Colloid and Interface Science* 12 (2007) p.213
- [3] McClements D. J., *Current Opinion in Colloid and Interface Science* (2004) p.305
- [4] Milanovic J., Petrovic L., Sovilj V., Katona J., *Food Hydrocolloids* 37 (2014) p.196

Acknowledgment

This work has been supported by the Ministry of Education Science and Technological Development of the Republic of Serbia (Grant Number III 46010).

Emulsion stabilized with biodegradables PLGA nanoparticles for pharmaceutical and cosmetic applications

C. Albert^{a,b}, N.Huang^{a,b}, N.Tsapis^{a,b}, G. Mekhloufi^{a,b}, E.Fattal^{a,b}, F. Agnely^a

^a*Univ Paris-Sud, Institut Galien Paris-Sud, LabEx LERMIT, Faculté de Pharmacie, 5 rue J.B. Clément, 92296 Châtenay-Malabry, France.*

^b*CNRS UMR 8612, Institut Galien Paris-Sud, LabEx LERMIT, 5 rue J.B. Clément, 92296 Châtenay-Malabry, France.*

claire.albert@u-psud.fr

Pickering emulsions are non-miscible liquid dispersions stabilized with particles instead of surfactants. In this study, we formulated long-term stabilized Pickering emulsions with biodegradable and biocompatible nanoparticles for pharmaceutical or cosmetic use. Such emulsions have the advantage of being potentially less toxic or irritant compared to emulsions stabilized with synthetic surfactants or mineral particles.

Here, we took full advantage of Poly(Lactic-co-Glycolic) Acid (PLGA), a biodegradable and biocompatible co-polymer, as nanoparticles to stabilize Miglyol in water emulsion for cutaneous use. We studied the impact of different formulations of nanoparticles on the stability of emulsions, particularly in changing the zeta potential of the particles by changing the polymers stabilizing the nanoparticles: polyvinyl alcohol, chitosan or Pluronic F68 for respectively neutrally, positively and negatively charged nanoparticles. The emulsion characterization and the study of their stability were performed. Interfacial rheology experiments were also conducted in order to clarify the kinetics and stabilization mechanism of the oil/water interface in presence of nanoparticles. We also studied the contribution of the polymers stabilizing the nanoparticles on the emulsion stability.

Those Pickering emulsions using PLGA nanoparticles are promising systems for the formulation of stable emulsions intended for topical administration allowing the encapsulation and the co-encapsulation of active ingredients.

Interfacial behavior of two-component monolayers of partially fluorinated alcohol (*F6H9OH*) and biomembrane constituents

H. Nakahara, M. Minamisono, and O. Shibata*

*Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences,
Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan*

wosamu@niu.ac.jp

We have investigated the mutual interaction in monolayers of partially fluorinated alcohols and biomembrane constituents[1-5]. In the present study, the binary interaction of (perfluorohexyl)nonanol (*F6H9OH*) with dipalmitoylphosphatidylcholine (DPPC), pentadecanol, and cholesterol was systematically studied at air–water interface. The thermodynamic property and phase morphology of the monolayers were investigated by isotherm measurements and several microscopic methods such as Brewster angle microscopy (BAM), fluorescence microscopy (FM), and atomic force microscopy (AFM). The excess Gibbs free energy change and interaction parameter (or energy) of the two components were calculated from the isotherm data. Both the phase transition pressure for the coexistence of ordered and disordered phases and collapse pressure of monolayers vary with the mole fraction of *F6H9OH*, indicating binary miscibility between *F6H9OH* and the lipids within a monolayer state. The miscibility is also confirmed visually by in situ and ex situ microscopy at micro- and nanometer scales.

References:

1. S. Nakamura, H. Nakahara, M.P. Krafft, O. Shibata, *Langmuir*, 23, 12634-12644 (2007).
2. H. Nakahara, M.P. Krafft, A. Shibata, O. Shibata, *Soft Matter*, 7, 7325–7333 (2011).
3. H. Nakahara, A. Ohmine, S. Kai, O. Shibata, *J. Oleo Sci.*, 62, 271–281 (2013).
4. H. Nakahara, C. Hirano, I. Fujita, O. Shibata, *J. Oleo Sci.* 62, 1017–1027 (2013).
5. H. Nakahara, C. Hirano, O. Shibata, *J. Oleo Sci.* 62, 1029–1039, (2013).

Characterisation of mixed monolayers formed by polyhedral oligomeric silsesquioxanes and carbon nanotubes

P. Szymański, M. Piechocka, M. Dudek, K. Prochaska,

*^aPoznan University of Technology, Institute of Chemical Technology and Engineering,
Berdychowo 4, 60-965 Poznań, Poland*

krystyna.prochaska@put.poznan.pl

Over the recent years a possibility of preparation of new organic-inorganic hybrid materials, which could handle specific tasks is in a great interest. One of the very promising is a hybrid material obtained by connection of polyhedral oligomeric silsesquioxanes (POSS) and carbon nanotubes (CNT). POSS are a very diversified group of chemical compounds of cube-octameric frameworks which chemical and physical properties are strongly dependable of structure of eight organic corner groups connected to silica-like core. Recent reports shows that the POSS/CNT hybrid material may possess tremendous thermal, electrical and mechanical properties of CNTs while the addition of POSS could improve them and allows to avoid problems with arrangement of CNTs. Unfortunately there are very few reports which describes the behavior of monolayer of such hybrid material what is crucial for its future development, improvement and application.

In this work results of experiments performed to investigate and describe a formation and a behavior of POSS/CNT hybrid material monolayers on the air/water interface are presented. Research of interfacial properties were carried out for various compositions of POSS/CNT hybrid material depending on the chemical structure of organic substituents of POSS molecules and the POSS-CNTs ratio. A Langmuir trough (KSV NIMA) equipped with Brewster angle microscope (BAM) and surface potential sensor (SPOT) as well as with interfacial stress rheometer (KSV NIMA ISR) were used to this end.

In general obtained experimental data allow to determine the influence of used fully condensed POSS derivative as well as the POSS-CNTs ratio on forming stable Langmuir monolayer at the air/water interface. Moreover, obtained data allows to find proper conditions for future transfer of various POSS/CNT hybrid Langmuir monolayers on solid material.

Acknowledgements:

This work was financially supported by Polish National Science Centre, Grant No. UMO-2012/05/B/ST02200

Interfacial Characterization of Langmuir Monolayers Containing Fluorinated Silsesquioxanes and Nanoparticles

K. Dopierala^a, K. Bojakowska^a, M. Piechocka^a, H. Maciejewski^b
K. Prochaska^a,

^a*Poznan University of Technology, Institute of Chemical Technology and Engineering,
Berdychowo 4, 60-965 Poznan, Poland*

^b*Adam Mickiewicz University, Faculty of Chemistry,
Umultowska 89b, 61-614 Poznań, Poland*

krystyna.prochaska@put.poznan.pl

Silsesquioxanes are compounds that present large potential as nanofillers in nanocomposites and in production of low surface energy coatings [1]. However, interfacial properties of these materials are poorly described [2-5]. Fluorinated silsesquioxanes are attractive as potential low- surface energy materials. However, addition of nanoparticles may increase roughness of coated surface. The combination of these two approaches allows obtaining water- repellent materials.

Our goal is to prepare ultrathin, non-wettable films by Langmuir-Blodgett technique using fluorinated silsesquioxanes and silica nanoparticles. In this report we present the first part of our study: interfacial characterization of mixed Langmuir monolayer formed by silsesquioxanes and silica nanoparticles. Interfacial properties were studied using Langmuir trough (KSV Nima) equipped with Brewster angle microscope and surface potential sensor. Moreover, the interfacial dilational viscoelasticity of the monolayers was determined by oscillating barriers method.

Literature:

- [1] Ganesh V.A., Nair A. S., Raut H.K., Yuan Tan T.T., He C., Ramakrishna S., Xu J., *J. Mater. Chem.*, **2012**, *22*, 18479-18485
- [2] Kim C., Esker A.R. , Runge F.E. , Yu H. *Macromolecules* **2006**, *39*, 4889-4893
- [3] Deng J., Farmer-Creely C. E., Viers B. D., Esker A.R., *Langmuir* **2004**, *20*, 2527-2530.
- [4] Wamke A., Dopierala K., Prochaska K., Maciejewski H., Biadasz A., Dudkowiak A *Coll. Surf. A* **2015**, *464*, 110–120
- [5] Dopierala K., Wamke A., Dutkiewicz M. Maciejewski H. Prochaska K., *J. Phys. Chem. C*, **2014**, *118* (42), 24548–24555

Acknowledgements:

This work was financially supported by Polish National Science Centre, Grant No. UMO-2012/05/B/ST02200

COMPARISON OF PROTEIN PHYSICAL PROPERTIES BY THEIR INTERACTION WITH BIG HYDROPHOBIC IONS

Leonor Pérez-Fuentes^{1,*}, Carlos Drummond², Jordi Faraudo³ and Delfi Bastos-González¹

¹Biocolloid and Fluid Physics Group, Department of Applied Physics, University of Granada, Spain, *lpfuentes@ugr.es

²CNRS, Centre de Recherche Paul Pascal (CRPP), Pessac, France

³Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, Barcelona, Spain

In the current work, we have studied the physical properties of three proteins: BSA, β -lactoglobulin and β -casein. The latter two are milk proteins very common in allergies. The knowledge of the behavior of these proteins in solution as well as their interactions with interfaces has a rising interest in order to develop techniques to detect and extract proteins in food.

With this purpose, we have carried out a comprehensive study that contains several experimental techniques. On the one hand, we have covered latex nanoparticles with the proteins. The surface of the obtained colloids shows the protein properties. These were physico-chemical characterized by electrophoretic and stability measurements. On the other hand, the adsorption of these proteins has been studied by a Quartz Crystal Microbalance with Dissipation monitoring device (QCM-D) [1], which is commonly used to determine the thickness and viscoelastic properties of nanofilms adsorbed over flat substrates.

Furthermore, we have used two big hydrophobic ions, which strongly interact with the proteins. These ions are the tetraphenylborate anion (Ph_4B^-) and the tetraphenylarsonium cation (Ph_4As^+). We have corroborated that these large ions present a great affinity toward the proteins and that this affinity depends on the hydrophobic character of the proteins. Moreover, we have also confirmed that the interaction of the anion is always stronger than that of the cation in spite of the very similar structural properties of both hydrophobic ions, as we expected from previous works [2,3].

Acknowledgements: This work has been sponsored by the projects CTS-6270 (Junta de Andalucía, Spain) and MAT2012-36270-C04-02 (Ministerio de Economía y Competitividad, Spain).

References:

- [1] Reviakine, I.; Johannsmann, D.; Richter, R.P. *Anal. Chem.* (2011), 83, 8838-8848.
- [2] Calero, C.; Faraudo, J.; Bastos-González, D. *J. Am. Chem. Soc.* (2011), 133, 15025-15035.
- [3] Pérez-Fuentes, L.; Drummond, C.; Faraudo, J.; Bastos-González, D. (submitted).

Surface Tension Distribution around a Camphor Boat Moving Spontaneously on a Water Surface

Y.Karasawa^a, T.Nomoto^a, T.Toyota^b, M.Fujinami^a

^a Dept. of Applied Chemistry & Biotechnology, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan

^b Dept. of Basic Science, The University of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153-8902, Japan

y.karasawa@chiba-u.jp

It is well-known that a camphor boat floated on an aqueous phase moves spontaneously. The inhomogeneous surface tension distribution around the camphor boat has been reported as the driving force [1]. However the difference in the surface tension between the front and the rear sides of the boat has never been measured *in situ* directly. A time-resolved quasi-elastic laser scattering (QELS) method enables us to measure the surface and interface tensions in a non-invasive manner, so that it is very suitable tool to apply the above-mentioned non-equilibrium phenomena [2]. In this work, the surface tension distributions around a camphor boat on an aqueous phase have been derived by QELS method and the driving force of the camphor boat is discussed.

The camphor boat consisted of a polyester film (thickness = 0.1 mm) with three camphor disks (diameter and thickness 3 mm and 1 mm, respectively) glued to the rear side. To construct the circular channel, a glass Petri dish (outer diameter: 82 mm) was placed inside a larger glass Petri dish (inner diameter: 125 mm). The mean circumference was estimated as 325 mm. The circular channel was filled to a height of 3 mm with an aqueous camphor solution (5.0, 6.5, 7.0, and 7.5 mmol⁻¹). The velocity of the boat was controlled by changing the camphor concentration in an aqueous phase and the boat moved uniformly along the circular channel.

A surface tension gradient was observed only at the rear side. To estimate the differences in surface tension between the front and rear sides, the data in the rear side were fitted to $\gamma(x)=\gamma_0+A\cdot\exp(x/l)$ and the data in the front side were fitted to a straight line. It was found that the surface-tension difference strongly depended on the velocity of the camphor boats. Furthermore, to clarify the contribution of Marangoni convection to the camphor-boat movement, we evaluated the A/l related to the surface tension gradient. The correlation between the A/l value and velocity of the camphor boat is quite small in comparison to that with the surface-tension difference. It was found that the deceleration of camphor boat by the Marangoni convective flow seemed to be small when the velocities are controlled by the aqueous-phase camphor concentration in the circular channel. It was proven experimentally that the camphor boat motion was chiefly driven by the difference in surface tension between the front and rear of the camphor boat.

[1] S. Nakata, Y. Iguchi, S. Ose, M. Kuboyama, *Langmuir* **13**, 4454 (1997).

[2] T. Nomoto, T. Toyota, M. Fujinami, *Anal. Sci.* **30**, 707 (2014).

Spontaneous Chemical Oscillation Mechanism in water/oil/water system: Effect of chemical species in the acceptor phase

S. Iko^a, K. Goto^a, T. Nomoto^a, T. Toyota^b, M. Fujinami^a

^a Dept. of Applied Chemistry & Biotechnology, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan

^b Dept. of Basic Science, The University of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153-8902, Japan

Satoshi_iko@chiba-u.jp

We used a time-resolved interfacial tension measurement method with quasi-elastic laser scattering to elucidate the mechanism of spontaneous chemical oscillation in donor/oil membrane/acceptor system. This three-phase oscillatory system is composed of surfactants and alcohol solution as the donor phase (W_d), nitrobenzene containing electrolyte as the oil membrane (O), and a electrolyte solution as the acceptor phase (W_a). It was found that the potential difference oscillation was generated by adsorption and desorption of surfactants at O/W_a , and instability of interfacial tension distribution determine the chemical oscillation pattern [1]. In this study, to elucidate the mechanism of oscillation phenomena, we varied chemical species systematically in W_a in W_d containing cationic surfactant or anionic surfactant. Cetyltrimethylammonium bromide (CTAB) was used as cationic surfactant, and sodium oleate as anionic surfactant.

In cationic CTAB system, we observed a strong halide ion dependence on the chemical oscillation pattern. Chloride ions stabilized the adsorption of CTA^+ ions and gave rise to large amplitude, short frequency interval and long relaxation time constant, while iodide ions with hydrophobic showed opposite results on them. Their mechanism has proposed on observation of the interfacial tension at the acceptor/oil interface and the convective flow due to the Marangoni effect.

In sodium oleate system, pH in the acceptor phase was varied. We found that the chemical oscillation was induced in more than pH 9 in W_a and the interfacial tension at O/W_a changed corresponding with potential difference. The amount of oleate ions in water/oil system strongly depended on pH in aqueous phase in equilibrium and it increased with pH in the region from pH 7 to pH 11. It was considered that oleate was protonated in less than pH 8 and dissolved in the oil phase immediately even if it was desorbed at O/W_a . The amount of oleate adsorption was too small to induce the Marangoni convective flow. It is, therefore, concluded that the three-phase oscillatory system is dominated by stability of surfactants at O/W_a and the mechanism can be explained by Marangoni convective flow induced by the inhomogeneous interfacial tension distribution.

References

[1] T. Nomoto *et al. Anal. Sci.*, **30**, 463 (2014).

Influence of Liquid Flow on Microbial Adhesion to Material Surfaces.

Klemen Bohinc^{*1}, Rok Fink¹, Martina Oder¹

¹Faculty of Health Sciences, University of Ljubljana, Ljubljana, Slovenia

* Corresponding author: Email: klemen.bohinc@zf.uni-lj.si, Phone: 00386 1 300 1170, Fax: 00386 1 300 11 19

Interactions between bacteria and material surfaces play an important role in biology and different process technologies [1, 2]. Environmental parameters dictate the conditions for both biofilm formation and deconstruction. The objective of this study is to investigate the influence of hydrodynamic and thermodynamic effects on the degree of biofilm detachment [3]. The study was made on material surfaces with different surface roughness. The preliminary results with *E.coli* show that turbulent flow removes significant more cells than laminar flow. The results indicate that the shear force influences the biofilm detaching. We also found that the detachment of cells was more efficient on material surface with lower roughness. The experimental findings will be related to the theoretical predictions.

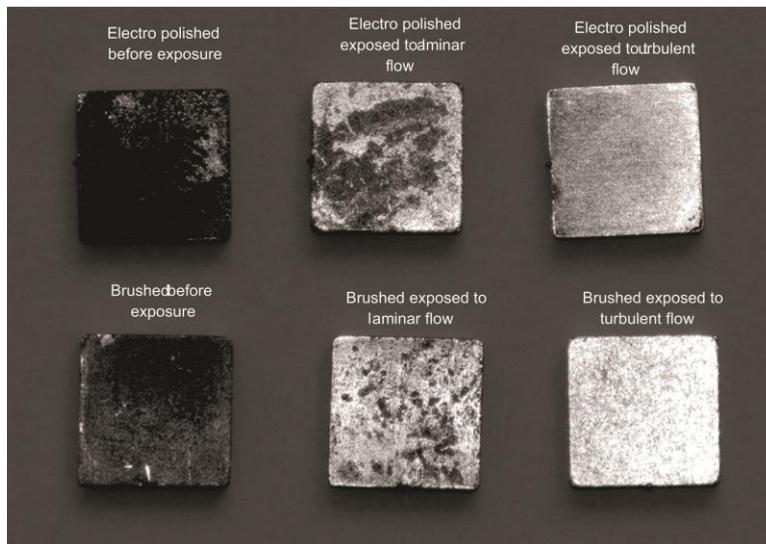


Figure: Photography of adhered bacteria on electro polished and brushed metal plates before and after exposure to laminar and turbulent flows. Stained surfaces were photographed with Nikon Coolpix P500 at 36 x optical zoom. Columns: before exposure, exposure to laminar flow and exposure to turbulent flow. First line corresponds to the electro polished surfaces whereas the second line corresponds to the brushed materials.

References:

1. K. Bohinc, G. Dražič, R. Fink, M. Oder, M. Jevšnik, D. Nipič, K. Godič Torkar, P. Raspor, Available surface dictates microbial adhesion capacity. *International journal of adhesion and adhesives*, 50(1) (2014) 265-272.
2. E. Preedy, S. Perni, D. Nipič, K. Bohinc, P. Prokopovich, Surface roughness mediated adhesion forces between borosilicate glass and gram-positive bacteria. *Langmuir*, 30(31) (2014) 9466-9476.
3. R. Fink, M. Oder, D. Rangus, P. Raspor, K. Bohinc, Microbial adhesion capacity. Influence of shear and temperature stress. *International Journal of Environmental Health Research*, in press 2015.

The relationship between chemical structure of Polyhedral Oligomeric Silsesquioxanes molecules and physicochemical properties of Langmuir monolayers formed at the air/water interphase

A. Wamke^a, K. Dopierała^a, H. Maciejewski^b, K. Prochaska^a,

^a*University of Technology, Institute of Chemical Technology and Engineering,
Berdychowo 4, 60-965 Poznan, Poland*

^b*Adam Mickiewicz University, Faculty of Chemistry,
Umultowska 89b, 61-614 Poznań, Poland*

anna.wamke@doctorate.put.poznan.pl

Polyhedral oligomeric silsesquioxanes (POSS) are an interesting class of hybrid inorganic–organic compounds, which carry strong potential as precursors for the preparation of new multifunctional materials. The attractiveness of POSS molecules is a result of their unique structure (POSS molecule contains inorganic Si-O core and organic substituents attached into Si atoms) and nanoscale. Due to the type and character of substituents, controlling of chemical properties of POSS molecules is possible.

Previous research of many scientists have been focused on describing interfacial properties of incompletely condensed POSS molecules. The results of studies on the nature of monolayers formed at the air/water interface by molecules of incompletely condensed POSS helped to understand the interfacial properties of POSS compounds, and explained their interaction with various polymers as blends. A lot of papers concerning different applications of POSS molecules have been issued. Unfortunately up to now there are very few reports describing interfacial properties of fully condensed POSS molecules.

In our report the properties of Langmuir monolayers formed by different types of POSS molecules (incompletely and fully condensed POSS) have been characterized and compared. The correlation between the chemical structure and behaviour of the POSS molecules at the air/water interface were discussed. To achieve this goal three groups of POSS of different chemical structure were considered: i) incompletely condensed POSS compounds possessing cage of different degree of opening; ii) fully condensed POSS molecules with eight identical substituents attached into Si-O core; iii) fully condensed POSS molecules possessing different types of substituents (reactive and unreactive). The surveys have been performed by Langmuir trough (KSV Nima), equipped with Brewster Angle Microscope and Surface Potential sensor. The experiments showed the influence of POSS chemical structure on compression isotherm as well as on surface potential at the air/water interface. It was found that the run of Π -A isotherm (phase transition) is affected by the structure of cage as well as by the character of substituents.

Acknowledgements:

This work was financially supported by Polish National Science Centre, Grant No. UMO-2012/05/B/ST02200

Is it possible to modify the viscoelasticity of cyclodextrin-based interfacial films?

Esther G. Merino^a, Jorge Hernández-Pascacio^b, Daniel Ondo^c, José Campos-Terán^d, Miguel Costas^b, Ángel Piñeiro^a

^a*Soft Matter and Molecular Biophysics Group, Dept. of Applied Physics, University of Santiago de Compostela, E-15782, Santiago de Compostela, Spain.*

^b*Dept. of Physical Chemistry, Faculty of Chemistry, Univ. Nacional Autónoma de México (UNAM), Ciudad Universitaria 04510, México D.F., México.*

^c*University of Chemistry and Technology, Department of Physical Chemistry Technicka 5, 16628 Prague 6, Czech Republic.*

^d*Dept. de Procesos y Tecnología, Universidad Autónoma Metropolitana, Unidad Cuajimalpa, Av. Vasco de Quiroga 4871, Col. Santa Fe, Delegación Cuajimalpa de Morelos, 05348, D.F., México.*

E-mail: esther.garcia.merino@rai.usc.es

Inclusion complexes based on cyclodextrins in aqueous solution are known to form aggregates that produce a film at the solution/air interface, whose physicochemical properties can be tuned by the addition of different guest molecules. [1–3]

The purpose of this study was to find new amphiphilic guest-molecules with the ability to improve the viscoelastic properties of the film formed at the interface. For that, an anionic surfactant, sodium tetradecyl sulfate (STS), was used as a guest-molecule. The properties of the film were characterized using Maximum Drop volumes and the resultant surface tension values. High surface tension values were found at specific concentrations/temperatures, corresponding to a 20 % increase when compared to pure water, comparable with the results of [1] obtained for another anionic surfactant, sodium dodecyl sulfate.

These results indicate that 1) a film is spontaneously formed at the air/water interface in the presence of STS, 2) the film presents a high viscoelasticity and 3) concentration and temperature play an important role in the modulation of the viscoelasticity of the film.

REFERENCES

1. J. Hernández-Pascacio, X. Banquy, S. Pérez-Casas, M. Costas, A. Amigo, and Á. Piñeiro, *J. Colloid Interface Sci.* **328**, 391 (2008).
2. J. Hernández-Pascacio, C. Garza, X. Banquy, N. Díaz-Vergara, A. Amigo, S. Ramos, R. Castillo, M. Costas, and Á. Piñeiro, *J. Phys. Chem. B* **111**, 12625 (2007).
3. Á. Piñeiro, X. Banquy, S. Pérez-Casas, E. Tovar, A. García, A. Villa, A. Amigo, A. E. Mark, and M. Costas, *J. Phys. Chem. B* **111**, 4383 (2007).

ACKNOWLEDGEMENTS

This work was financially supported by MICINN-Spain by the project MAT2011-25501 09 and, through the scholarship BES-2012-057842 granted to Esther G. Merino.

Development, Characterization, and Stability Evaluation of Submicron Emulsions for Incorporation of Hydrophobic Naphthoquinones

L.S. Diniz,^a R.M.G. Sousa,^a F.V.S. Rodrigues,^a P.L. Goto,^b T.M. Gonçalves,^a C.R.M. Araújo,^a L.A. Rolim,^a A.C. Tedesco,^b M.P. Siqueira-Moura^{a*}

^a*Colegiado Acadêmico de Ciências Farmacêuticas, Universidade Federal do Vale do São Francisco (UNIVASF), Petrolina-PE, Brazil*

^b*Departamento de Química, Laboratório de Nanotecnologia e Engenharia Tecidual, FFCLRP, Universidade de São Paulo (USP), Ribeirão Preto-SP, Brazil*

*marigilson.moura@univasf.edu.br

Natural naphthoquinones, such as lapachol and β -lapachone, have demonstrated promising biological activities. However, these quinones present low systemic biodisponibility due to its poor aqueous solubility. Nanoemulsions (submicrometer-size droplets) formed by oily core are able to incorporate hydrophobic molecules thus enabling them to be dispersed into an aqueous phase in which they are normally insoluble. Submicron emulsions can be prepared by low-energy methods which present advantages such as prevent the potential degradation of fragile encapsulated molecules and potential industrial scale-up [1]. The present work reports the development, characterization, and physical stability of nanoemulsion containing lapachol. The physicochemical parameters analyzed and stability profile were dependent on pair of surfactants and oil type present in each formulation. The formulation chosen to incorporate naphthoquinone showed droplet size in nanometric scale with homogeneous size distribution (PDI <0.2), negative zeta potential (about -30 mV), and lapachol loading about 90%. Besides that, good physical stability of the formulation was demonstrated by analytical centrifugation with photometric detection. Nanoemulsion containing lapachol presented a reddish aspect but the incorporation of this naphthoquinone did not change the main physicochemical parameters resulting in a stable formulation. Therefore, submicron emulsions could be considered promising delivery systems applied to hydrophobic drugs of naturally occurring.

Literature:

1- Anton, N., Vandamme, T.F. The universality of low-energy nano-emulsification. *Int. J. Pharm.* 377 (2009) 142–147.

Acknowledgements: This study was supported by Grant BIC-1693-4.03/14 from the Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE), Brazil.

Supercritical CO₂ hops extract as active substance in cleansing compositions

E. Sikora*, J. Ogonowski, M. Zak, M. Kaptur
Institute of Organic Chemistry and Technology, Cracow University of Technology,
Krakow, Poland
*esikora@pk.edu.pl

Extracts of hop (*Humulus a magnifying ulus*), due to the reach content of active substances are increasingly used as cosmetic ingredients. Among other components, hops extracts contain: fraction of resins (*lupulone*, humulone, isohumulone), flavonoids (e.g. xanthohumol, isoxanthohumol, 8-prenylnaringenin), essential oil and tannins (derivatives of gallic acid, chlorogenic or protocatechinic acids). Thanks such the composition, the hops extracts showe antioxidant, antimicrobial, estrogenic and sedative properties. Moreover it influences the secretion of the sebaceous glands [1-4].

The aim of our work was an elaboration of cleansing compositions, containing as an antimicrobial and sebostatic active, hops extract obtained by supercritical CO₂ extraction (SC-CO₂ hops extract). Series of the products consisting of mild surfactants (lauryl polyglucoside, glutamate and glycinate) and different amount of the extract (0.1 up to 0.5%) were obtained. The physicochemical and user properties of the formulations were studied. The foam ability, foam durability index, surface tension, wettability, pH and reological properties were determined. Additionally, for the selected products, their effect on skin conditions were investigated, using AramoTS skin diagnosis system (Aram HUVIS Co.,Ltd).

The obtained result showed that the SC-CO₂ hops extract could be successfully used in cleansing formulations designed for the care of greasy and acne skin. The prepared products exhibited the high stability and, due to the hops extract addition, antibacterial, astringent and antioxidant properties.

Acknowledgement

The research (work) was supported by NCBiR, „The development of a new generation of environmentally friendly, safe in the use of cosmetics and household products involving plant extracts obtained under supercritical CO₂., contract no PBS1/A5/18/2012

References

- [1]. N. Yamaguchi, K. Satoh-Yamaguchi, O. Mitsunori: In vitro evaluation of antibacterial, anticollagenase, antioxidant activities of hop components (*Humulus lupulus*) addressing acne vulgaris, *Phytomed*, 16, 369-76, (2009)
- [2]. M. Van Cleemput, K. Cattoor, K. De Bosscher i wsp: Hop (*Humulus lupulus*) – derived bitter acids as multipotent bioactive compounds, *J Nat Prod*, 72,1220-30, (2009)
- [3]. C. Gerhäuser: Broad spectrum antiinfective potential of xanthohumol from hop (*Humulus lupulus* L.) in comparison with activities of other hop constituents and xanthohumol metabolites, *Mol Nutr Food Res*, 49,827-31, (2005)
- [4].S. Possemiers, S. Bolca, C. Grootaert i wsp: The prenylflavonoid isoxanthohumol from hops (*Humulus lupulus* L.) is activated into the potent phytoestrogen 8-prenylnaringenin in vitro and in the human intestine, *J Nutr* , 136,1862-1867, (2006)

Preparation and Colloid-Chemical Study of Titania-Modified Glass Membranes

A.V. Volkova,^a D.A. Vaganov,^a T.V. Antropova,^b L.E. Ermakova^a

^a *Institute of Chemistry Saint-Petersburg state university, Saint-Petersburg, Russia*

^b *Institute of Silicate Chemistry of Russian Academy of Sciences, Saint-Petersburg, Russia*

anna.volkova@chem.spbu.ru

The preparation of novel highly efficient and ecologically safe sorbents, selective membranes and photocatalysts for water purification from organic and inorganic pollutants, viruses, bacteria, etc. is in a focus of many researches during last years. The functional properties and effectivity of well-known materials using in membrane technologies can be improved by the fabrication on their base the composite membranes due to synergistic effect of support and active layers.

Porous glasses (PGs) can be successfully used as active supports possessing thermal, chemical and microbiological stability along with controllable structure parameters and adjustable adsorption and optical properties. Deposition of thin titanium oxide layers on internal and external surfaces of porous glass should enhance the sorption and photocatalytic properties of titania and selectivity of glass membrane.

Taking this into account we have prepared disk-shaped macroporous glass membranes on the base of initial two-phase sodium borosilicate (SBS) glasses by consequent acid and alkali leaching and used atomic layer deposition (ALD) (installation "Solar-MN") for membrane modification. Morphology, structural, equilibrium and transport properties of porous glasses before and after modification were studied in wide range of background solution concentrations and pH. Scanning electron microscopy did not show any notable changes in membrane morphology after ALD cycles proving the formation of smooth nano-scale layers. The titanium oxide deposition was confirmed by number of analytical methods and observed differences between the electro-surface properties of initial and titania-modified membranes.

This research used resources of the "Innovative technologies of composite nanomaterials", "Interdisciplinary Resource Center for Nanotechnology", "Center for Chemical Analysis and Material Research" and "Centre for Physical Methods of Surface Investigation" of SPbSU. This work was supported by the Russian Foundation for Basic Research, project No. 14-03-01062.

Variable Angle Spectroscopic Ellipsometry Study of PEDOT:PSS Thin Films in Contact with Air

G. Pathak^a, D. Čakara^{a,b}

^aCentre for Micro and Nano Sciences and Technologies, University of Rijeka, Rijeka, HR-51000 Croatia

^bDepartment of Biotechnology, University of Rijeka, Rijeka, HR-51000 Croatia

dcakara@uniri.hr

Variable angle spectroscopic ellipsometry (VASE) is a powerful technique for studying the dielectric properties of thin films as well as their thickness. We report a VASE study in the visible and NIR region for poly(3,4-ethylenedioxythiophene) : polystyrene sulfonate (PEDOT:PSS), a polyplex frequently used in production of soft electronic devices, spun onto silicon (100) in contact with air. The measured ellipsometric angles $[\psi, \Delta]$ for varied angle of incidence and wavelength, can be interpreted in terms of the stratified optical layers model, which involves the complex refractive index of the film $\tilde{n}(\lambda)$. The latter can be rationalized in terms of a dielectric function, which depends on the electrodynamic behavior of the charge carriers in the film. Thus VASE data of the studied PEDOT:PSS films of varied thicknesses, can be fitted by applying various models, whereby we compare the outcomes obtained by Tauc-Lorentz and Drude-Lorentz models.

Fine Emulsions Without Emulsifier.

Pickering Nanoemulsions Stabilized by Non-Aggregated Solid Nanoparticles

Laure Ridel ^{*}, Marie-Alexandrine Bolzinger, Hatem Fessi, Yves Chevalier

– University of Lyon 1, LAGEP, CNRS UMR 5007, 69622 Villeurbanne, France.

* - ridel@lagep.univ-lyon1.fr

Nanoemulsions can be defined as “ultrafine” emulsions. Their submicron droplet size provides them with better long-term stability. One possible drawback of nanoemulsions is the high demand for emulsifiers coming from the large interfacial area to be covered. Pickering (surfactant-free) emulsions are attractive because the classical emulsifier is replaced by solid particles. Nanoemulsions can be prepared either by means of high energy processes such as ultrasounds dispersion, or by mild methods involving solvent shifting methods. The later method called “spontaneous emulsification” is preferred.

This work was aimed at the formulation of Pickering nanoemulsions by spontaneous emulsification. Since the diameter of oil droplets is in the sub-micron range (~100 nm), the diameter of the particles which stabilize the oil-water interface should be significantly below 100 nm. Most Pickering emulsions investigated so far were stabilized by either solid microparticles, nanoparticles with diameter in the 100 nm range, or aggregates of small elementary particles.

The area is quite new and the three following questions are coming: Can such ultrafine nanoparticles stabilize Pickering emulsions? Do such ultrafine nanoparticles allow the fabrication of Pickering nanoemulsions? Can high and low energy methods allow the fabrication of such emulsions?

The present work considers a model o/w Pickering emulsion system. Non-aggregated bare silica nanoparticles of approximately 30 nm diameter from the Ludox™ series were used; and diisopropyl adipate was chosen as model oil that has already been shown to give stable Pickering emulsions stabilized by bare (hydrophilic) fumed silica (1). Non-aggregated solid nanoparticles of very small size (10 - 30 nm) are efficient stabilizers of o/w Pickering emulsions. Several experiments based on light scattering, optical microscopy, and transmission electron microscopy show the feasibility of Pickering nanoemulsions. Fig.1 shows that spontaneous emulsification allows the fabrication of Pickering nanoemulsions with diisopropyl adipate as oil and silica and also with other components than ones used in the model system.

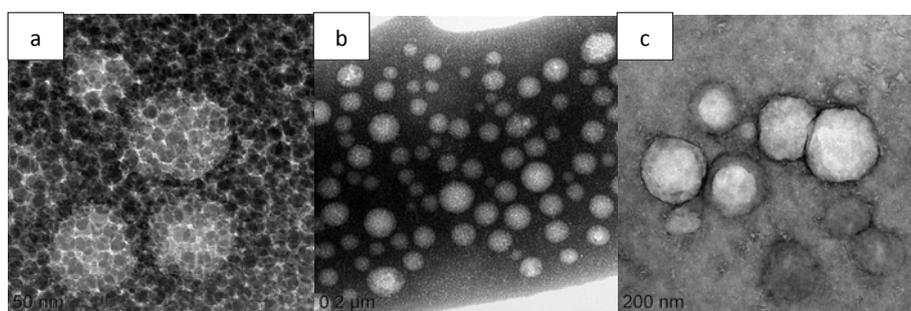


Fig. 1: O/w Pickering nanoemulsions of (a) diisopropyl adipate oil stabilized by Ludox™ AS40 (b) Castor oil stabilized by Ludox™ AS40 (c) Mineral oil stabilized by Laponite® XLG

1. Frelichowska J., Bolzinger M.-A., Chevalier Y. (2009). Pickering emulsions with bare silica, Colloids Surfaces A, 343, 70–74.

Multiple Emulsions controlled by stimuli-responsive polymers

L. Besnard,^{a,b,c} M. Protat,^{a,b,c} N. Bodin,^{a,b} F. Malloggi,^c J. Daillant,^d F. Cousin,^e
N. Pantoustier,^{a,b} P. Guenoun,^c P. Perrin,^{a,b}

^a *ESPCI, ParisTech, PSL Research University, Sciences et Ingénierie de la Matière Molle (SIMM), CNRS UMR 7615, 10 Rue Vauquelin, 75005, Paris, France*

^b *Sorbonne-Universités, UPMC Univ Paris 06, SIMM, 10 Rue Vauquelin, 75005, Paris, France*

^c *LIONS (DSM/IRAMIS/NIMBE) UMR3299 CEA-CNRS, Saclay, F91191 Gif sur Yvette, France*

^d *Synchrotron Soleil, L'Orme Les Merisiers, St Aubin-BP48, F-91192, Gif sur Yvette, France.*

^e *Lab Léon Brillouin LLB, UMR12, CEA-CNRS, CEA-Saclay, F-91191, Gif sur Yvette, France*

Patrick.perrin@espci.fr

Emulsions are currently used quite often in everyday life and their applications in numerous industrial domains need an adequate control of their stability and types [oil in water, O/W; water in oil, W/O; and multiple, Water in O/W (W/O/W) or Oil in W/O (O/W/O)]. Moreover, most applications like encapsulation/release of active species or enhanced oil recovery, to name but a few, require easy to use efficient stimuli (pH, ionic strength, temperature, light...) to either break emulsions or change their types.

We describe several water and oil emulsion systems (oil = toluene) stabilized by styrene (S)/(dimethyl aminoethyl methacrylate) (DMAEMA) based-diblock copolymers synthesized by Atom Transfer radical Polymerization (ATRP) with various structure, molar mass and composition (PS-*b*-PDMAEMA, PS-*b*-P(S-*st*-DMAEMA)). The copolymers are used to study the conditions under which the different types of emulsions (simple and multiple) are either stabilized or destabilized by changing pH, T or ionic strength as the polymers are indeed stimuable by pH, T or ionic strength^{(1),(2)}. To rationalize our results, the conformation of the different polymers at the oil/water interface was determined by SANS and neutron reflectivity at liquid/liquid interface. The distribution of the polymers between the aqueous and oil phases was measured by UV spectroscopy. Interfacial tensions were determined both by spinning and rising/pendant drop tensiometers.

Overall, our results show that the oil/water interfacial curvature (positive or negative as the copolymer chains extend preferentially towards water or oil respectively) give reliable predictions of emulsion types (O/W or W/O). In the region of near zero curvature, stable but stimuable multiple emulsions are observed. Quite interestingly and indeed original, the multiple emulsions are prepared using a unique polymer emulsifier and a one-step preparation method (a classical Ultra-Turrax type of mixing). We discuss their formation and argue that the oil/aqueous phases distribution of the polymer is a key parameter to predict the stability of the multiple emulsion. The encapsulation/release properties of species in the inner droplets of the multiple emulsions is hence versatile in our system as the oil/water phases polymer distribution can be controlled not only by polymer chemistry (molar mass, structure and composition of polymer chains) but also by a great number of stimuli such as pH, T and ionic strength.

We also demonstrate that the one-step making of stimuable multiple emulsions formulated with a single emulsifier can be extended to fully biocompatible systems (PDMS/PDMAEMA based copolymers and mygliol or isopropyl myristate as oils) using a similar approach.

(1) (2) : L. Besnard *et al.* *Adv. Mater.*25, 2844 (2013) ; *Soft Matter* 10, 7013 (2014)

Dispersing carbon nanotubes with ionic surfactants under controlled conditions: comparisons and molecular insight

Ricardo Fernandes,^{a,b} Matat Buzaglo,^c Oren Regev,^c István Furó,^c and Eduardo F. Marques^a

^a*Centro de Investigação em Química, Dept. Chem. and Biochem., University of Porto, Porto, Portugal.*

^b*Dept. Chem., Royal Institute of Technology, Stockholm, Sweden.*

^c*Dept. Chem. Eng. and Ilse Katz Institute for Nanotechnology, Ben-Gurion University of the Negev, Beer-Sheva, Israel.*

efmarque@fc.up.pt

The ability of surfactants to disperse carbon nanotubes (CNTs) in water has been widely explored, and yet the variety of processing conditions used seems to obscure a coherent vision. [1] Besides, the detailed molecular picture behind surfactant-CNT interactions still awaits consensus.[2,3] There is need for well controlled methodologies and reliable comparative metrics, which could not only lead to a more fundamental understanding of the mechanisms of dispersion, in connection with molecular simulations, but also provide rational optimization of the dispersability.[4] Here, our goal has been to determine and compare the dispersion ability of several ionic surfactants, differing in headgroup chemistry and chain length, towards both single and multi-walled carbon nanotube. For that, we used a stringently controlled sonication-centrifugation method for the preparation of the dispersions. The CNT concentration was accurately measured as a function of surfactant concentration (below and well above critical micelle concentration, *cmc*), using calibration curves obtained from thermogravimetric analysis and UV-vis absorption spectroscopy. The dispersion curves allowed us to determine quantitative parameters, such as critical surfactant concentration for dispersion, maximum dispersed CNT concentration, and respective surfactant concentration at that point, dispersion effectiveness and dispersion efficiency for each surfactant. The effects of nanotube morphology, surfactant aromatic rings, alkyl chain length, headgroup charge and *cmc* on the dispersability of CNTs are presented and rationalized.

[1] Kharissova, O. V.; Kharisov, B. I.; de Casas Ortiz, E. G. *RSC Adv.* **2013**, *3*, 24812.

[2] Blanch, A. J.; Lenehan, C. E.; Quinton, J. S. *Carbon* **2011**, *49*, 5213.

[3] Fernandes, R. M. F.; Buzaglo, M.; Shtein, M.; Pri Bar, I.; Regev, O.; Marques, E. F.; Furó, I. *J. Phys. Chem. C* **2014**, *118*, 582.

[4] Angelikopoulos, P.; Bock, H. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9546.

The Separative Recovery of Rare-Earth Metals such as Europium and Yttrium by Using Fatty Acids and/or Crown Ethers

Ho-Cheol Kang^{*}, Jong Mok Park, Dea Seon Sim
Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Korea
**hckang@kriict.re.kr*

ABSTRACT

KEYWORDS

There has been a great demand of rare earth metals such as europium, ytterium, etc. due to their native physical and chemical properties as the new constituents for electronic, optical and magnetic devices. The effective separation by solvent extraction of rare earth elements such as europium and yttrium has been investigated by using fatty acid with crown ether as an additive. Macrocyclic ligands as host-guest compounds form more stable complexes with metal ions which have the similar size of the cavity of crown ether. The synergistic separation effect of the two metals has been investigated in fatty acid solution with a crown ether such as 18-crown-6 ether, 15-crown-5 ether, and 12-crown-4 ether. Also the recovery of the elements has been carried out by using fatty acid with various alkyl chains. When 0.05 M hexanoic acid and 0.002M 15-crown-5 ether was used for the separation of the metals, the separation ratio is the highest value of 1.72, it is about twice of using only hexanoic acid. Moreover, the metal ion is solvated with three molecules of hexanoic acid monomer like MR_3 in the concentration.

Key words : fatty acids, crown ethers, solvent extraction, europium, yttrium, rare earth metals

Double emulsion for fragrance encapsulation

Margot Stasse,^{a-b} Valérie Héroguez,^{b*} Véronique Schmitt^{a+}

^a Centre of Research Paul Pascal, CNRS - University of Bordeaux
Avenue Dr Albert Schweitzer, PESSAC, FRANCE

^b Laboratoire de Chimie des Polymères Organique, UMR 5629, 16 avenue Pey Berland,
PESSAC, FRANCE

*heroguez@enscbp.fr

+schmitt@crpp-bordeaux.cnrs.fr

Oil-in-water-in-oil (O/W/O) double emulsions are dispersions of a direct emulsion in an oil continuous phase. These emulsions are interesting systems to encapsulate hydrophobic substances in the inner oil phase. Double emulsions enable a good protection of encapsulated agents against external environment, and a controlled release thereof. Despite their interest, they are still not widespread in industrial applications because of the difficulty to formulate stable systems. Indeed they require the presence of two antagonistic types of stabilizers: a more hydrophilic surfactant to stabilize the direct emulsion, and a more hydrophobic one to disperse the water droplets in the oil phase.

Herein, we propose to study both simple emulsions needed to elaborate the double emulsion. Each emulsion requires specific properties in order to lead to a kinetically stable double emulsion. For example, the reverse emulsion should be composed of large enough water globules in order to contain several fragrance droplets (of the direct emulsion). This latter, on the contrary should be of small sizes. Furthermore, the difference in sizes for the globules and droplets has to be significant enough for an efficient two-step emulsification process.

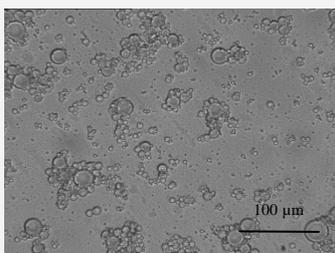


Fig. 1 : Microscopy observation of an inverse emulsion

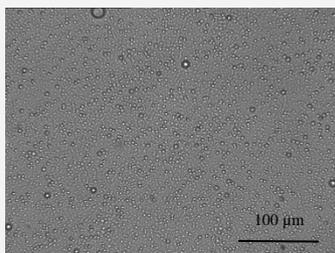


Fig.2: Microscopy observation of a direct emulsion

Photoresponsive self-assemblies based on fatty acids

Audrey Arnould^a, Cedric Gaillard^a, Marc Anton^a, Regine von Klitzing^b & Anne-Laure Fameau^a

^a INRA, Biopolymères Interactions Assemblages, Nantes, France

^b Stranski-Laboratorium für Physikalische und Theoretische Chemie, TU Berlin, Berlin, Germany

audrey.arnould@nantes.inra.fr

Stimuli-responsive surfactants self-assemble into various structures, which can be tuned by changes in environmental conditions or by an external stimulus¹. Light as stimulus displays many advantages to tune surfactant self-assemblies in solution, since it is a non-invasive trigger with micro-scale resolution¹. Fatty acids are a simple class of pH-responsive green surfactant. A pH change tunes the fatty acid ionization degree, the effective headgroup area and the self-assembly in water. To produce photoresponsive fatty acid self-assemblies we combined fatty acid self-assemblies with a photoacid generator that releases protons under UV². A multi-scale approach was used to study the effect of UV irradiation by combining infrared spectroscopy, small angle neutron scattering and microscopy experiments. Before UV illumination, fatty acids were ionized and formed spherical micelles. After UV illumination, the pH of the solution decreased. Ionized and protonated fatty acids coexisted. The change of fatty acid ionization state led to an increase of the packing parameter and self-assembly transition. By modifying the fatty acid chain length, transitions from spherical micelles to vesicles, lamellar phases or tubes were observed under UV light (Figure 1).

This simple approach to induce self-assemblies transitions by UV light is an asset for potential applications in which both stimuli-responsive systems and green molecules are needed.

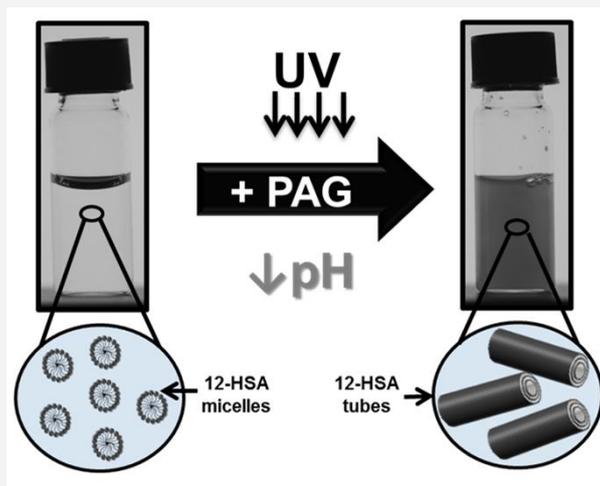


Figure 1: 12hydroxystearic acid (12HSA) self-assemblies transition with a photoacid generator (PAG) induced by UV.

- (1) Brown, P. *Soft Matter* **2013**, 9, 2365.
- (2) Fameau, A.-L. *Chem. Commun.* **2015**, 51, 2907.

The effect of dipropylene glycol on the hydrogel composed of a crude lecithin mixture and hexadecanol

Y. Nakagawa ^a, H. Nakazawa ^b, S. Kato ^b

^aKracie Home Products, Ltd., Yokohama-city, Kanagawa, Japan

^bKwansei Gakuin University, Sanda-city, Hyogo, Japan

y.nakagawa@khp.kracie.co.jp

Polyol is widely used as a moisturizing ingredient in the cosmetic industry because it usually has a good moisturizing effect derived from the multiple hydroxyl groups. Among them, dipropylene glycol (DPG) is commonly contained in skin care products because it has not only moisturizing effect but also dry touch. We investigated the effect of DPG on the structures and physicochemical properties of the hydrogel we had found previously in the lipid system composed of a crude lecithin mixture (PC70) and hexadecanol (HD) [1] by freeze-fracture electron microscopy, optical microscopy, differential scanning calorimetry and synchrotron X-ray diffraction. We found that a great increase of DPG-to-water ratio in the PC70/HD bilayer system caused disintegration of the hydrogel, a decrease in the chain-melting phase transition temperature and ordered stacking of the PC70/HD bilayers. Structural analyses suggested that the disintegration of the hydrogel was closely coupled with the formation of multi-lamellar structures. In the absence of DPG, the hydrogel is formed as a result of the homogeneous distribution of sheet-like bilayers throughout the solution because the bilayer has a surface charge derived from the charged lipids in the PC70 as described in the previous study [1]. The addition of DPG, which has lower dielectricity than water, may modify the electric double layer repulsion between the bilayers so as to give a secondary minimum in the interbilayer interaction energy as a function of interbilayer distance and subsequently reduce the energy barrier to form the multi-lamellar aggregates, keeping their sheet-like morphology. The formation of the multi-lamellar aggregates with a shorter interbilayer distance causes the phase separation of the solvent (water/DPG) phase, leading to the disintegration of the homogeneous hydrogel.

[1] Y. Nakagawa, H. Nakazawa, S. Kato, *J. Colloid Interface Sci.*, 376 (2012) 146-151

Glucose-Responsive Hybrid Nanoassemblies in Aqueous Solutions: Ordered Phenylboronic Acid within Intermixed Poly-(4-hydroxystyrene)-*block*-Poly(Ethylene oxide) Block Copolymer

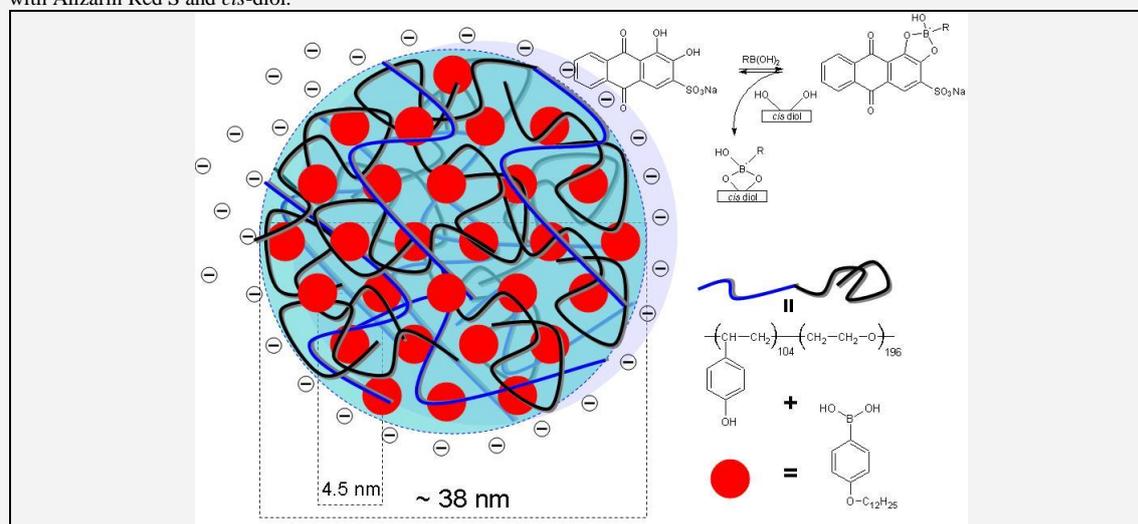
M. Uchman

Department of Physical and Macromolecular Chemistry Faculty of Science, Charles University
in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic.

uchman@natur.cuni.cz

Co-assembly behavior of the double hydrophilic block copolymer poly-(4-hydroxystyrene)-*block*-poly(ethylene oxide) (PHOS-PEO) with three amphiphilic phenylboronic acids (PBA) differing in hydrophobicity, *p*-dodecyloxyphenylboronic acid (C12), *p*-octyloxyphenylboronic acid (C8) and *p*-isobutoxyphenylboronic acid (*i*Bu) was studied in alkaline aqueous solutions and in mixtures of NaOH_{aq}/THF by ¹H NMR spectroscopy, static, dynamic and electrophoretic light scattering and SAXS. The study reveals that only the coassembly of C12 with PHOS-PEO provides spherical nanoparticles with intermixed PHOS and PEO blocks, containing densely packed C12 micelles. NMR measurements have shown that spatial proximity of PHOS-PEO and C12 leads to the formation of ester bonds between –OH of PHOS block and hydroxyl groups of –B(OH)₂. Due to the PBA moieties, the release of compounds with 1,2- or 1,3-dihydroxy groups loaded in the coassembled PHOS-PEO/PBA nanoparticles by covalent binding to PBA can be triggered by addition of a surplus of glucose that bind to PBA competitively. The latter feature has been confirmed by fluorescence measurements using Alizarin Red as a model compound.

Drawing of the Coassembled Structure in Solution of PHOS-PEO/C12 as seen by SAXS and Competitive Binding of Boronic Acid with Alizarin Red S and *cis*-diol.



The authors would like to acknowledge the financial support of the Grant Agency of the Czech Republic P205/14-14608S

Rheological properties of wormlike micellar gels formed by novel bio-based isosorbide surfactants

Miho Kamada^{1, 2*}, Christel Pierlot³, Jean-Marie Aubry³ and Kenji Aramaki²

¹ Beauty Care Laboratory, Kracie Home Products, Ltd., Yokohama, Japan

² Graduate School of Environment and Information Sciences, Yokohama National University, Japan

³ Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Equipe CISCO, Université Lille1, Villeneuve d'Ascq, Cedex, France
m.kamada@khp.kracie.co.jp

Isosorbide surfactants having an isosorbide group as a building block is one of bio-based surfactants. There are some reports on significant aqueous phase behavior^[1], foaming properties, Krafft temperatures and critical micellar concentrations^[2]. In this presentation, we report a wormlike micelle formation with a mixture of sodium dodecyl isosorbide (SDSS) and 2-*O*- or 5-*O*-dodecylisosorbide (EXO or ENDO, respectively).

Fig.1 shows viscosity behavior of the 3wt% NaCl aq./SDSS system with EXO or ENDO at constant surfactant concentration (5wt%). A maximum of viscosity was given at the same surfactant mixing composition (X) for both systems but the maximum viscosity is higher in the ENDO system. In addition, X giving high viscosity is wider composition range in the ENDO system. This interesting result was caused by isomeric molecule structure of the cosurfactant. We have also studied dynamic rheological behavior. Oscillatory-shear (frequency sweep) measurements were performed on the viscoelastic samples formed around the viscosity maximum composition. Liquid-like behavior ($G' < G''$) was observed at low frequency region whereas solid-like behavior ($G' > G''$) was observed at high frequency region. Maxwell-type oscillatory rheological behavior of viscous micellar solutions can be related to the transient network formed by the entanglement of wormlike micelles. Maxwell equations were also fitted to the data, indicating wormlike micelle formation.

[1] A. Lavergne, et al., *Colloids Surf.*, A, 404 (2012) 56.

[2] A. Lavergne, et al., *J. Colloid Interface Sci.*, 360 (2011) 645.

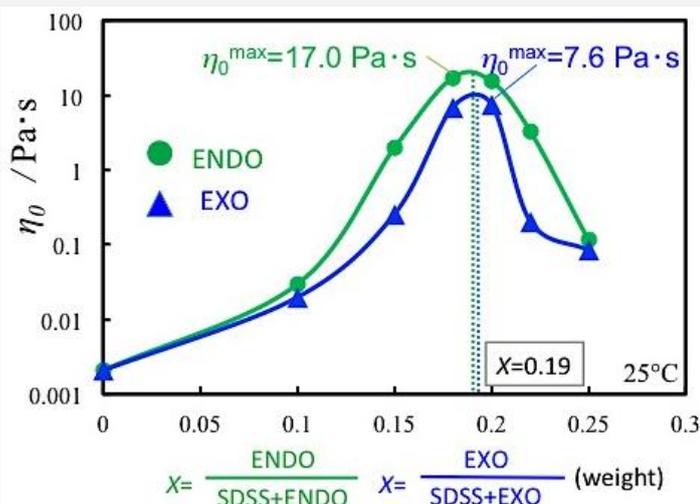


Fig.1 Zero-shear viscosity η_0 plot against surfactant mixing fraction.

Formation, Stability and Time Development of Polyelectrolyte Assemblies

B. Plazzotta^a, J. S. Diget^b, KaiZheng Shu^b, B. Nystrom^b and J. S. Pedersen^a

^aAarhus University, Department of Chemistry and iNano Center, Gustav Wieds Vej 14, 8000 Aarhus, Denmark

^bOslo University, Department of Chemistry, Sem Sælands Vei 26, 0371 Oslo, Norway
beapla@chem.au.dk

Owing to the advances in organic synthesis, the availability of well-defined synthetic charged polymers has increased widely in the past years, allowing more systematic studies on the interactions between charged species in solution; most of the work so far has been focused on interactions between polyions and small oppositely charged molecules or between oppositely charged homopolymers. Here we studied the case of anionic block copolymers constituted of a hydrophilic chain covalently linked to a polyelectrolyte chain interacting with short chain homocations. The chosen blocks were poly(*N*-isopropylacrylamide) for the hydrophobic part, Poly(styrene sulfonate) as polyanionic block. The samples were mixed as diluted aqueous solutions and characterized mainly by Small-Angle X-Ray Scattering (SAXS) and Photon Cross Correlation Spectroscopy (PCCS).

Most of the samples have a limpid appearance and the assemblies were found to be nano-sized globular micellar-like structures, with a core formed by the charge-neutralized polyelectrolytes and an outer shell formed by the hydrophilic component of the block copolymers. It was possible to relate the SAXS data of those assemblies to that of the pure polyelectrolyte and to obtain a reliable value of aggregation number (found to be between 50 and 100) from the scattered intensity.

Samples containing block copolymers with a long hydrophobic tail show a time development from a turbid to a limpid solution containing globular micelles. This evolution was followed by SAXS and PCCS. Presence of added salt was seen to influence strongly the kinetic and phase state of the systems. Adding low amount of electrolytes increases the stability of the assemblies in solution and speeds the aggregation; however, increasing salt concentration a critical point is reached where the polyelectrolytes form a separate solid phase.

Microemulsion Properties and Phase Behavior of (Dimeric Ammonium Surfactant – Heavy Crude Oil – Connate Water) System

Ronald Nguele^a, Kyuro Sasaki^a, Hikmat Said-Al Salim^b, Yuichi Sugai^a and Masanori Nakano^c

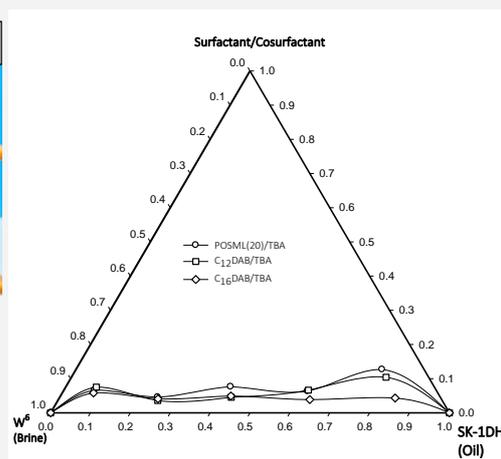
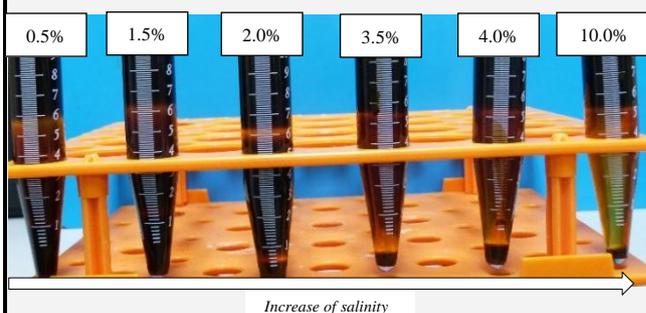
^aKyushu University, Fukuoka-city, Japan

^bUCSI University, Kuala Lumpur, Malaysia

^cResearch Center, Japan Petroleum Exploration Co. LTD, Tokyo, Japan

nguele.odou.548@s.kyushu-u.ac.jp

Recovery methods of untapped crude oils require injection of foreign material in the reservoir which subsequently induces the displacement of oil. In chemical enhanced oil recovery, the microscopic sweep efficiency depends on achievement of a low interfacial tension ($IFT \leq 10^{-3}$ mN/m). The present work discusses about the phase behavior and the properties of microemulsion generated by contacting a dimeric ammonium surfactant, heavy dead crude oil at various salinities. Two gemini ammonium surfactants were considered and their potentials as micellar solutions were gauged with a conventional non-ionic surfactant. The oleic phase consisted of dead heavy crudes. An ultra-low IFT, 5% lesser than a conventional surfactant, was achieved even at low concentrations of active surfactant. Salinity tolerance was significantly influenced by the increase in carbon number of the hydrophobic chain. A submicellar aggregation along with a possible self-coiling of dimeric surfactants was observed when secondary alcohols and diols were used as cosolvent. Interestingly, spectral analyses highlighted an inhibiting acidity activity for gemini surfactants.



A. Bera, K. Ojha, A. Mandal, and T. Kumar, "Interfacial tension and phase behavior of surfactant-brine-oil system," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 383, no. 1–3, pp. 114–119, 2011.

Effect of cholesterol on zeta potential of positively-charged liposomes with lecithin and alkyl quaternary ammonium salts.

Y.Watanabe¹, K.Aramaki¹, Y.Konno², A.Ogata²

¹Graduate School of Environment and Information Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

²Research and Development Division, KOSÉ Corporation, Japan

watanabe-yuki-vy@ynu.jp

Liposomes are widely used as drug delivery carriers and also for some functional cosmetics due to biocompatibility and encapsulation ability of active molecules. As liposomes are applied for transdermal drug delivery systems, positively-charged liposomes are known to improve delivery efficiency compared to negatively-charged lecithin liposomes since skin surface is negatively charged. [1] Cholesterol is often mixed to liposomes for stabilization of liposome membrane. We report effect of cholesterol mixing on zeta potential behavior of positively-charged liposomes prepared with soybean lecithin and dimethyldistearylammonium chloride ($2C_{18}DAC$).

Figure 1 shows the effect of cholesterol on zeta potential behavior. X indicates the mole fraction of cholesterol in liposomes. Zeta potential of soybean lecithin liposome ($X=0$) was about $-40mV$. It dramatically increased by substituting small fraction of lecithin with cationic surfactants and, then, degree of increment was gradually reduced at higher cationic surfactant fraction. Finally zeta potential reached to a maximum value, about $40mV$. Upon increasing X up to 0.3, the maximum zeta potential value was gradually increased. However, zeta potential curve was dramatically shifted at $X=0.4$. DSC and X-ray scattering measurements revealed the transition from α -type crystalline state in bilayer membranes to the intermediate gel phase or the liquid-ordered phase [2] at $X=0.4$. This phase transition in the bilayer membrane could induce the dramatic change in zeta potential behavior at $X=0.4$.

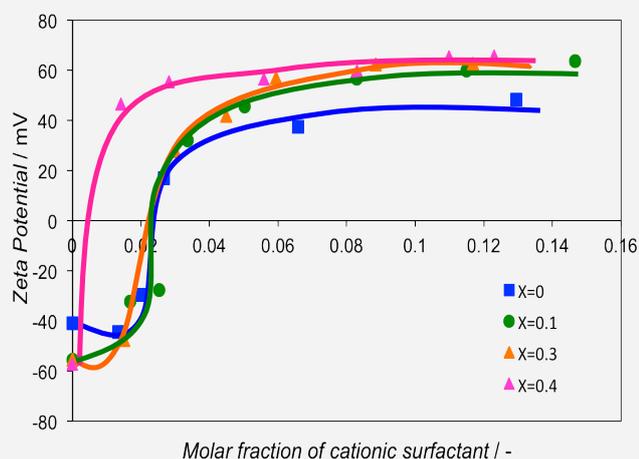


Figure 1 Zeta potential values of the liposomes at 25°C are plotted.

[1] Kitagawa, S., Kasamaki, M., *Chem. Pharm. Bull.*, **2006**, 54, 242-244

[2] Ipsen, J. H., G. Karlstrom, O. G. Mouritsen, H. Wennerstrom, and M. J. Zuckermann, *Biochim. Biophys. Acta.*, **1987**, 905, 162-172.

Revealing the Formation and Stability of PDADMAC Monolayers on Mica via Electrokinetic and Colloid Enhancement Techniques

A. Michna, Z. Adamczyk, P. Batys

Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Cracow, Poland

ncmichna@cyf-kr.edu.pl

The formation and the stability of cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) monolayers were established *in situ* by the streaming potential and colloid deposition measurements.

Firstly, the PDADMAC adsorption and desorption on mica were studied using the streaming potential measurements. The obtained results were quantitatively interpreted in terms of the electrokinetic model postulating a 3D adsorption of molecules as discrete particles. The calibration dependencies allowed one to evaluate the PDADMAC desorption kinetics. It was found that the desorption of the polyelectrolyte at the ionic strength range 0.001–0.15 M was minor over the time of 20 h. Furthermore, the desorption constants, the equilibrium adsorption constants and the binding energies of PDADMAC were determined. It was concluded that the calculated energies agree with the proposed model of discrete electrostatic interactions among ion pairs.

The structure of PDADMAC monolayer and PDADMAC chain orientation were determined by the colloid deposition method. The negative latex microspheres were used as the polyelectrolyte chain markers. The dependence of maximum coverage of microspheres as a function of PDADMAC coverage was determined for ionic strength in the range 0.01 – 0.15 M. It was found that one colloid particle is irreversibly immobilized by one single PDADMAC chain in 0.15 M and for the PDADMAC coverage below 0.1%. For ionic strength below 0.15 M, irreversible adsorption of latex microspheres can occur only at the adsorption sites formed by a few closely adsorbed PDADMAC molecules. The obtained experimental results were quantitatively interpreted in terms of the random sequential adsorption model.

The obtained results confirmed the side-on adsorption mechanisms of PDADMAC for the above ionic strength range.

Acknowledgements: This work was supported financially by the NCN Grant UMO-2012/07/B/ST4/00559.

Phase Behavior of a Diglycerol-based Surfactant: Formation of Stable Nanostructured Dispersions Mediated by a Polymeric Stabilizer.

J.R. Magana, C.Solans

Instituto de Química Avanzada de Cataluña, Consejo Superior de Investigaciones Científicas (IQAC-CSIC) and Biomedical Research Networking Center in Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Jordi Girona, 18-26, 08034 Barcelona, Spain

jmrnqb@cid.csic.es

Glycerol-based nonionic surfactants are focusing considerable attention in the food, cosmetic and pharmaceutical industries due their biocompatibility and biodegradability compared with other conventional nonionic surfactants. Their amphiphilic character allows self-aggregation in water, forming a wide range of structures. However, commercial glycerol based surfactants usually contain a large portion of unreacted polyglycerols that could influence the phase behavior. In addition, glycerol has four hydroxyl groups and most industrial synthetic strategies lead to a complicated mixture of polyglycerol surfactants. There have been few studies of the phase behaviour of these commercial surfactants despite of their importance in industry.

In this context the phase behavior of a commercially available diglycerol-monoisostearate surfactant, abbreviated as C41V, was studied. C41V is a complex mixture of C14, C16 and C18 hydrocarbonated chains. One attractive feature of this surfactant is that all the raw materials used for the synthesis are from natural resources, making this an ideal surfactant for "eco-friendly" and biocompatible applications. C41V forms an inverse hexagonal liquid crystalline phase (H_{II}) coexisting with water from low surfactant concentrations up to 96 wt%. Dispersions of H_{II} were formed at high water content stabilized by a block copolymer. The particle size, polydispersity and stability were assessed by dynamic light scattering and backscattering light techniques. As the concentration of stabilizer polymer is increased the size of the particles decreases and the stability is enhanced. SAXS results suggest a strong adsorption of the stabilizer at the water/hexosome interface. The release of an incorporated model drug in the liquid crystalline dispersion was studied as a function of pH; it was found a higher release of the model drug at high pH values making these ideal candidates for oral administration protecting drugs from the acidic conditions of the stomach and delivering at the intestine.

Phosphonic acids / titania hybrids. Study of the functionalization parameters and in deep characterizations.

L. Baldaccioni^a, G. Soliveri^a, D. Meroni^a, G. Panzarasa^b, G. Cappelletti^a,
R. Annunziata^a, S. Ardizzone^a

^aDipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

^bDipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale
"Amedeo Avogadro", Alessandria, Italy

guido.soliveri@unimi.it

The growing excitement in molecular self-assembly at oxide surfaces, in fields ranging from corrosion to microelectronic, urges a better understanding of the mechanism of formation and organization of such surfactants at the interface. Notwithstanding the titanium dioxide surfaces are ubiquitous in literature, thanks principally to their biocompatibility and semiconductor behavior, only few papers have deepened the interactions between adsorbed molecules and the TiO₂[1]. Especially, phosphonic acids, thanks to their facility to graft at the oxides, are emerging in many different areas of material and surface science, *e.g.* field effect transistors, nanoparticle protection, etc. As recently well discussed by Peukert *et al.*[2], the deep investigation of defects, order and organization of such layers can be critical for the final application.

Here, we go in deep in the grafting of titania by phosphonic acids. Especially, we examined two molecules with different functionalities: a linear alkyl chain, octylphosphonic acid, and an aromatic one, phenylphosphonic acid. The functionalization was performed by a wet procedure both on smooth titania films and on nanoparticles, both synthesized *ad hoc* in our lab. Films are composed by pure phase anatase, while in the case of powders both anatase and mixed phase (anatase/brookite) polymorphs are used. The substrates were previously deeply characterized by AFM, XRD and BET. The functionalized substrates were investigated by the relevant combination of surface free energy measurements, solid state NMR and FTIR analysis. Eventually, we proved the formation of a lotus leaf-like superhydrophobic coating, simply by spin-coating the functionalized nano-powders from an alcoholic suspension.

[1] G. Soliveri *et al.*, *J.Phys.Chem.C*, **2012**, *116*, 26405;

[2] C. Meltzer *et al.*, *J.Am.Chem.Soc.* **2014**, *136*, 10718.

Fatty acid droplets and vesicles as a route to compartmentalization.

Garenne. D.¹, Houinsou Housou. B.², Fameau A-L.², Navailles. L.³, Nallet. F.³, Zhendre. V.⁴, Grélard. A.⁴, Gaillard. C.², Dufourc. E.⁴ and Douliez. J-P.^{1*}

1 UMR 1332, biologie et pathologie du fruit, INRA, centre de Bordeaux, 33883 Villenave d'Ornon, France. 2 UR 1268 Biopolymères Interactions et Assemblages, INRA, rue de la Géraudière, 44316 Nantes, France. 3 Centre de recherche Paul Pascal, CNRS, av. A. Schweitzer, 33600 Pessac, France. 4 Institute of Chemistry and Biology of Membranes and Nano-objects, UMR 5248, CNRS, Univ. Bordeaux, Institut Polytechnique Bordeaux, 33600 Pessac, France.

Corresponding Authors

David GARENNE, email : David.garenne@bordeaux.inra.fr

Jean-Paul DOULIEZ, email : Jean-Paul.Douliez@bordeaux.inra.fr

Compartmentalization is of importance for our understanding of the emergence of life on earth but also for the development and design of minimal cells and bioreactors. Here, we introduce a model built from saturated long chain fatty acids and guanidium. This system, characterised by NMR and small angle neutron scattering, can form both membranous vesicles and membrane-free coacervate-like droplets that results from clouding. Droplets can transit toward vesicles by varying the pH (reversible) and upon addition of alkanol (irreversible). We have first shown using organic colored dyes that droplet can sequester solutes depending on their charge and lipophilicity. We also demonstrated (i) that Yellow Fluorescent Protein (YFP) is sequestered specifically within droplets and (ii) that this protein is further recovered within vesicles after transition occurs from droplets. So, these experiments allowed to encapsulate biomolecules from an « open » membrane-free system (droplets), to a « close » membranous system (vesicles). These systems should be of interest in fields of synthetic biology to encapsulate biological material for design of bioreactors, and to build by a bottom-up approach minimal cells.

Development, Characterization, and Stability Evaluation of Submicron Emulsions for Incorporation of Hydrophobic Naphthoquinones

L.S. Diniz,^a R.M.G. Sousa,^a F.V.S. Rodrigues,^a P.L. Goto,^b T.M. Gonçalves,^a C.R.M. Araújo,^a L.A. Rolim,^a A.C. Tedesco,^b M.P. Siqueira-Moura^{a*}

^a*Colegiado Acadêmico de Ciências Farmacêuticas, Universidade Federal do Vale do São Francisco (UNIVASF), Petrolina-PE, Brazil*

^b*Departamento de Química, Laboratório de Nanotecnologia e Engenharia Tecidual, FFCLRP, Universidade de São Paulo (USP), Ribeirão Preto-SP, Brazil*

*marigilson.moura@univasf.edu.br

Natural naphthoquinones, such as lapachol and β -lapachone, have demonstrated promising biological activities. However, these quinones present low systemic biodisponibility due to its poor aqueous solubility. Nanoemulsions (submicrometer-size droplets) formed by oily core are able to incorporate hydrophobic molecules thus enabling them to be dispersed into an aqueous phase in which they are normally insoluble. Submicron emulsions can be prepared by low-energy methods which present advantages such as prevent the potential degradation of fragile encapsulated molecules and potential industrial scale-up [1]. The present work reports the development, characterization, and physical stability of nanoemulsion containing lapachol. The physicochemical parameters analyzed and stability profile were dependent on pair of surfactants and oil type present in each formulation. The formulation chosen to incorporate naphthoquinone showed droplet size in nanometric scale with homogeneous size distribution (PDI <0.2), negative zeta potential (about -30 mV), and lapachol loading about 90%. Besides that, good physical stability of the formulation was demonstrated by analytical centrifugation with photometric detection. Nanoemulsion containing lapachol presented a reddish aspect but the incorporation of this naphthoquinone did not change the main physicochemical parameters resulting in a stable formulation. Therefore, submicron emulsions could be considered promising delivery systems applied to hydrophobic drugs of naturally occurring.

Literature:

1- Anton, N., Vandamme, T.F. The universality of low-energy nano-emulsification. *Int. J. Pharm.* 377 (2009) 142–147.

Acknowledgements: This study was supported by Grant BIC-1693-4.03/14 from the Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE), Brazil.

Supercritical CO₂ hops extract as active substance in cleansing compositions

E. Sikora*, J. Ogonowski, M. Zak, M. Kaptur
*Institute of Organic Chemistry and Technology, Cracow University of Technology,
Krakow, Poland*
*esikora@pk.edu.pl

Extracts of hop (*Humulus a magnifying ulus*), due to the reach content of active substances are increasingly used as cosmetic ingredients. Among other components, hops extracts contain: fraction of resins (*lupulone*, humulone, isohumulone), flavonoids (e.g. xanthohumol, isoxanthohumol, 8-prenylnaringenin), essential oil and tannins (derivatives of gallic acid, chlorogenic or protocatechinic acids). Thanks such the composition, the hops extracts showe antioxidant, antimicrobial, estrogenic and sedative properties. Moreover it influences the secretion of the sebaceous glands [1-4].

The aim of our work was an elaboration of cleansing compositions, containing as an antimicrobial and sebostatic active, hops extract obtained by supercritical CO₂ extraction (SC-CO₂ hops extract). Series of the products consisting of mild surfactants (lauryl polyglucoside, glutamate and glycinate) and different amount of the extract (0.1 up to 0.5%) were obtained. The physicochemical and user properties of the formulations were studied. The foam ability, foam durability index, surface tension, wettability, pH and reological properties were determined. Additionally, for the selected products, their effect on skin conditions were investigated, using AramoTS skin diagnosis system (Aram HUVIS Co.,Ltd).

The obtained result showed that the SC-CO₂ hops extract could be successfully used in cleansing formulations designed for the care of greasy and acne skin. The prepared products exhibited the high stability and, due to the hops extract addition, antibacterial, astringent and antioxidant properties.

Acknowledgement

The research (work) was supported by NCBiR, „The development of a new generation of environmentally friendly, safe in the use of cosmetics and household products involving plant extracts obtained under supercritical CO₂., contract no PBS1/A5/18/2012

References

- [1]. N. Yamaguchi, K. Satoh-Yamaguchi, O. Mitsunori: In vitro evaluation of antibacterial, anticollagenase, antioxidant activities of hop components (*Humulus lupulus*) addressing acne vulgaris, *Phytomed*, 16, 369-76, (2009)
- [2]. M. Van Cleemput, K. Cattoor, K. De Bosscher i wsp: Hop (*Humulus lupulus*) – derived bitter acids as multipotent bioactive compounds, *J Nat Prod*, 72,1220-30, (2009)
- [3]. C. Gerhäuser: Broad spectrum antiinfective potential of xanthohumol from hop (*Humulus lupulus* L.) in comparison with activities of other hop constituents and xanthohumol metabolites, *Mol Nutr Food Res*, 49,827-31, (2005)
- [4].S. Possemiers, S. Bolca, C. Grootaert i wsp: The prenylflavonoid isoxanthohumol from hops (*Humulus lupulus* L.) is activated into the potent phytoestrogen 8-prenylnaringenin in vitro and in the human intestine, *J Nutr* , 136,1862-1867, (2006)

Preparation and Colloid-Chemical Study of Titania-Modified Glass Membranes

A.V. Volkova,^a D.A. Vaganov,^a T.V. Antropova,^b L.E. Ermakova^a

^a *Institute of Chemistry Saint-Petersburg state university, Saint-Petersburg, Russia*

^b *Institute of Silicate Chemistry of Russian Academy of Sciences, Saint-Petersburg, Russia*

anna.volkova@chem.spbu.ru

The preparation of novel highly efficient and ecologically safe sorbents, selective membranes and photocatalysts for water purification from organic and inorganic pollutants, viruses, bacteria, etc. is in a focus of many researches during last years. The functional properties and effectivity of well-known materials using in membrane technologies can be improved by the fabrication on their base the composite membranes due to synergistic effect of support and active layers.

Porous glasses (PGs) can be successfully used as active supports possessing thermal, chemical and microbiological stability along with controllable structure parameters and adjustable adsorption and optical properties. Deposition of thin titanium oxide layers on internal and external surfaces of porous glass should enhance the sorption and photocatalytic properties of titania and selectivity of glass membrane.

Taking this into account we have prepared disk-shaped macroporous glass membranes on the base of initial two-phase sodium borosilicate (SBS) glasses by consequent acid and alkali leaching and used atomic layer deposition (ALD) (installation "Solar-MN") for membrane modification. Morphology, structural, equilibrium and transport properties of porous glasses before and after modification were studied in wide range of background solution concentrations and pH. Scanning electron microscopy did not show any notable changes in membrane morphology after ALD cycles proving the formation of smooth nano-scale layers. The titanium oxide deposition was confirmed by number of analytical methods and observed differences between the electro-surface properties of initial and titania-modified membranes.

This research used resources of the "Innovative technologies of composite nanomaterials", "Interdisciplinary Resource Center for Nanotechnology", "Center for Chemical Analysis and Material Research" and "Centre for Physical Methods of Surface Investigation" of SPbSU. This work was supported by the Russian Foundation for Basic Research, project No. 14-03-01062.

Variable Angle Spectroscopic Ellipsometry Study of PEDOT:PSS Thin Films in Contact with Air

G. Pathak^a, D. Čakara^{a,b}

^aCentre for Micro and Nano Sciences and Technologies, University of Rijeka, Rijeka, HR-51000 Croatia

^bDepartment of Biotechnology, University of Rijeka, Rijeka, HR-51000 Croatia

dcakara@uniri.hr

Variable angle spectroscopic ellipsometry (VASE) is a powerful technique for studying the dielectric properties of thin films as well as their thickness. We report a VASE study in the visible and NIR region for poly(3,4-ethylenedioxythiophene) : polystyrene sulfonate (PEDOT:PSS), a polyplex frequently used in production of soft electronic devices, spun onto silicon (100) in contact with air. The measured ellipsometric angles $[\psi, \Delta]$ for varied angle of incidence and wavelength, can be interpreted in terms of the stratified optical layers model, which involves the complex refractive index of the film $\tilde{n}(\lambda)$. The latter can be rationalized in terms of a dielectric function, which depends on the electrodynamic behavior of the charge carriers in the film. Thus VASE data of the studied PEDOT:PSS films of varied thicknesses, can be fitted by applying various models, whereby we compare the outcomes obtained by Tauc-Lorentz and Drude-Lorentz models.

Fine Emulsions Without Emulsifier.

Pickering Nanoemulsions Stabilized by Non-Aggregated Solid Nanoparticles

Laure Ridel ^{*}, Marie-Alexandrine Bolzinger, Hatem Fessi, Yves Chevalier

– University of Lyon 1, LAGEP, CNRS UMR 5007, 69622 Villeurbanne, France.

* - ridel@lagep.univ-lyon1.fr

Nanoemulsions can be defined as “ultrafine” emulsions. Their submicron droplet size provides them with better long-term stability. One possible drawback of nanoemulsions is the high demand for emulsifiers coming from the large interfacial area to be covered. Pickering (surfactant-free) emulsions are attractive because the classical emulsifier is replaced by solid particles. Nanoemulsions can be prepared either by means of high energy processes such as ultrasounds dispersion, or by mild methods involving solvent shifting methods. The later method called “spontaneous emulsification” is preferred.

This work was aimed at the formulation of Pickering nanoemulsions by spontaneous emulsification. Since the diameter of oil droplets is in the sub-micron range (~100 nm), the diameter of the particles which stabilize the oil-water interface should be significantly below 100 nm. Most Pickering emulsions investigated so far were stabilized by either solid microparticles, nanoparticles with diameter in the 100 nm range, or aggregates of small elementary particles.

The area is quite new and the three following questions are coming: Can such ultrafine nanoparticles stabilize Pickering emulsions? Do such ultrafine nanoparticles allow the fabrication of Pickering nanoemulsions? Can high and low energy methods allow the fabrication of such emulsions?

The present work considers a model o/w Pickering emulsion system. Non-aggregated bare silica nanoparticles of approximately 30 nm diameter from the Ludox™ series were used; and diisopropyl adipate was chosen as model oil that has already been shown to give stable Pickering emulsions stabilized by bare (hydrophilic) fumed silica (1). Non-aggregated solid nanoparticles of very small size (10 - 30 nm) are efficient stabilizers of o/w Pickering emulsions. Several experiments based on light scattering, optical microscopy, and transmission electron microscopy show the feasibility of Pickering nanoemulsions. Fig.1 shows that spontaneous emulsification allows the fabrication of Pickering nanoemulsions with diisopropyl adipate as oil and silica and also with other components than ones used in the model system.

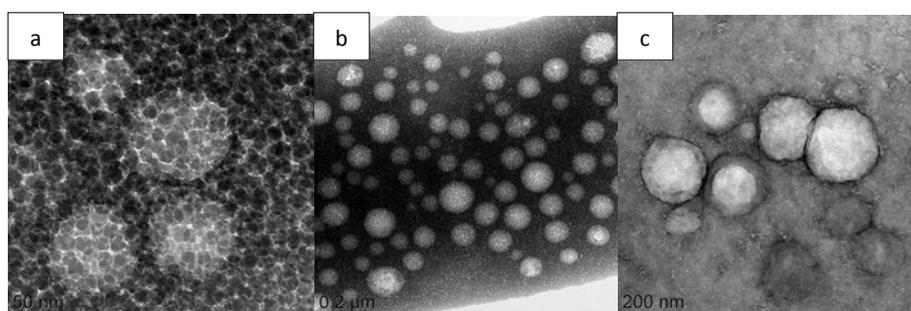


Fig. 1: O/w Pickering nanoemulsions of (a) diisopropyl adipate oil stabilized by Ludox™ AS40 (b) Castor oil stabilized by Ludox™ AS40 (c) Mineral oil stabilized by Laponite®XLG

1. Frelichowska J., Bolzinger M.-A., Chevalier Y. (2009). Pickering emulsions with bare silica, Colloids Surfaces A, 343, 70–74.

Multiple Emulsions controlled by stimuli-responsive polymers

L. Besnard,^{a,b,c} M. Protat,^{a,b,c} N. Bodin,^{a,b} F. Malloggi,^c J. Daillant,^d F. Cousin,^e
N. Pantoustier,^{a,b} P. Guenoun,^c P. Perrin,^{a,b}

^a *ESPCI, ParisTech, PSL Research University, Sciences et Ingénierie de la Matière Molle (SIMM), CNRS UMR 7615, 10 Rue Vauquelin, 75005, Paris, France*

^b *Sorbonne-Universités, UPMC Univ Paris 06, SIMM, 10 Rue Vauquelin, 75005, Paris, France*

^c *LIONS (DSM/IRAMIS/NIMBE) UMR3299 CEA-CNRS, Saclay, F91191 Gif sur Yvette, France*

^d *Synchrotron Soleil, L'Orme Les Merisiers, St Aubin-BP48, F-91192, Gif sur Yvette, France.*

^e *Lab Léon Brillouin LLB, UMR12, CEA-CNRS, CEA-Saclay, F-91191, Gif sur Yvette, France*

Patrick.perrin@espci.fr

Emulsions are currently used quite often in everyday life and their applications in numerous industrial domains need an adequate control of their stability and types [oil in water, O/W; water in oil, W/O; and multiple, Water in O/W (W/O/W) or Oil in W/O (O/W/O)]. Moreover, most applications like encapsulation/release of active species or enhanced oil recovery, to name but a few, require easy to use efficient stimuli (pH, ionic strength, temperature, light...) to either break emulsions or change their types.

We describe several water and oil emulsion systems (oil = toluene) stabilized by styrene (S)/(dimethyl aminoethyl methacrylate) (DMAEMA) based-diblock copolymers synthesized by Atom Transfer radical Polymerization (ATRP) with various structure, molar mass and composition (PS-*b*-PDMAEMA, PS-*b*-P(S-*st*-DMAEMA)). The copolymers are used to study the conditions under which the different types of emulsions (simple and multiple) are either stabilized or destabilized by changing pH, T or ionic strength as the polymers are indeed stimuable by pH, T or ionic strength^{(1),(2)}. To rationalize our results, the conformation of the different polymers at the oil/water interface was determined by SANS and neutron reflectivity at liquid/liquid interface. The distribution of the polymers between the aqueous and oil phases was measured by UV spectroscopy. Interfacial tensions were determined both by spinning and rising/pendant drop tensiometers.

Overall, our results show that the oil/water interfacial curvature (positive or negative as the copolymer chains extend preferentially towards water or oil respectively) give reliable predictions of emulsion types (O/W or W/O). In the region of near zero curvature, stable but stimuable multiple emulsions are observed. Quite interestingly and indeed original, the multiple emulsions are prepared using a unique polymer emulsifier and a one-step preparation method (a classical Ultra-Turrax type of mixing). We discuss their formation and argue that the oil/aqueous phases distribution of the polymer is a key parameter to predict the stability of the multiple emulsion. The encapsulation/release properties of species in the inner droplets of the multiple emulsions is hence versatile in our system as the oil/water phases polymer distribution can be controlled not only by polymer chemistry (molar mass, structure and composition of polymer chains) but also by a great number of stimuli such as pH, T and ionic strength.

We also demonstrate that the one-step making of stimuable multiple emulsions formulated with a single emulsifier can be extended to fully biocompatible systems (PDMS/PDMAEMA based copolymers and mygliol or isopropyl myristate as oils) using a similar approach.

(1) (2) : L. Besnard *et al.* *Adv. Mater.*25, 2844 (2013) ; *Soft Matter* 10, 7013 (2014)

Dispersing carbon nanotubes with ionic surfactants under controlled conditions: comparisons and molecular insight

Ricardo Fernandes,^{a,b} Matat Buzaglo,^c Oren Regev,^c István Furó,^c and Eduardo F. Marques^a

^a*Centro de Investigação em Química, Dept. Chem. and Biochem., University of Porto, Porto, Portugal.*

^b*Dept. Chem., Royal Institute of Technology, Stockholm, Sweden.*

^c*Dept. Chem. Eng. and Ilse Katz Institute for Nanotechnology, Ben-Gurion University of the Negev, Beer-Sheva, Israel.*

efmarque@fc.up.pt

The ability of surfactants to disperse carbon nanotubes (CNTs) in water has been widely explored, and yet the variety of processing conditions used seems to obscure a coherent vision. [1] Besides, the detailed molecular picture behind surfactant-CNT interactions still awaits consensus.[2,3] There is need for well controlled methodologies and reliable comparative metrics, which could not only lead to a more fundamental understanding of the mechanisms of dispersion, in connection with molecular simulations, but also provide rational optimization of the dispersability.[4] Here, our goal has been to determine and compare the dispersion ability of several ionic surfactants, differing in headgroup chemistry and chain length, towards both single and multi-walled carbon nanotube. For that, we used a stringently controlled sonication-centrifugation method for the preparation of the dispersions. The CNT concentration was accurately measured as a function of surfactant concentration (below and well above critical micelle concentration, *cmc*), using calibration curves obtained from thermogravimetric analysis and UV-vis absorption spectroscopy. The dispersion curves allowed us to determine quantitative parameters, such as critical surfactant concentration for dispersion, maximum dispersed CNT concentration, and respective surfactant concentration at that point, dispersion effectiveness and dispersion efficiency for each surfactant. The effects of nanotube morphology, surfactant aromatic rings, alkyl chain length, headgroup charge and *cmc* on the dispersability of CNTs are presented and rationalized.

[1] Kharissova, O. V.; Kharisov, B. I.; de Casas Ortiz, E. G. *RSC Adv.* **2013**, *3*, 24812.

[2] Blanch, A. J.; Lenehan, C. E.; Quinton, J. S. *Carbon* **2011**, *49*, 5213.

[3] Fernandes, R. M. F.; Buzaglo, M.; Shtein, M.; Pri Bar, I.; Regev, O.; Marques, E. F.; Furó, I. *J. Phys. Chem. C* **2014**, *118*, 582.

[4] Angelikopoulos, P.; Bock, H. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9546.

The Separative Recovery of Rare-Earth Metals such as Europium and Yttrium by Using Fatty Acids and/or Crown Ethers

Ho-Cheol Kang^{*}, Jong Mok Park, Dea Seon Sim
Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Korea
**hckang@kriict.re.kr*

ABSTRACT

KEYWORDS

There has been a great demand of rare earth metals such as europium, yttrium, etc. due to their native physical and chemical properties as the new constituents for electronic, optical and magnetic devices. The effective separation by solvent extraction of rare earth elements such as europium and yttrium has been investigated by using fatty acid with crown ether as an additive. Macrocyclic ligands as host-guest compounds form more stable complexes with metal ions which have the similar size of the cavity of crown ether. The synergistic separation effect of the two metals has been investigated in fatty acid solution with a crown ether such as 18-crown-6 ether, 15-crown-5 ether, and 12-crown-4 ether. Also the recovery of the elements has been carried out by using fatty acid with various alkyl chains. When 0.05 M hexanoic acid and 0.002M 15-crown-5 ether was used for the separation of the metals, the separation ratio is the highest value of 1.72, it is about twice of using only hexanoic acid. Moreover, the metal ion is solvated with three molecules of hexanoic acid monomer like MR_3 in the concentration.

Key words : fatty acids, crown ethers, solvent extraction, europium, yttrium, rare earth metals

Double emulsion for fragrance encapsulation

Margot Stasse,^{a-b} Valérie Héroguez,^{b*} Véronique Schmitt^{a+}

^a Centre of Research Paul Pascal, CNRS - University of Bordeaux
Avenue Dr Albert Schweitzer, PESSAC, FRANCE

^b Laboratoire de Chimie des Polymères Organique, UMR 5629, 16 avenue Pey Berland,
PESSAC, FRANCE

*heroguez@enscbp.fr

+schmitt@crpp-bordeaux.cnrs.fr

Oil-in-water-in-oil (O/W/O) double emulsions are dispersions of a direct emulsion in an oil continuous phase. These emulsions are interesting systems to encapsulate hydrophobic substances in the inner oil phase. Double emulsions enable a good protection of encapsulated agents against external environment, and a controlled release thereof. Despite their interest, they are still not widespread in industrial applications because of the difficulty to formulate stable systems. Indeed they require the presence of two antagonistic types of stabilizers: a more hydrophilic surfactant to stabilize the direct emulsion, and a more hydrophobic one to disperse the water droplets in the oil phase.

Herein, we propose to study both simple emulsions needed to elaborate the double emulsion. Each emulsion requires specific properties in order to lead to a kinetically stable double emulsion. For example, the reverse emulsion should be composed of large enough water globules in order to contain several fragrance droplets (of the direct emulsion). This latter, on the contrary should be of small sizes. Furthermore, the difference in sizes for the globules and droplets has to be significant enough for an efficient two-step emulsification process.

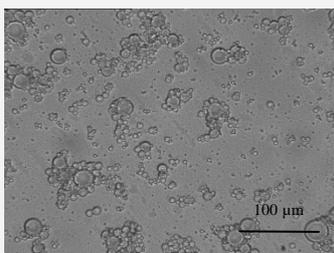


Fig. 1 : Microscopy observation of an inverse emulsion

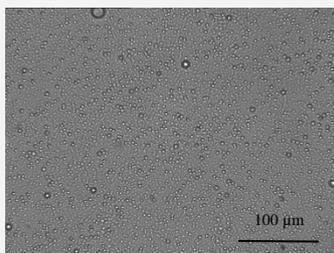


Fig.2: Microscopy observation of a direct emulsion

Photoresponsive self-assemblies based on fatty acids

Audrey Arnould^a, Cedric Gaillard^a, Marc Anton^a, Regine von Klitzing^b & Anne-Laure Fameau^a

^a INRA, Biopolymères Interactions Assemblages, Nantes, France

^b Stranski-Laboratorium für Physikalische und Theoretische Chemie, TU Berlin, Berlin, Germany

audrey.arnould@nantes.inra.fr

Stimuli-responsive surfactants self-assemble into various structures, which can be tuned by changes in environmental conditions or by an external stimulus¹. Light as stimulus displays many advantages to tune surfactant self-assemblies in solution, since it is a non-invasive trigger with micro-scale resolution¹. Fatty acids are a simple class of pH-responsive green surfactant. A pH change tunes the fatty acid ionization degree, the effective headgroup area and the self-assembly in water. To produce photoresponsive fatty acid self-assemblies we combined fatty acid self-assemblies with a photoacid generator that releases protons under UV². A multi-scale approach was used to study the effect of UV irradiation by combining infrared spectroscopy, small angle neutron scattering and microscopy experiments. Before UV illumination, fatty acids were ionized and formed spherical micelles. After UV illumination, the pH of the solution decreased. Ionized and protonated fatty acids coexisted. The change of fatty acid ionization state led to an increase of the packing parameter and self-assembly transition. By modifying the fatty acid chain length, transitions from spherical micelles to vesicles, lamellar phases or tubes were observed under UV light (Figure 1).

This simple approach to induce self-assemblies transitions by UV light is an asset for potential applications in which both stimuli-responsive systems and green molecules are needed.

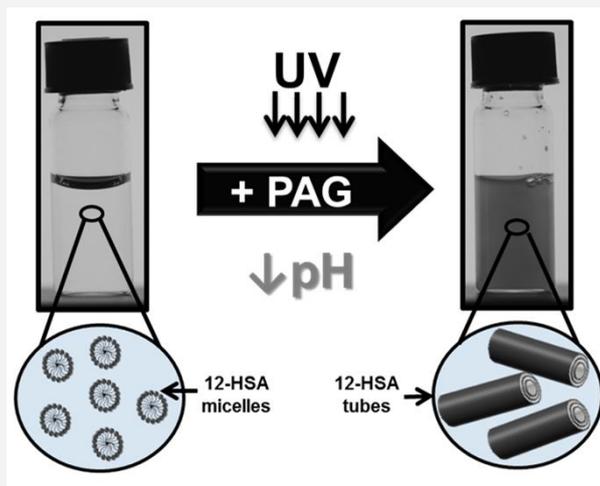


Figure 1: 12hydroxystearic acid (12HSA) self-assemblies transition with a photoacid generator (PAG) induced by UV.

- (1) Brown, P. *Soft Matter* **2013**, 9, 2365.
- (2) Fameau, A.-L. *Chem. Commun.* **2015**, 51, 2907.

The effect of dipropylene glycol on the hydrogel composed of a crude lecithin mixture and hexadecanol

Y. Nakagawa ^a, H. Nakazawa ^b, S. Kato ^b

^a*Kracie Home Products, Ltd., Yokohama-city, Kanagawa, Japan*

^b*Kwansei Gakuin University, Sanda-city, Hyogo, Japan*

y.nakagawa@khp.kracie.co.jp

Polyol is widely used as a moisturizing ingredient in the cosmetic industry because it usually has a good moisturizing effect derived from the multiple hydroxyl groups. Among them, dipropylene glycol (DPG) is commonly contained in skin care products because it has not only moisturizing effect but also dry touch. We investigated the effect of DPG on the structures and physicochemical properties of the hydrogel we had found previously in the lipid system composed of a crude lecithin mixture (PC70) and hexadecanol (HD) [1] by freeze-fracture electron microscopy, optical microscopy, differential scanning calorimetry and synchrotron X-ray diffraction. We found that a great increase of DPG-to-water ratio in the PC70/HD bilayer system caused disintegration of the hydrogel, a decrease in the chain-melting phase transition temperature and ordered stacking of the PC70/HD bilayers. Structural analyses suggested that the disintegration of the hydrogel was closely coupled with the formation of multi-lamellar structures. In the absence of DPG, the hydrogel is formed as a result of the homogeneous distribution of sheet-like bilayers throughout the solution because the bilayer has a surface charge derived from the charged lipids in the PC70 as described in the previous study [1]. The addition of DPG, which has lower dielectricity than water, may modify the electric double layer repulsion between the bilayers so as to give a secondary minimum in the interbilayer interaction energy as a function of interbilayer distance and subsequently reduce the energy barrier to form the multi-lamellar aggregates, keeping their sheet-like morphology. The formation of the multi-lamellar aggregates with a shorter interbilayer distance causes the phase separation of the solvent (water/DPG) phase, leading to the disintegration of the homogeneous hydrogel.

[1] Y. Nakagawa, H. Nakazawa, S. Kato, *J. Colloid Interface Sci.*, 376 (2012) 146-151

Glucose-Responsive Hybrid Nanoassemblies in Aqueous Solutions: Ordered Phenylboronic Acid within Intermixed Poly-(4-hydroxystyrene)-*block*-Poly(Ethylene oxide) Block Copolymer

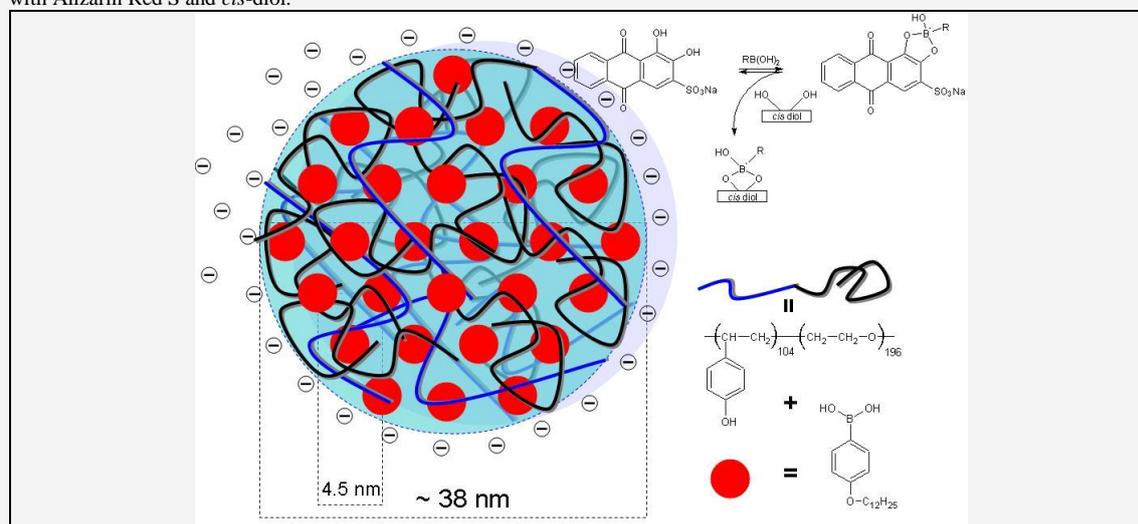
M. Uchman

Department of Physical and Macromolecular Chemistry Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic.

uchman@natur.cuni.cz

Co-assembly behavior of the double hydrophilic block copolymer poly-(4-hydroxystyrene)-*block*-poly(ethylene oxide) (PHOS-PEO) with three amphiphilic phenylboronic acids (PBA) differing in hydrophobicity, *p*-dodecyloxyphenylboronic acid (C12), *p*-octyloxyphenylboronic acid (C8) and *p*-isobutoxyphenylboronic acid (*i*Bu) was studied in alkaline aqueous solutions and in mixtures of NaOH_{aq}/THF by ¹H NMR spectroscopy, static, dynamic and electrophoretic light scattering and SAXS. The study reveals that only the coassembly of C12 with PHOS-PEO provides spherical nanoparticles with intermixed PHOS and PEO blocks, containing densely packed C12 micelles. NMR measurements have shown that spatial proximity of PHOS-PEO and C12 leads to the formation of ester bonds between –OH of PHOS block and hydroxyl groups of –B(OH)₂. Due to the PBA moieties, the release of compounds with 1,2- or 1,3-dihydroxy groups loaded in the coassembled PHOS-PEO/PBA nanoparticles by covalent binding to PBA can be triggered by addition of a surplus of glucose that bind to PBA competitively. The latter feature has been confirmed by fluorescence measurements using Alizarin Red as a model compound.

Drawing of the Coassembled Structure in Solution of PHOS-PEO/C12 as seen by SAXS and Competitive Binding of Boronic Acid with Alizarin Red S and *cis*-diol.



The authors would like to acknowledge the financial support of the Grant Agency of the Czech Republic P205/14-14608S

Rheological properties of wormlike micellar gels formed by novel bio-based isosorbide surfactants

Miho Kamada^{1, 2*}, Christel Pierlot³, Jean-Marie Aubry³ and Kenji Aramaki²

¹ Beauty Care Laboratory, Kracie Home Products, Ltd., Yokohama, Japan

² Graduate School of Environment and Information Sciences, Yokohama National University, Japan

³ Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Equipe CISCO, Université Lille1, Villeneuve d'Ascq, Cedex, France
m.kamada@khp.kracie.co.jp

Isosorbide surfactants having an isosorbide group as a building block is one of bio-based surfactants. There are some reports on significant aqueous phase behavior^[1], foaming properties, Krafft temperatures and critical micellar concentrations^[2]. In this presentation, we report a wormlike micelle formation with a mixture of sodium dodecyl isosorbide (SDSS) and 2-*O*- or 5-*O*-dodecylisosorbide (EXO or ENDO, respectively).

Fig.1 shows viscosity behavior of the 3wt% NaCl aq./SDSS system with EXO or ENDO at constant surfactant concentration (5wt%). A maximum of viscosity was given at the same surfactant mixing composition (X) for both systems but the maximum viscosity is higher in the ENDO system. In addition, X giving high viscosity is wider composition range in the ENDO system. This interesting result was caused by isomeric molecule structure of the cosurfactant. We have also studied dynamic rheological behavior. Oscillatory-shear (frequency sweep) measurements were performed on the viscoelastic samples formed around the viscosity maximum composition. Liquid-like behavior ($G' < G''$) was observed at low frequency region whereas solid-like behavior ($G' > G''$) was observed at high frequency region. Maxwell-type oscillatory rheological behavior of viscous micellar solutions can be related to the transient network formed by the entanglement of wormlike micelles. Maxwell equations were also fitted to the data, indicating wormlike micelle formation.

[1] A. Lavergne, et al., *Colloids Surf.*, A, 404 (2012) 56.

[2] A. Lavergne, et al., *J. Colloid Interface Sci.*, 360 (2011) 645.

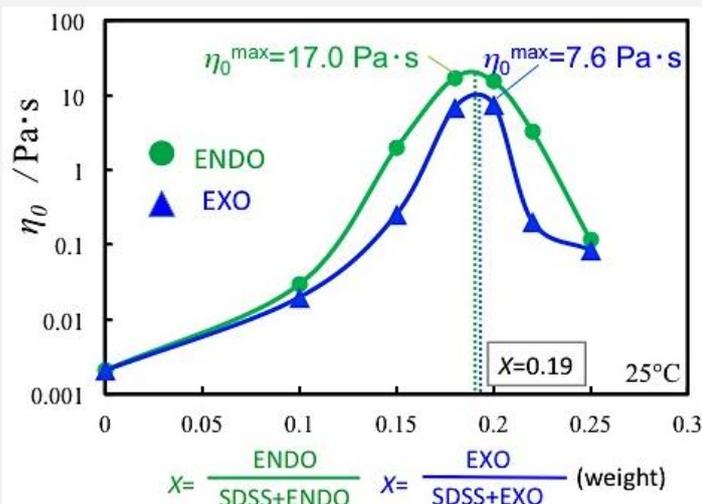


Fig.1 Zero-shear viscosity η_0 plot against surfactant mixing fraction.

Formation, Stability and Time Development of Polyelectrolyte Assemblies

B. Plazzotta^a, J. S. Diget^b, KaiZheng Shu^b, B. Nystrom^b and J. S. Pedersen^a

^aAarhus University, Department of Chemistry and iNano Center, Gustav Wieds Vej 14, 8000 Aarhus, Denmark

^bOslo University, Department of Chemistry, Sem Sælands Vei 26, 0371 Oslo, Norway
beapla@chem.au.dk

Owing to the advances in organic synthesis, the availability of well-defined synthetic charged polymers has increased widely in the past years, allowing more systematic studies on the interactions between charged species in solution; most of the work so far has been focused on interactions between polyions and small oppositely charged molecules or between oppositely charged homopolymers. Here we studied the case of anionic block copolymers constituted of a hydrophilic chain covalently linked to a polyelectrolyte chain interacting with short chain homocations. The chosen blocks were poly(*N*-isopropylacrylamide) for the hydrophobic part, Poly(styrene sulfonate) as polyanionic block. The samples were mixed as diluted aqueous solutions and characterized mainly by Small-Angle X-Ray Scattering (SAXS) and Photon Cross Correlation Spectroscopy (PCCS).

Most of the samples have a limpid appearance and the assemblies were found to be nano-sized globular micellar-like structures, with a core formed by the charge-neutralized polyelectrolytes and an outer shell formed by the hydrophilic component of the block copolymers. It was possible to relate the SAXS data of those assemblies to that of the pure polyelectrolyte and to obtain a reliable value of aggregation number (found to be between 50 and 100) from the scattered intensity.

Samples containing block copolymers with a long hydrophobic tail show a time development from a turbid to a limpid solution containing globular micelles. This evolution was followed by SAXS and PCCS. Presence of added salt was seen to influence strongly the kinetic and phase state of the systems. Adding low amount of electrolytes increases the stability of the assemblies in solution and speeds the aggregation; however, increasing salt concentration a critical point is reached where the polyelectrolytes form a separate solid phase.

Microemulsion Properties and Phase Behavior of (Dimeric Ammonium Surfactant – Heavy Crude Oil – Connate Water) System

Ronald Nguete^a, Kyuro Sasaki^a, Hikmat Said-Al Salim^b, Yuichi Sugai^a and Masanori Nakano^c

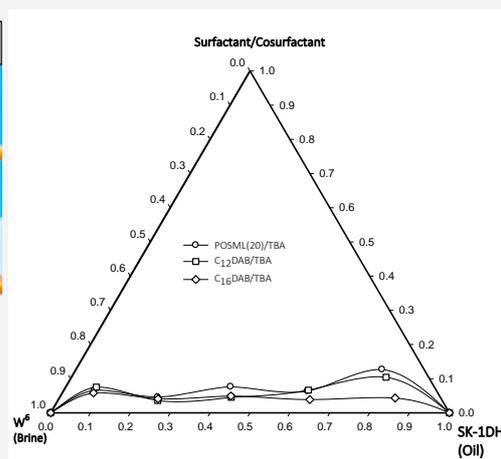
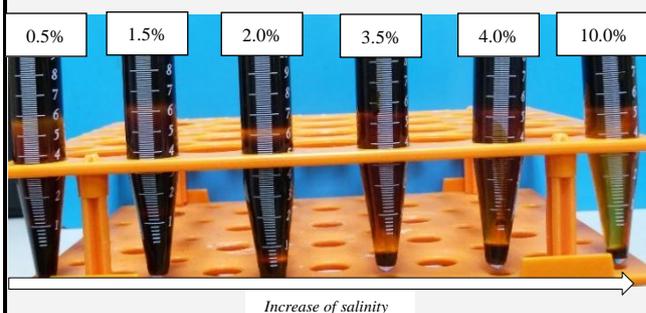
^aKyushu University, Fukuoka-city, Japan

^bUCSI University, Kuala Lumpur, Malaysia

^cResearch Center, Japan Petroleum Exploration Co. LTD, Tokyo, Japan

nguele.odou.548@s.kyushu-u.ac.jp

Recovery methods of untapped crude oils require injection of foreign material in the reservoir which subsequently induces the displacement of oil. In chemical enhanced oil recovery, the microscopic sweep efficiency depends on achievement of a low interfacial tension ($IFT \leq 10^{-3}$ mN/m). The present work discusses about the phase behavior and the properties of microemulsion generated by contacting a dimeric ammonium surfactant, heavy dead crude oil at various salinities. Two gemini ammonium surfactants were considered and their potentials as micellar solutions were gauged with a conventional non-ionic surfactant. The oleic phase consisted of dead heavy crudes. An ultra-low IFT, 5% lesser than a conventional surfactant, was achieved even at low concentrations of active surfactant. Salinity tolerance was significantly influenced by the increase in carbon number of the hydrophobic chain. A submicellar aggregation along with a possible self-coiling of dimeric surfactants was observed when secondary alcohols and diols were used as cosolvent. Interestingly, spectral analyses highlighted an inhibiting acidity activity for gemini surfactants.



A. Bera, K. Ojha, A. Mandal, and T. Kumar, "Interfacial tension and phase behavior of surfactant-brine-oil system," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 383, no. 1–3, pp. 114–119, 2011.

Effect of cholesterol on zeta potential of positively-charged liposomes with lecithin and alkyl quaternary ammonium salts.

Y.Watanabe¹, K.Aramaki¹, Y.Konno², A.Ogata²

¹Graduate School of Environment and Information Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

²Research and Development Division, KOSÉ Corporation, Japan

watanabe-yuki-vy@ynu.jp

Liposomes are widely used as drug delivery carriers and also for some functional cosmetics due to biocompatibility and encapsulation ability of active molecules. As liposomes are applied for transdermal drug delivery systems, positively-charged liposomes are known to improve delivery efficiency compared to negatively-charged lecithin liposomes since skin surface is negatively charged. [1] Cholesterol is often mixed to liposomes for stabilization of liposome membrane. We report effect of cholesterol mixing on zeta potential behavior of positively-charged liposomes prepared with soybean lecithin and dimethyldistearylammonium chloride ($2C_{18}DAC$).

Figure 1 shows the effect of cholesterol on zeta potential behavior. X indicates the mole fraction of cholesterol in liposomes. Zeta potential of soybean lecithin liposome ($X=0$) was about $-40mV$. It dramatically increased by substituting small fraction of lecithin with cationic surfactants and, then, degree of increment was gradually reduced at higher cationic surfactant fraction. Finally zeta potential reached to a maximum value, about $40mV$. Upon increasing X up to 0.3, the maximum zeta potential value was gradually increased. However, zeta potential curve was dramatically shifted at $X=0.4$. DSC and X-ray scattering measurements revealed the transition from α -type crystalline state in bilayer membranes to the intermediate gel phase or the liquid-ordered phase [2] at $X=0.4$. This phase transition in the bilayer membrane could induce the dramatic change in zeta potential behavior at $X=0.4$.

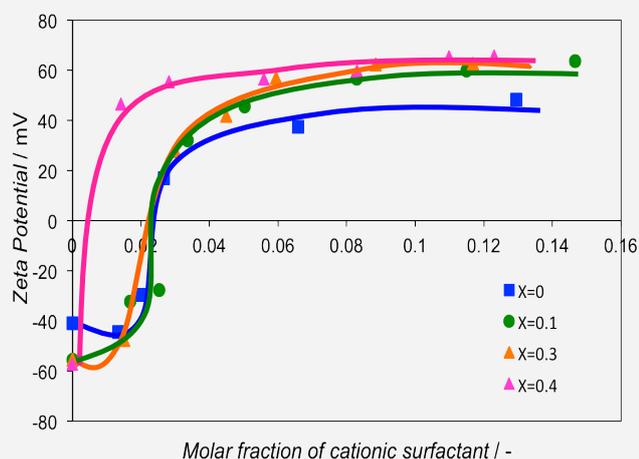


Figure 1 Zeta potential values of the liposomes at 25°C are plotted.

[1] Kitagawa, S., Kasamaki, M., *Chem. Pharm. Bull.*, **2006**, 54, 242-244

[2] Ipsen, J. H., G. Karlstrom, O. G. Mouritsen, H. Wennerstrom, and M. J. Zuckermann, *Biochim. Biophys. Acta.*, **1987**, 905, 162-172.

Revealing the Formation and Stability of PDADMAC Monolayers on Mica via Electrokinetic and Colloid Enhancement Techniques

A. Michna, Z. Adamczyk, P. Batys

Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Cracow, Poland

ncmichna@cyf-kr.edu.pl

The formation and the stability of cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) monolayers were established *in situ* by the streaming potential and colloid deposition measurements.

Firstly, the PDADMAC adsorption and desorption on mica were studied using the streaming potential measurements. The obtained results were quantitatively interpreted in terms of the electrokinetic model postulating a 3D adsorption of molecules as discrete particles. The calibration dependencies allowed one to evaluate the PDADMAC desorption kinetics. It was found that the desorption of the polyelectrolyte at the ionic strength range 0.001–0.15 M was minor over the time of 20 h. Furthermore, the desorption constants, the equilibrium adsorption constants and the binding energies of PDADMAC were determined. It was concluded that the calculated energies agree with the proposed model of discrete electrostatic interactions among ion pairs.

The structure of PDADMAC monolayer and PDADMAC chain orientation were determined by the colloid deposition method. The negative latex microspheres were used as the polyelectrolyte chain markers. The dependence of maximum coverage of microspheres as a function of PDADMAC coverage was determined for ionic strength in the range 0.01 – 0.15 M. It was found that one colloid particle is irreversibly immobilized by one single PDADMAC chain in 0.15 M and for the PDADMAC coverage below 0.1%. For ionic strength below 0.15 M, irreversible adsorption of latex microspheres can occur only at the adsorption sites formed by a few closely adsorbed PDADMAC molecules. The obtained experimental results were quantitatively interpreted in terms of the random sequential adsorption model.

The obtained results confirmed the side-on adsorption mechanisms of PDADMAC for the above ionic strength range.

Acknowledgements: This work was supported financially by the NCN Grant UMO-2012/07/B/ST4/00559.

Phase Behavior of a Diglycerol-based Surfactant: Formation of Stable Nanostructured Dispersions Mediated by a Polymeric Stabilizer.

J.R. Magana, C.Solans

Instituto de Quimica Avanzada de Cataluña, Consejo Superior de Investigaciones Cientificas (IQAC-CSIC) and Biomedical Research Networking Center in Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Jordi Girona, 18-26, 08034 Barcelona, Spain

jmrnqb@cid.csic.es

Glycerol-based nonionic surfactants are focusing considerable attention in the food, cosmetic and pharmaceutical industries due their biocompatibility and biodegradability compared with other conventional nonionic surfactants. Their amphiphilic character allows self-aggregation in water, forming a wide range of structures. However, commercial glycerol based surfactants usually contain a large portion of unreacted polyglycerols that could influence the phase behavior. In addition, glycerol has four hydroxyl groups and most industrial synthetic strategies lead to a complicated mixture of polyglycerol surfactants. There have been few studies of the phase behaviour of these commercial surfactants despite of their importance in industry.

In this context the phase behavior of a commercially available diglycerol-monoisostearate surfactant, abbreviated as C41V, was studied. C41V is a complex mixture of C14, C16 and C18 hydrocarbonated chains. One attractive feature of this surfactant is that all the raw materials used for the synthesis are from natural resources, making this an ideal surfactant for "eco-friendly" and biocompatible applications. C41V forms an inverse hexagonal liquid crystalline phase (H_{II}) coexisting with water from low surfactant concentrations up to 96 wt%. Dispersions of H_{II} were formed at high water content stabilized by a block copolymer. The particle size, polydispersity and stability were assessed by dynamic light scattering and backscattering light techniques. As the concentration of stabilizer polymer is increased the size of the particles decreases and the stability is enhanced. SAXS results suggest a strong adsorption of the stabilizer at the water/hexosome interface. The release of an incorporated model drug in the liquid crystalline dispersion was studied as a function of pH; it was found a higher release of the model drug at high pH values making these ideal candidates for oral administration protecting drugs from the acidic conditions of the stomach and delivering at the intestine.

Phosphonic acids / titania hybrids. Study of the functionalization parameters and in deep characterizations.

L. Baldaccioni^a, G. Soliveri^a, D. Meroni^a, G. Panzarasa^b, G. Cappelletti^a,
R. Annunziata^a, S. Ardizzone^a

^aDipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

^bDipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale
"Amedeo Avogadro", Alessandria, Italy

guido.soliveri@unimi.it

The growing excitement in molecular self-assembly at oxide surfaces, in fields ranging from corrosion to microelectronic, urges a better understanding of the mechanism of formation and organization of such surfactants at the interface. Notwithstanding the titanium dioxide surfaces are ubiquitous in literature, thanks principally to their biocompatibility and semiconductor behavior, only few papers have deepened the interactions between adsorbed molecules and the TiO₂[1]. Especially, phosphonic acids, thanks to their facility to graft at the oxides, are emerging in many different areas of material and surface science, *e.g.* field effect transistors, nanoparticle protection, etc. As recently well discussed by Peukert *et al.*[2], the deep investigation of defects, order and organization of such layers can be critical for the final application.

Here, we go in deep in the grafting of titania by phosphonic acids. Especially, we examined two molecules with different functionalities: a linear alkyl chain, octylphosphonic acid, and an aromatic one, phenylphosphonic acid. The functionalization was performed by a wet procedure both on smooth titania films and on nanoparticles, both synthesized *ad hoc* in our lab. Films are composed by pure phase anatase, while in the case of powders both anatase and mixed phase (anatase/brookite) polymorphs are used. The substrates were previously deeply characterized by AFM, XRD and BET. The functionalized substrates were investigated by the relevant combination of surface free energy measurements, solid state NMR and FTIR analysis. Eventually, we proved the formation of a lotus leaf-like superhydrophobic coating, simply by spin-coating the functionalized nano-powders from an alcoholic suspension.

[1] G. Soliveri *et al.*, *J.Phys.Chem.C*, **2012**, *116*, 26405;

[2] C. Meltzer *et al.*, *J.Am.Chem.Soc.* **2014**, *136*, 10718.

Fatty acid droplets and vesicles as a route to compartmentalization.

Garenne. D.¹, Houinsou Housou. B.², Fameau A-L.², Navailles. L.³, Nallet. F.³, Zhendre. V.⁴, Grélard. A.⁴, Gaillard. C.², Dufourc. E.⁴ and Douliez. J-P.^{1*}

1 UMR 1332, biologie et pathologie du fruit, INRA, centre de Bordeaux, 33883 Villenave d'Ornon, France. 2 UR 1268 Biopolymères Interactions et Assemblages, INRA, rue de la Géraudière, 44316 Nantes, France. 3 Centre de recherche Paul Pascal, CNRS, av. A. Schweitzer, 33600 Pessac, France. 4 Institute of Chemistry and Biology of Membranes and Nano-objects, UMR 5248, CNRS, Univ. Bordeaux, Institut Polytechnique Bordeaux, 33600 Pessac, France.

Corresponding Authors

David GARENNE, email : David.garenne@bordeaux.inra.fr

Jean-Paul DOULIEZ, email : Jean-Paul.Douliez@bordeaux.inra.fr

Compartmentalization is of importance for our understanding of the emergence of life on earth but also for the development and design of minimal cells and bioreactors. Here, we introduce a model built from saturated long chain fatty acids and guanidium. This system, characterised by NMR and small angle neutron scattering, can form both membranous vesicles and membrane-free coacervate-like droplets that results from clouding. Droplets can transit toward vesicles by varying the pH (reversible) and upon addition of alkanol (irreversible). We have first shown using organic colored dyes that droplet can sequester solutes depending on their charge and lipophilicity. We also demonstrated (i) that Yellow Fluorescent Protein (YFP) is sequestered specifically within droplets and (ii) that this protein is further recovered within vesicles after transition occurs from droplets. So, these experiments allowed to encapsulate biomolecules from an « open » membrane-free system (droplets), to a « close » membranous system (vesicles). These systems should be of interest in fields of synthetic biology to encapsulate biological material for design of bioreactors, and to build by a bottom-up approach minimal cells.

EFFECT OF TEMPERATURE ON SUPPORTED DPPC* BILAYERS; STRUCTURE AND LUBRICATION PERFORMANCE

Min Wang¹, Thomas Zander³, Xiaoyan Liu¹, Chao Liu¹, **Akanksha Raj**¹, DC Florian Wieland³, Vasyl M. Garamus³, Regine Willumeit-Römer³, Per Martin Claesson^{1,2}, Andra Dedinaite^{1,2}

¹ *KTH Royal Institute of Technology, School of Chemical Sciences and Engineering, Dept. of Chemistry, Surface and Corrosion Science, Drottning Kristinas Väg 51, 10044 Stockholm, Sweden*

² *SP Technical Research Institute Of Sweden, SP Chemistry, Materials and Surfaces, Box 5607, 11486 Stockholm, Sweden*

³ *Helmholtz Zentrum Geesthacht, Institute for Materials Research, Max Planck-Strasse 1, 21502 Geesthacht, Germany*

rajaka@kth.se

Phospholipids are important in joint lubrication. They are among the biolubricants that sustain low friction between cartilage surfaces bathed in synovial fluid. Thus, in this work we have investigated how the friction force and load bearing capacity of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) bilayers on silica surfaces are affected by temperature, covering the temperature range of 25–52 °C. Using AFM colloidal probe technique we demonstrated that DPPC bilayers are able to provide low friction forces over the whole studied temperature interval. Interestingly, as compared to lower temperatures, higher load bearing capacity is realised at higher temperatures, where phospholipid bilayer failure is less likely. This is attributed to lower rigidity and self-healing ability of DPPC in liquid disordered state compared to the gel state.

Wang M, Zander T, Liu X, Liu C, Raj A, Wieland DC, Garamus VM, Willumeit-Römer R, Claesson PM, Dédinaite A, *J Colloid Interface Sci.* 445 (2015) 84

DPPC* - dipalmitoylphosphatidylcholine

Preparation and Investigation of Solid Lipid Nanoparticles for Drug Delivery

G. D. Kalaycioglu, N. Aydogan

Hacettepe University, Chemical Engineering Department, Ankara, Turkey

anihal@hacettepe.edu.tr

Solid lipid nanoparticles (SLNs), which can be prepared by using various physiologically related lipids, emulsifiers and water have been used as an alternative nanocarrier since 1990s. Due to possessing adjustable release kinetics depend on the synthesis method and biocompatibility, stability and availability/efficiency to encapsulate various active materials into the different parts of its structure, SLNs are ideal to be used in body with various administration routes [1]. In our study, 12 types of SLNs with different size and formulations were synthesized by using “microemulsion method”, because of its user friendly nature like avoidance of high pressure, temperature, organic solvents and formation of monodisperse particles. Various techniques have been used in the characterization of SLNs such as Atomic Force Microscopy and Scanning Electron Microscopy. In addition, surface charge densities of each particle were obtained. After the synthesis of SLNs, encapsulation and release studies were performed by using ascorbic acid (AA) and methylene blue (MB) as model molecules. AA was loaded into the SLNs during the preparation of microemulsion whereas MB was entrapped on the surface of SLNs via electrostatic interaction dominantly. Although the performance of synthesized SLNs shows some variations, the optimum result is obtained for SLN to whom 95% of the AA can be loaded and 90% of the drug was released within 24 hours. It was observed that, MB can be entrapped on the surface of SLNs with an efficiency of ~%90. The release kinetic was directly proportional to the surface charge density of the particles. After all, this study can be considered as a step in the improvement of controlled drug delivery systems as well as development of an understanding.

[1] Cavalli et. al., International Journal of Pharmaceutics, 2002.

Zeta Potential and Surface Charge of DPPC and DOPC Liposomes in the Presence of PLC Enzyme

E. Chibowski, A. Szczes

*^aMaria Curie-Sklodowska University, Faculty of Chemistry, Department of Physical Chemistry-
Interfacial Phenomena, 20-031 Lublin, Poland
email: emil.chibowski@umcs.pl*

Zeta potential of liposomes is often measured in studies of their properties and/or applications. However, there are not many papers published in which zeta potential was determined during enzymatic reaction of a lipid. Therefore in this paper size, polydispersity index, and zeta potentials of 1,2-dipalmitoylsn-glycero-3-phosphatidylcholine (DPPC) and 1,2-dioleoyl-sn-glycero-3-phosphatidylcholine (DOPC) liposomes were investigated in 1 mM NaCl (pH = 6.2) and phosphate buffer (pH = 8.1) during 60 min of phospholipase C action at 20°C and 37°C. The hydrocarbon chains saturation differ these two phospholipids what appears in some differences in the zeta potential changes during the hydrolysis reaction run. The polydispersity index of the liposomes indicates that they are relatively stable and monodisperse except for DPPC in phosphate buffer. However, in the buffer their zeta potential practically does not change during PLC action. Also the changes of zeta potential of DOPC liposomes are minor although their negative values are much smaller than those of DPPC at both temperatures. These small changes of the potential may be due to compression of the diffuse double layer by present phosphate buffer. The distinct changes of the zeta potentials in the presence of PLC take place in NaCl solution. The observed changes can be explained by reorientation of the phospholipid polar heads and different density on the DPPC and DOPC on the surface of liposomes. From the zeta potentials the surface potentials of the liposomes and percentage of their charge surface were calculated. It was found that only 2-3.5 % of the surface was charged. A scheme of the electrical potential profile across the DOPC bilayer, based on the literature data will be presented. Although it appeared that the zeta potential is not very sensitive parameter for the hydrolysis reaction tracking in phosphate buffer, generally the obtained results deliver interesting information about electrokinetic properties of the studied systems.

Acknowledgements: Support from Marie Curie Initial Training Network "ComplexWetting Phenomena" (Project number 607861) is highly appreciated.

Controlled redox-mediated drug release from diblock copolymer micelles

A. Justies,^a A. Lu,^b V. Ravaine,^a S. Lecommandoux,^b P. Barthélémy^c

^a Université de Bordeaux, UMR 5255 Groupe NsysA, ISM ENSCBP,
33607 Pessac Cedex, France

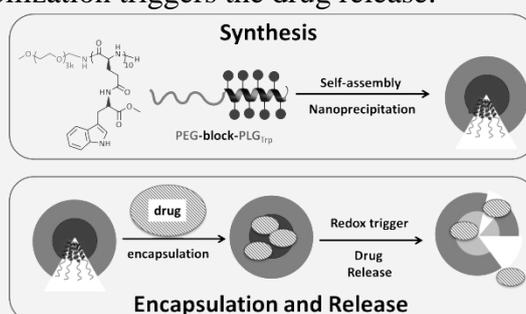
^b Université de Bordeaux, Bordeaux INP, LCPO, UMR 5629, 33600 Pessac, France

^c Université de Bordeaux, ChemBioMed, INSERM U869
33076 Bordeaux Cedex, France

aileen.justies@enscbp.fr

Materials for loading and controlled release on-demand, with the ability to return into a steady state, are of tremendous interest for drug administration.

The aim of this work is to design materials based on the self-assembly of biocompatible polymers and to tailor their loading/release properties by redox triggers. Known redox-responsive materials are based on *e.g.* disulfide bonds or ferrocene inclusion complexes.^[1] The introduction of biocompatible, hydrophobic, redox-responsive moieties into a hydrophilic biocompatible polypeptide backbone would lead to a new generation of redox-responsive materials.^[2] As the polymer scaffold a poly(ethylene glycol)-*block*-poly(L-glutamate) PEG-*b*-PGA diblock copolymer was used.^[3] L-Tryptophan (Trp) was coupled onto the polymer via the acidic groups of PGA in order to introduce redox-responsive properties, thus obtaining PEG-*b*-PLG_{Trp}. Such a modification is of particular interest as, in addition to its redox-response, its change in redox state influences its hydrophobic nature, which alters the self-assembly behavior of the polymer.^[4] The resulting PEG-*b*-PLG_{Trp} copolymers form well-defined micelles, which are able to encapsulate hydrophobic molecules. The release of these molecules can be achieved by electrochemical or chemical oxidation. These triggers change the loading ability of the micelle, by decreasing the hydrophobicity of the tryptophan. The resulting micelle destabilization triggers the drug release.



[1] aL. Zhang, W. Liu, L. Lin, D. Chen, M. H. Stenzel, *Biomacromolecules* **2008**, *9*, 3321-3331; bY. Ma, W.-F. Dong, M. A. Hempenius, H. Mohwald, G. Julius Vancso, *Nature Materials* **2006**, *5*, 724-729.

[2] A. Carlsen, S. Lecommandoux, *Current Opinion in Colloid & Interface Science* **2009**, *14*, 329-339.

[3] W. Agut, A. Brûlet, D. Taton, S. Lecommandoux, *Langmuir* **2007**, *23*, 11526-11533.

[4] N. T. Nguyen, M. Z. Wrona, G. Dryhurst, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1986**, *199*, 101-126.

Effect of hyaluronan hydrophobization on its interactions with surfactants

M. Pekař,^a F. Mravec,^a D. Pihíková,^a T. Venerová,^a J. Mondek,^a
^a*Brno University of Technology, Brno, Czech Republic*

pekar@fch.vutbr.cz

Hyaluronan-surfactant aggregates represent colloids combining biocompatible hydrophilic biopolymer with hydrophobic moieties capable of solubilizing non-polar substances. These systems can find applications as delivery systems for hydrophobic drugs equipped also with targeting properties due to the existence of, e.g., overexpressed hyaluronan receptors on cancer cells. Systems formed by hyaluronan and oppositely (positively) charged surfactant have been studied in most previous works. Attaching hydrophobic alkyl chains onto hyaluronan backbone is supposed to support its interactions with various types of surfactants and to promote formation of micelles anchored on the hyaluronan chain. These systems, to the best of our knowledge, have not been studied thus far.

Here we report on the results of fluorescence probe study of interactions of sodium caproyl hyaluronate (degree of substitution 10-20%) of two molecular weights (17 and 206 kDa) with selected non-ionic (Triton X-100), cationic (cetyl trimethylammonium bromide) and anionic (sodium dodecyl benzenesulphonate) surfactants. Modified hyaluronan at sufficient concentration (5 g/l in contrast to 1 g/l) showed self-aggregation behavior leading to the formation of hydrophobic domains. Addition of hydrophobized hyaluronan at the concentration of 0.1 g/l significantly affected aggregation behavior of ionic surfactants whereas negligible effect was observed in the case of non-ionic surfactant. The critical micellar concentration of ionic surfactants was significantly decreased in the presence of hyaluronan especially in the case of 206 kDa preparation. Fluorescence probes showed two distinct concentration ranges of surfactant – at lower concentrations hyaluronan-induced micelles are formed whereas at higher concentrations, around the standard critical micellar value, standard free micelles occur. The charge of hydrophobized hyaluronan-cationic surfactant aggregates can be reversed by changing the surfactant concentration.

The study demonstrated that the modification of hyaluronan with alkyl chain in the length of only six carbon atoms significantly affects its interactions with ionic surfactants and promotes surfactant aggregation at concentrations much lower than their standard critical micellar concentration.

This work was supported by project LO1211 (Czech Ministry of Education, National Sustainability Programme I) and COST action CM1101 (WG 3).

Cholesterol-Enhanced Physical Stability of Catanionic Vesicles Composed of Ion Pair Amphiphile and Double-Chain Ionic Surfactant

C.-H. Chang, A.-T. Kuo, C.-L. Tu

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

changch@mail.ncku.edu.tw

Catanionic surfactant is formed of a mixture of cationic and anionic surfactants. After the counterions are removed from catanionic surfactant, the residue is called ion pair amphiphile. Ion pair amphiphile can be considered as pseudodouble-chain surfactant and has the potential to be applied to the formation of vesicular structure, or catanionic vesicle.

In this study, charged catanionic vesicles of ion pair amphiphile/double-chain ionic surfactant were successfully fabricated with the addition of cholesterol. The effects of cholesterol on physical stability of the catanionic vesicles were then investigated by size, zeta potential, and bilayer fluidity analyses. It was found that the presence of cholesterol in the catanionic vesicles could significantly improve the physical stability of the catanionic vesicles in association with enhanced bilayer fluidity and surface charge character.

The molecular dynamics simulations suggested that by adding cholesterol into the vesicular bilayers of ion pair amphiphile/double-chain ionic surfactant, one could reduce the conformational order in the fore and terminal segments of the molecular hydrocarbon chains, resulting in the observed cholesterol-enhanced bilayer fluidity. In addition, the presence of cholesterol would decrease the molecule-occupied area in the vesicular bilayers and the counterion binding ability on the vesicle surfaces, which could explain the observed cholesterol-enhanced surface charge character.

The results demonstrated that the presence of cholesterol in the vesicular bilayers of ion pair amphiphile/double-chain ionic surfactant not only adjusted the intra-vesicular molecular packing but also enhanced the inter-vesicular electrostatic repulsion, leading to improved physical stability of the catanionic vesicles. One is thus able to fabricate catanionic vesicles with controlled physical stability and charge character from mixed ion pair amphiphile/double-chain ionic surfactant/cholesterol systems.

Surface activity of esterquat surfactants – influence of hydrolysis

G. Para,^a J. E. Jarek,^a J. Łuczynski,^b M. K.A.Wilk,^b P. Warszynski^a

^a*Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, niezapomianejk 8, 30-239
Krakow Poland*

^b*Faculty of Chemistry, Wrocław University of Technology, ul. Wybrzeże Wyspiańskiego 27, 50-
370 Wrocław, Poland*

ncwarszy@cyf-kr.edu.pl

We considered both experimentally and theoretically adsorption of selected cleavable cationic esterquat surfactants. We studied derivatives having –O-CO- bond between quaternary amine and hydrophobic tail: N,N,N-trimethyl-2-(dodecanoyloxy)ethan ammonium bromide (DMM-11) and N,N,N-trimethyl-2-(dodecanoyloxy)-1-methylethan ammonium bromide (DMP2M-11)), and derivatives with –CO-O- bond: dodecyloxycarbonyl-methyl-N,N,N-trimethyl ammonium bromide (DMGM-12)), and dodecyloxycarbonyl-1-ethyl-N,N,N-trimethyl ammonium bromide (DMALM-12)). These compounds are stable in the acidic conditions but in neutral and basic pH undergo hydrolysis. The hydrolysis of investigated esterquats results in formation of non-surface active salt (choline - in case of DMM-11) and surface active dodecanoate anion, which at low pH can be protonated to get dodecanoic acid. For dodecyl betaines the basic hydrolysis results in non-surface active, zwitterionic amino acid (trimethylglycine, betaine in case of DMGM-12) and surface active dodecanol.

The extended “surface quasi two-dimensional electrolyte” (STDE) model of ionic surfactant adsorption was applied for the description of hydrolysis influenced surface activity of investigated surfactants.

We found that surface activity of the mixture resulting from the esterquat hydrolysis increases with time and it is higher when the ester carbonyl group is located near to the quaternary amine with respect to the inverted (betaine ester type) arrangement. That is a consequence of strong synergistic effect between the cationic esterquat surfactant and the anionic product of its hydrolysis - dodecanoate ion. At pH 10 the rate of hydrolysis becomes faster and increase of surface activity is observed. However, in case of DMGM-12 it is limited by solubility of dodecanol. Addition of CH₃ in the surfactant headgroup slows down the hydrolysis. We also determined surface activity of esterquats mixture with anionic polyelectrolyte (polystyrene sulphonate). Addition of polyanion had the least effect on DMM-11 surface tension because of surface charge neutralization by decanoic acid.

Acknowledgements:

This work was partially financed by NCN project UMO-2011/03/B/ST4/01217, and statutory activity subsidy for the Faculty of Chemistry of WUT

Controlled release from liposomes using electroporation

Aleš Zadražil^a, Ivana Pivarníková^a, Jaroslav Hanuš^a, Martin Ullrich^a, František Štěpánek^a, John McCaskill^b

^a*Department of Chemical Engineering, University of Chemistry and Technology, Prague, Technická 3, 166 28 Prague 6, Czech Republic*

^b*Microsystems Chemistry and BioIT (BioMIP), Ruhr-University-Bochum, Universitätsstr. 150, 44801 Bochum, Germany*

ales.zadrazil@vscht.cz

Liposomes are phospholipid vesicles that can be used as carriers for the encapsulation, targeted delivery and controlled release of bioactive molecules. It is well known that the lipid bi-layer can undergo a reversible phase transition by an increase of temperature; it can also be stabilised by the presence of surfactants or osmotic shocks. More recent methods of triggered release from liposomes include ultrasound, stimulation by laser or the application of electric field – the so-called electroporation. By imposing liposomes to a high gradient of electric field (~1000 V/m) the lipid bi-layer can be locally destabilised leading to the release of the encapsulated content. So far, the liposomes were dispersed in the bulk and the release thus occurred in the whole solution volume.

In the present work, we investigate electroporation-controlled release from liposomes that are adsorbed to a patterned gold-coated surface. By applying an electric field, the electroporation of the lipid bilayer was observed and the effect of electric field gradient, time sequence and the composition of the lipid bi-layer (e.g. the presence of charged lipids) on the extent of electroporation was investigated. Carboxyfluorescein was encapsulated in the liposomes as a model payload and its release and electroporation progress was monitored by a time-dependent fluorescence spectroscopy. The electroporation was investigated in two configurations: on macroscopic electrodes forming a channel with characteristic dimension of 1-2 mm, and on a microelectrode array (dimensions 10 x 10 mm) with a characteristic electrode size of 100x100 μ m. The formation of spatiotemporal patterns by creating local electric field gradients was explored.

Solvophobic Self-Assembly and Nanostructure in Protic Ionic Liquids

G.G. Warr^a, R. Atkin^b, H. Jiang^a, A. Dolan^a, T. Murphy^b and S. Imberti^c

^a*School of Chemistry, The University of Sydney, NSW 2006 Australia*

^b*The University of Newcastle, Newcastle, Australia*

^c*STFC, Rutherford Appleton Laboratory, Didcot, United Kingdom*

gregory.warr@sydney.edu.au

Protic ionic liquids (PILs) have been extensively examined over the past decade due to their ability to promote self-assembly by surfactants and amphiphilic polymers.[1-3] This has been attributed to their high cohesive energy density resulting from electrostatic and H-bonding interactions. Recently it has been shown by neutron diffraction that many PILs are nanostructured, forming a bicontinuous network of polar and non-polar domains, while others behave more like molten salts.[4-6] Whereas in aqueous solution the notions of hydrophobicity/philicity are understood, designing surfactants for PILs requires an understanding of their counterparts: solvophobicity and solvophilicity.

We have examined the self-assembly of nonionic and cationic amphiphiles into micelles, as well as the self-assembly of alkanols in PILs by SAXS/WAXS, SANS and neutron diffraction. Together these yield a high-resolution picture of the H-bond network and nanostructure of the PILs, and also how they solvate moieties such as -OH, -CH₂CH₂O- and (C₂-C₁₂) alkyl chains in molecular solutions and in micelles, and the larger scale structures formed as functional groups and counterions in the amphiphiles and PIL are varied.

Polar domain structure of PILs is critical in determining the behaviour of solvophilic groups, but long chains are sensitive only to the average solvent environment, as the solute cannot be accommodated within the existing solvent nanostructure, and drives self-assembly into micelles, microemulsions and lyotropic phases.

[1] M.U. Araos, G.G. Warr, *Langmuir* 24, (2008) 9354.

[2] R. Atkin and G.G. Warr, *J. Phys. Chem. B* 111, (2007) 9309.

[3] R. Atkin, L.-M. da Fina, U. Kiederling, G.G. Warr, *J. Phys. Chem. B* 113, (2009) 12201.

[4] R. Atkin, G.G. Warr, *J. Phys. Chem. B* 112, (2008) 4164.

[5] R. Hayes, S. Imberti, G.G. Warr, R. Atkin, *Angew. Chemie Intl Ed.* 52, (2013) 4623.

[6] R. Hayes, S. Imberti, G. G. Warr, R. Atkin, *Phys. Chem. Chem. Phys.* 13, (2011) 13544.

Study of Langmuir monolayers formed by phospholipids and POSS compounds at the air/water surface

M. Rojewska, P. Szymański, M. Dudek, M. Piechocka, and K. Prochaska
*Poznan University of Technology, Institute of Chemical Technology and Engineering,
ul. Berdychowo 4, 60-965 Poznan, Poland*

monika.rojewska@put.poznan.pl

The unique structure, size and properties of polyhedral oligomeric silsesquioxane molecules (POSS) allow to use these substance in many fields such as biochemistry, polymer science, pharmacy as well as medicine i.e. as: hybrid medical devices, nanocarriers in drug delivery systems or in formation of biomaterials like dental nanocomposites . From the point of view of possible medical applications of POSS crucial is to analyze the interactions occurring between POSS molecules and model biological membrane at molecular level. In general, this approach allows to predict the impact of POSS contained in biomaterials and cosmetics onto a living organism.

The main goal of our study was to analyzed the morphology and stability of Langmuir monolayers formed by POSS, phospholipids (DPPC) and their mixtures at the air/water surface. Moreover, the rheological properties of these monolayers were also studied.

The measurements were carried out by use a Langmuir balance (KSV Nima) integrated with the Brewster Angle Microscope BAM and SPOT potential meter. Internal reflection-absorption infrared spectra (IRRAS) were recorded using a Bruker Equinox 55 spectrometer equipped with a TGS detector. The relaxation experiment was carried out to test the monolayer stability. During all measurements the temperature was kept constant and changed in the range 25-36.6 °C (± 0.1 °C).

Our studies indicate that both the stability and morphology of the monolayer formed depends on the chemical structure of POSS and composition of mixtures analyzed. Moreover, the results obtained revealed the influence of temperature on the stability of Langmuir monolayers.

Acknowledgement

The research was financially supported by 03/32/DSMK/0515 and 03/32/DS-PB/0501.

A quantitative model of photoswitch of cloud point and aqueous assemblies of azobenzene-containing copolymers.

Christophe Tribet, Emmanuelle Marie

^aEcole Normale Supérieure, Dpt Chemistry, Biophysical Chemistry Group, Paris, France.

Emmanuelle.marie@ens.fr

We tailor azobenzene-modified poly(acrylate) to allow for remote control by exposure to light of hydrophobicity^{1,2} and degree of ionization³ of polymer chains. In mixed aqueous solutions of TX100 with copolymers, we assessed assemblies by measurements of the fractions of polymer-bound micelles and of micelle-bound azobenzene side groups by capillary electrophoresis and spectrophotometry. The binding propensity and magnitude of photoswitch can be captured by a model based solely on one parameter: the threshold length of a polymer segment allowing for binding.¹ This model enabled us to reproduce the non-monotonic variations of the low critical solubility temperature (LCST) of azobenzene-containing poly-N-isopropylacrylamide (PNIPAM) that were recently experimentally evidenced.^{2,4}

(1) J. Ruchman, S. Sebai, C. Tribet, *Macromolecules*, 2011, 44, 604-611.

(2) Yan-Jun Liu *et al.*, *Soft Matter* 2012, 8, 8446-8455,

(3) Jing Sun *et al.*, *Macromolecules* 2014, 47 (5), 1684-1692.

(4) A. Laschewsky *et al.* *Macromol. Chem Phys.* 2013, 214, 1504-1514.

Bile Salt-Based Bolaamphiphiles: Building Blocks for Supramolecular Architectures

M. Gubitosi,^{a,c} L. Galantini,^a N. V. Pavel,^a A. D'Annibale,^a S. Sennato,^b K. Schillén,^c U. Olsson,^c

^aDepartment of Chemistry, Sapienza University of Rome, Rome, Italy

^bInstitute of Complex Systems (ISC) – CNR, UOS Sapienza, Rome, Italy

^cDivision of Physical Chemistry, Lund University, Lund, Sweden

marta.gubitosi@fkem1.lu.se

In recent years an increasing interest towards nano-organized systems for various applicative purposes have been developed, and molecular self-assembly has been established as a practical strategy for their fabrication in a *bottom up* approach. Bile salts, because of their steroidal backbone, appear to be suitable precursors in the synthesis of non-conventional rigid amphiphiles,[1] and such derivatives show very often uncommon aggregation features.[2,3] Here we report on two novel sugar-bile salt-based bolaamphiphiles NaManLC and NaGluLC, obtained by introducing a monosaccharide unit (mannose and glucose, respectively) on carbon 3 of sodium lithocholate (NaLC), and whose structures differ only for the orientation of an hydroxyl group on the sugar residue. Even with substantial differences, both compounds exhibit a peculiar aggregation behavior in aqueous solutions, with the formation of metastable phases of tubular structures in many experimental conditions, similarly to what observed for the natural precursor. As a further step, two component mixtures comprising the natural bile salt and the bolaamphiphilic derivatives were investigated and show an ideal behavior in wide concentration ranges, with the formation of tubular assemblies with intermediate cross section diameters, which can be conveniently tuned by varying the stoichiometric ratio of the two compounds. The stability of these structures and the equilibrium phase behavior will also be discussed.

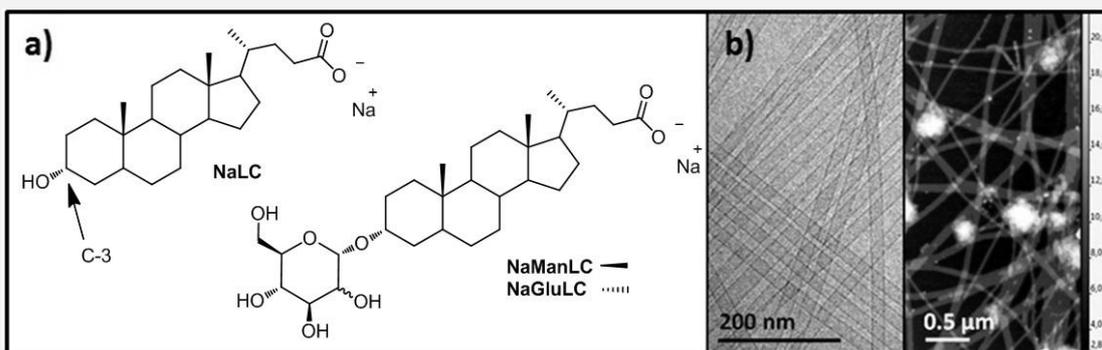


Fig.1 a) Molecular structures of NaManLC, NaGluLC and their precursor; b) Cryo-TEM and AFM images of supramolecular nanotubes formed by NaManLC.

[1] D. Madenci et al. *Curr. Opin. Colloid In.* **2010**, *15*, 109.

[2] U. Maitra et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 2281.

[3] V. H. Soto Tellini et al. *Adv. Mater.* **2007**, *19*, 1752.

Supported POPC/POPE lipid bilayer modified with quantum dots.

M.Wlodek,^a M.Kolasinska-Sojka,^a P.Warszynski,^a

^a*Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Cracow, Poland*

ncwlodek@cyf-kr.edu.pl

Fabrication of polyelectrolyte – lipid films with embedded hydrophobic nanoparticles are promising systems since they combine the response of polymers to external stimuli with properties of nanoparticles as well as potential of lipid bilayer to act as cell-membrane models or biosensors. Such novel nanostructures may have unique properties and promising applications for nanotechnology, biomaterials and biotechnology. Preparation of polyelectrolyte – lipid films with incorporation of nano – objects, characterized by specific properties determining their functionality, is still a scientific challenge.

The main goal of presented studies was the incorporation of hydrophobic nanoparticles (cadmium sulphide quantum dots, QD with size ranging from 1.6nm to 5.4nm) into POPC:POPE lipid bilayers supported on polyelectrolyte multilayers (PEMs). Polyelectrolyte cushions with different number of layers, applied as a support for lipid bilayer with quantum dots, were constructed by the layer by layer deposition of polycations (PEI, PLL, PDADMAC) and polyanions (PGA, PSS) on quartz or silicon surface. Nanoparticles were inserted directly into the hydrophobic part of lipid bilayer during its preparation as lipid vesicles. Deposition on vesicles with QD on polyelectrolyte films was studied in situ using QCM-D technique. Fluorimetric experiments were performed to confirm the presence of fluorescent nanoparticles within liposome structure and in the supported lipid bilayer after spreading of the vesicles on the polyelectrolyte multilayers.

We have demonstrated that quantum dots used as model hydrophobic nanoparticles can be successively embedded into hydrophobic part of lipid bilayers. Moreover, we observed the differences in the structure of studied hybrid materials dependent on the size of nanoparticles used.

Acknowledgement: The work presented was financed by the National Science Centre, Contract No. DEC-2011/01/DST5/04913 and the COST Action CM1101.

Stabilising lamellar stacks of lipid bilayers with soft confinement and steric effects

K. Bougis^a, R. Leite Rubim^a, N. Ziane^a, J. Peyencet^a, A. Bentaleb^a, A. Février^a,
C. L. Pinto de Oliveira^b, E. Andreoli de Oliveira^b, F. Nallet^a, and L. Navailles^a

^a*Université de Bordeaux, Centre de recherche Paul-Pascal–CNRS, 115 avenue du Docteur-Schweitzer, F-33600 Pessac, France.*

^b*Universidade de São Paulo, Instituto de Física-GFCx, P.O.B. 66318, São Paulo, SP 05314-970, Brazil.*

bougis@crpp-bordeaux.cnrs.fr

Structure and interactions stabilising the lyotropic lamellar stack of mixed lipid bilayers in their fluid state are investigated by means of small-angle x-ray scattering. The (electrically-neutral) bilayers are composed of a mixture of lecithin, a zwitterionic phospholipid, and Simulsol, a non-ionic cosurfactant with an ethoxylated polar head provided by the french company SEPPIC. Such self-assembled systems present some potential applications. They can be doped with some nanoobjects as DNA rods¹ and sheared in order to create oignons², i.e multilamellar vesicles. Thus, these nanoobjects can potentially serve for vectorization application as gene therapy.

The challenge here is to understand the mechanisms origin responsible for the formation of these supramolecular assemblies which are not based on electrostatic interactions commonly used. In this aim, we are interested in entropic and interfacial mechanisms linked to the membrane flexibility and specific interactions between adjacent bilayers. The cosurfactant used, whose the hydrophilic part is longer than the lecithin one, takes therefore its key role. Moreover, a soft nanoconfinement is applied on the lamellar stack thanks to the systematic variation of the hydration of the system. With the use of a theoretical model³, we extract from small-angle x-ray experiments some interesting physic parameters to characterize the lamellar stack of the lamellar phase, the elastic properties and interactions between adjacent bilayers. A smooth structural transition between two different lamellar phases is so brought out at low hydration. At higher hydration, the swelling of the lamellar stacks occurs with a significant, but continuous evolution in the mixed bilayer structure. The bilayer structural changes result from a coupling between lateral and vertical confinements.

References

¹E.R. T. Da Silva et al, Eur. Phys. J. E, 34, 83 (2011).

²T. Pott and D. Roux, FEBS Letters 511 (2002) 150-154

³F. Nallet, R. Laversanne and D. Roux, J. Phys. II France, 3, 487-502 (1993).

The New Stimuli Responsive Lipid Nanotube for Protein Entrapment and Release: From Molecular Design to Application

H. Unsal,^a N. Aydogan*,^a

^a*Hacettepe University, Department of Chemical Engineering, Ankara, Turkey*
anihal@hacettepe.edu.tr

Lipid nanotubes have various advantages such as high biocompatibility, simple production, high inner volume etc. which make them preferential especially as carriers for different guests. Here, the usability of the recently designed AQUA (AQ-NH-(CH₂)₁₀COOH, where AQ is anthraquinone) nanotubes for protein transport and release is investigated. The loading capacities and release profiles of hemoglobin (Hb) and BSA (Bovine serum albumin) are determined. Due to the tubular geometry and the rational molecular design, relatively higher loading capacities are achieved. The π - π stacking, electrostatic and hydrogen bonding interactions provided by AQ and COOH groups, contribute this high entrapment efficiency. The loading capacities and release profiles of the proteins change with pH and temperature. AQUA nanotubes release a high portion of the entrapped BSA, but, the released Hb amount is very low which are attributed to the smart design of AQUA molecule. The quite high and low release amounts for BSA and Hb are both promising for different purposes and reveal the usability of AQUA nanotubes in the controlled release and artificial blood applications, respectively.

On the self assembly of an adamantyl substituted sodium deoxycholate

L. Galantini,^a M. C. di Gregorio,^a M. Gubitosi,^a L. Travaglini,^a N. V. Pavel,^a S. Sennato,^b V. H. Soto Tellini,^c A. Jover,^d F. Meijide,^d J. Vázquez Tato.^d

^a*Dipartimento di Chimica, Università di Roma "La Sapienza", P. le A. Moro 5, 00185, Roma, Italy*

^b*Institute of Complex Systems (ISC) – CNR, UOS Sapienza, P.le Aldo Moro 2, 00185 Rome, Italy*

^c*Escuela de Química Universidad de Costa Rica, San José, Costa Rica*

^d*Facultad de Ciencias, Universidad de Santiago de Compostela, Avenida Alfonso X El Sabio s/n, 27002 Lugo, Spain*

luciano.galantini@uniroma1.it

In the last decades several efforts have been made to fabricate self assembling micro- and nano- supramolecular structures with interesting applicative potentials. Within the building blocks, biological molecules have been those firstly studied and among them relevant attentions have been drawn to bile acids (BAs) due to their unique self assembly features which are different from those of conventional surfactants and mainly dictated by the peculiar molecular structure (presence of a rigid backbone, several positions for intramolecular hydrogen bonds and complex distribution of hydrophobic/hydrophilic regions). In the recent years the fundamental study of BAs has been accompanied by innovative research streams aimed at the synthesis of BA derivatives that showed an enlarged array of morphologies,^{1,2} sometimes presenting also stimuli responsive features.³ In this context the work finds its relevance by reporting the characterization of a new deoxycholate derivative bearing an adamantyl group at C3 on the steroidal nucleus instead of the original OH. The analysis was focused on the temoresponsive evolution of the supramolecular structures. Planar sheets turned out to form at room temperature and transform into helically wrapped nanotubes at 50 °C (Figure a). The morphological transformation, that is rapid and reversible, was highlighted by circular dichroism (Figure b), light scattering and microscopy techniques.

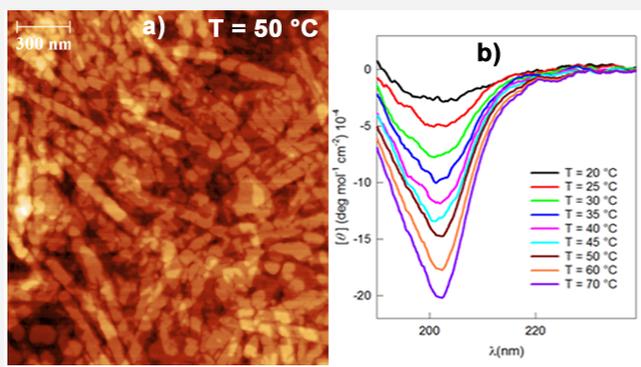


Figure: BA derivative nanotubes and circular dichroism spectra evolution as function of temperature

[1] Travaglini, L. et al. Chem. Commun. 2012, 48, 12011.

[2] Gubitosi, M. et al. Langmuir 2014, 30, 6358.

[3] di Gregorio, M. C. et al. RSC Adv. 2015, 5, 37800.

Effect of anionic surfactants on the stability ratio and electrophoretic mobility of colloidal hematite particles

M. Kobayashi, S. Yuki, and Y. Adachi
University of Tsukuba, Tsukuba, Japan
kobayashi.moto.fp@u.tsukuba.ac.jp

The effect of anionic surfactants on the charging and aggregation of hematite particles was investigated. Charging behavior was studied by the measurement of the electrophoretic mobility. The stability ratio of hematite suspension was obtained from the temporal change of turbidity. These experiments were performed as functions of types of surfactant, surfactant dosage, and surfactant chain length.

Electrophoretic mobility of bare hematite was positive at pH 4. The mobility went down to zero and became negative with increasing surfactant dosage. Required surfactant concentration reaching zero mobility decreased as the chain length of surfactant increased. The stability ratios (W) show the minimum around the concentration of zero mobility (Fig. 1). That is, the destabilization of the suspension is induced by charge neutralization due to the adsorption of surfactants onto the hematite. The values of minimum stability are almost unity irrespective of the chain length; the fastest aggregation rate with surfactants equals the salt-induced rate. Therefore, in the case of surfactant, charge-patch attraction and steric hindrance do not significantly work around zero mobility concentration.

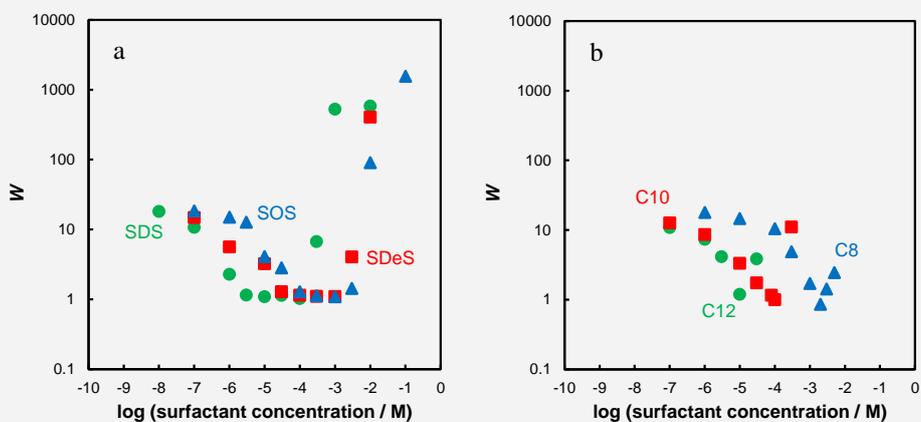


Fig. 1 Stability ratio (W) against surfactant concentration: (a) ● sodium dodecyl sulfate (SDS), ■ sodium decyl sulfate (SDeS), ▲ sodium octyl sulfate (SOS) and (b) ● sodium dodecanoate (C12), ■ sodium decanoate (C10), ▲ sodium octanoate (C8). All the data were taken at pH 4 in 10 mM NaCl.

Formation of Hollow Capsules from Monodisperse Kinetically Stabilised Vesicles

Katharina Bressel, S. Bayer, H. Yalcinkaya, M. Gradzielski
Stranski-Laboratory, Technische Universität Berlin, Berlin, Germany

katharina.bressel@tu-berlin.de

We study the formation of monodisperse vesicles and based on that knowledge use them as templates to synthesize spherical hollow silica and polymer capsules.

Monodisperse vesicles are formed in mixtures of TDMAO (tetradecyldimethylamine oxide) and LiPFOS (lithium perfluorooctylsulfonate). Their size depends on the mechanism of formation, which proceeds via a disc-like micellar state, where disc-like micelles grow until the energy of the disc rim exceeds the bending energy of the bilayer.¹⁻⁴

The vesicle size is controlled by stabilising the disc rim by the presence of amphiphilic polymers of the pluronic type (EO_n-PO_m-EO_n), which reduce the line tension (λ) and thereby the cut-off disc radius $R_{disc,max}=2(\kappa+\lambda)/\lambda$ and the resulting initial vesicle radius. In addition the polymer prevents vesicle ageing by fusion processes due to steric interactions between polymer decorated vesicles.⁵

Stable monodisperse vesicles offer the opportunity to use them as templates for silica formation with TMOS (tetramethyl orthosilicate) or for polymerisation with styrene or with alkylacrylates. The incorporation of these precursors into the bilayer was studied by turbidity and Dynamic Light Scattering (DLS) measurements. The preservation of the vesicle structure was investigated by DLS measurements and by Small Angle Neutron Scattering (SANS). Polymerisations were performed as UV induced radical polymerisations.

The potential of this approach to produce well-defined capsules by a self-assembled system is critically evaluated.

References

- [1] S. Schmolzer, D. Gräbner, M. Gradzielski, T. Narayanan, *Phys Rev. Lett.* **88**, 258301 (2002)
- [2] T. Weiss, T. Narayanan, C. Wolf, M. Gradzielski, P. Panine, S. Finet, W. Helby, *Phys Rev. Lett.* **94**, 0388303 (2005)
- [3] T. Weiss, T. Narayanan, M. Gradzielski, *Langmuir* **24**, 3759-3766 (2008)
- [4] K. Bressel, M. Muthig, S. Prévost, I. Grillo, M. Gradzielski, *Colloid. Polym. Sci.* **288**, 827-840 (2010)
- [5] K. Bressel, M. Muthig, S. Prévost, J. Gummel, T. Narayanan, M. Gradzielski, *ACS Nano* **6**, 5858-5865 (2012)

Supramolecular systems based on gemini surfactants for enhancing solubility of special probes and drugs in aqueous solution

Alla Mirgorodskaya,^{a,b} Lucia Zakharova,^{a,b} Ekaterina Yackevich,^a Svetlana Lukashenko,^a
Oleg Sinyashin.^{a,b}

^a*A.E. Arbutov Institute of Organic and Physical Chemistry of Kazan Scientific Centre of Russian Academy of Sciences, Kazan, Russia*

^b*Kazan National Research Technological University, Kazan, Russia*

mirgoralla@mail.ru

One of the key properties of the supramolecular surfactant based systems is their ability to solubilize nonpolar organic compounds, thereby increasing their solubility in aqueous media. The solubilizing effect is determined by the chemical structure of the surfactant. It varies depending on the charge of the surfactant head group, the volume of the hydrophobic domain, and of the specific interactions between the micelle and the substrate.

In this paper the aggregation behavior and solubilization properties of micellar systems based on cationic gemini surfactant of the *m-s-m* type are compared. As a solubilize hydrophobic polyaromatic compounds, namely an indicator thymolphthalein, a dye Orange OT, and drugs indomethacin and bibenzimidazole have been investigated.

The solubilization capacity of the micellar solutions of surfactants of the *m-s-m* series has been evaluated. It was shown that their use makes it possible to enhance the solubility of the hydrophobic substrates by 5-10 times. The efficiency of the surfactant increases with the elongation of the spacer and of the hydrophobic tail. As exemplified by thymolphthalein the solubilization is accompanied by a change in the pK_a of the indicator and of the pH range of the color transition. In the case of indomethacin the change in its hydrolytic stability was found with the transfer from water to micellar solution.

Acknowledgement. This work is supported by Russian Scientific Foundation, grant no. 14-23-00073.

The effect of additives on rheological properties of ionic amphiphiles

A. Mirgorodskaya,^{1,2} S. Zakharov,² D. Kuryashov,^{1,2} F. Valeeva,¹ S. Lukashenko,¹
N. Bashkirtseva,² L. Zakharova.^{1,2}

¹*A. E. Arbutov Institute of Organic and Physical Chemistry of Kazan Scientific Center of
Russian Academy of Sciences, Kazan, Russia*

²*Kazan National Research Technological University, Kazan, Russia*

mirgoralla@mail.ru

One of the important tools for the control of the functional activity of surfactants consists in the modification of their morphological behavior. Structural transitions of aggregates, e.g. sphere-rod or micelle-vesicle are conjugated with changes in the surface potential, aggregation numbers and size, which in turn affect their solubilization capacity, catalytic activity, etc. Herein self-assembling behavior of cationic surfactant 4-aza-1-hexadecyl-1-azoniabicyclo[2.2.2]octane bromide (DABCO-16) is studied in the presence of typical hydrotropic compounds, i.e. salts of aromatic acids as well as non-electrolyte such as thymol. Data obtained are compared with those of typical cationic surfactant cetyltrimethylammonium bromide. A decrease in critical micelle concentration (cmc) and electrokinetic potential is shown, which is due to the strong binding of organic counterions with cationic head groups, with their charge partially neutralized. The counterion effect increases as follows: benzoate<tosylate<salicylate. For DABCO-16 micellar solution, viscoelastic behavior occurs in the presence of sodium tosylate and sodium salicylate, while benzoate-ion exerts little effect. Rheological behavior of the binary systems is shown to be described by Maxwell model for viscoelastic liquid with one relaxation time. Further we considered the influence of a thymol additive on the properties of DABCO-16. Dynamic light scattering data show the presence of aggregates of a higher hydrodynamic diameter than that of typical cationic micelles at concentrations significantly lower than cmc. It was established that the viscosity of the binary system can be controlled by varying the concentrations of the surfactant and thymol. Viscosity in the DABCO-16/thymol system increases by more than two orders of magnitude as compared to individual micelles.

This work is supported by Russian Foundation for Basic Researches, grant no15-43-02490.

Solubilization of *n*-alkylbenzenes into micelles of gemini surfactants with different spacer chains

H. Nakahara,^a H. Nishizaka,^a K. Iwasaki,^a Y. Moroi,^a M. Nakaya,^b K. Kanie,^b A. Muramatsu,^b and O. Shibata^{a,*}.

^a *Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan,*

^b *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan*

wosamu@niu.ac.jp

Solubilization behavior of benzene, toluene, ethylbenzene, *n*-propylbenzene, and *n*-butylbenzene into micelles of decanediyl-1-10-bis(dimethyltetradecylammonium bromide) (14-10-14,2Br⁻) was investigated in the aqueous medium [1]. In this report, it was indicated that the solubilization is entropy-driven and that the location of the solubilizates moves into the inner core of the micelle with an elongation of their alkyl chains. The movement on the location is also supported by the results of absorption spectra, Fourier transform infrared (FTIR) spectra, and two-dimensional nuclear Overhauser effect spectroscopy (2-D NOESY). Thus, in this study, we have elucidated the solubilization into the micelles of 14-2-14,2Br⁻ and 14-6-14,2Br⁻ in the same manner to understand the effect of space length.

References

1. H. Nakahara, Y. Kojima, Y. Moroi, O. Shibata, *Langmuir* 30 (2014) 5771–5779.

X-shaped bolapolyphilic molecules cause demixing of phosphatidylcholine membranes

B.-D. Lechner,^a A. Beerlink,^b S. Werner,^c H. Ebert,^a K. Bacia,^c C. Tschierske,^a A. Blume^a

^a*Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Germany*

^b*ZIK HALOmem, Halle (Saale), Germany*

^c*HASYLAB at the DESY, Hamburg, Germany*

bob-dan.lechner@chemie.uni-halle.de

Interactions of peptides or proteins with lipid bilayer membranes have been intensively studied in the past decades to understand the mechanism of structure and pore formation or diffusion processes through membranes.^[1] Model membranes have been used to reduce the complexity of these systems. Although many studies concerning function and dynamic properties have been performed, the principles of structure formation of foreign molecules in membranes and the underlying mechanism of pore formation are still not completely clear.

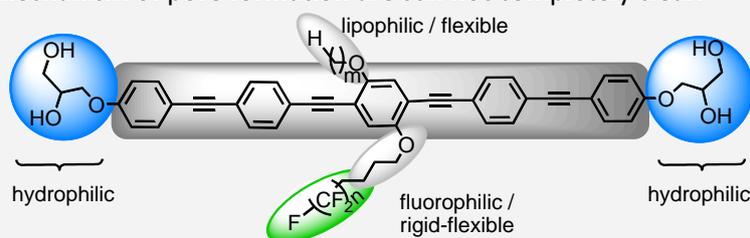


Fig. 1: Chemical structure of the X-shaped bola-polyphiles **Fm-n**.

Here we present investigations on the interaction of the synthetic bolapoliphilic molecules **Fm-n**^[2] (Fig. 1) with lipid model membranes. The molecules **Fm-n** consist of a rod-like rigid oligo-phenyl-alkynyl central core and two hydrophilic glycerol head groups giving the molecules a bolaamphiphile-like structure. At one side of the core, a flexible alkyl chain and at the other side a more rigid semi-perfluoralkyl chain is attached, causing the x-shaped structure. The molecules **Fm-n** themselves form liquid-crystalline bulk phases. The interplay of different affinities (hydrophilic, lipophilic and fluorophilic) and the combination of rigid and flexible units within the molecules, allow for the formation of a variety of structures when interacting with lipid membranes. The incorporation of the molecules into lipid bilayers leads to the formation of large **Fm-n** domains within the membrane and a separation into two lamellar species (Fig. 2).

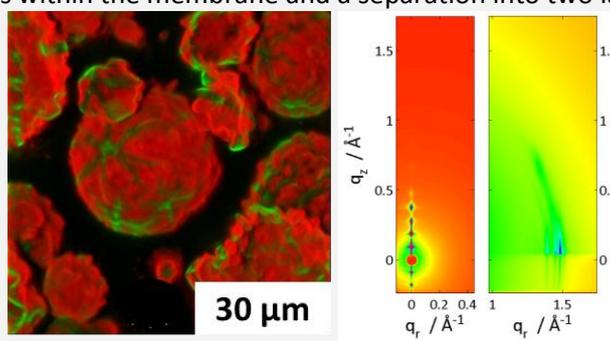


Fig. 2: CLSM image of the mixture of **F18-10**:DPPC (1:10) at 20°C (left) and GIXD pattern of the mixture of **F18-6**:DPPC (1:4) at 25°C (right).

References

[1] M. S. Bretschner, *Science*, 1973, 181, 622-629. b) T. A. Harroun, N. Kucerka, M.-P. Nieh, J. Katsaras, *Soft Matter*, 2009, 5, 2694-2703.

[2] H. Ebert, Diploma thesis, MLU Halle-Wittenberg, 2009.

Preparation, Characterization and Investigation of the Process Parameters on the Formation of Nanostructured Lipid Carriers (NLC)

G.S. Korkmaz, N. Aydogan

Hacettepe University, Department of Chemical Engineering, Ankara, Turkey

kmglnr09@hacettepe.edu.tr

Nanostructured lipid carriers (NLC) are new type of lipid nanoparticles consist solid/lipid matrix entrapping liquid oil. NLC can be considered as drug delivery system administered via dermal, oral, ocular and pulmonary routes because of their advantages such as improved drug loading capacity, biocompatibility and sustained drug release ability [1].

The purpose of this study was to synthesize NLC for appropriate drug delivery route with a desired size and investigate the drug release mechanism in vivo. NLC were prepared by solvent-diffusion method in aqueous system using stearic acid (SA) as the solid lipid, oleic acid (OA) as the liquid lipid and ethanol-acetone mixture as organic phase. Several parameters were investigated to synthesize NLC with desired size and morphology, such as the ratio of lipids used, stirring speed, reaction time and storage conditions at different temperatures. It was determined that the OA content significantly affects the size and morphology of NLC. The optimum OA content was found as 30wt%. Characterization of NLC was done by Dynamic Light Scattering, Atomic Force Microscopy, Differential Scanning Calorimetry and X-Ray Diffraction. In addition, zeta potential values of each particle were obtained. The size of particles was determined to be in range of 75-210 nm which is strongly depend on synthesis conditions. Also, the stability of these systems was determined via macroscopic observation and some stabilizers were added to improve the stability of NLC. Moreover with in the content of this study drug loading and release properties were also investigated by using model drug molecule.

Directional motion and speed of micro-plates depending on the position and frequency of the produced bubbles

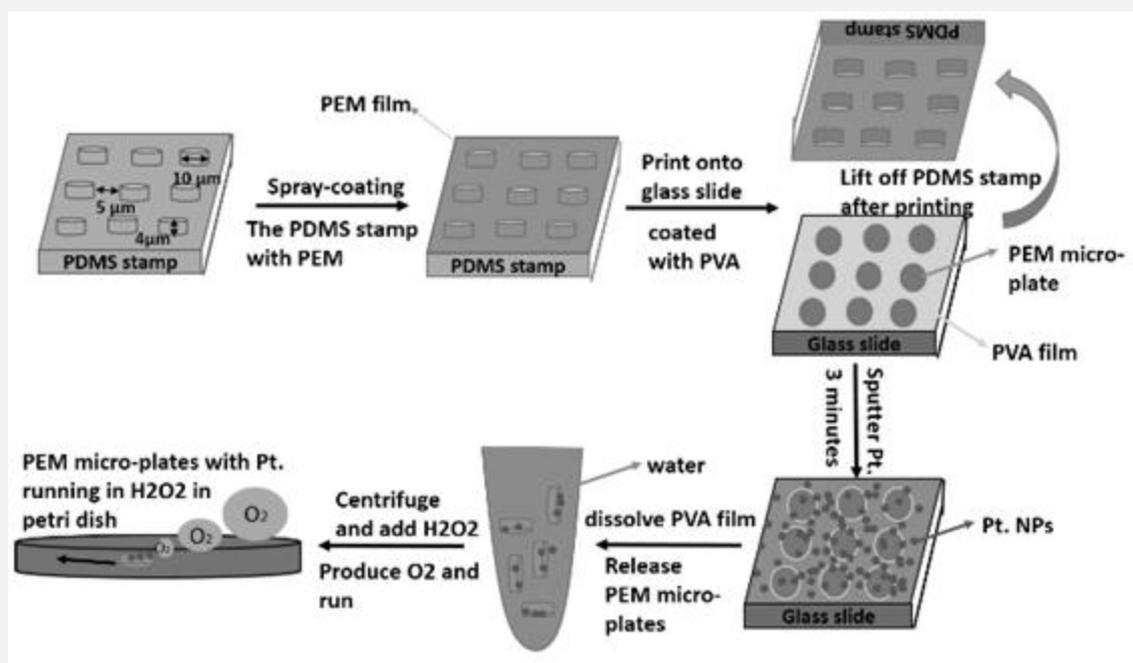
Meiyu Gai,^{a,b+} Johannes Frue,^a Gleb Sukhorukov,^{b+} Qiang He^a

^aHarbin Institute of Technology, Harbin, China

^bQueen Mary University of London, E14NS, London, Enland

+johannes.frueh@hit.edu.cn, +M.Gai@qmul.ac.uk

We hereby present a novel approach and formalism of determining and forecasting the future movement of Polyelectrolyte multilayer (PEM) plates produced by the well known layer-by-layer deposition procedure¹ propelled by catalytic decomposition of hydrogen peroxide solution in water.² The motion direction depends on the nucleation site of the oxygen bubbles on the PEM plate, which can be more than one, with the bubble positions being at arbitrary amount and angular positions to each other. The final direction depends on the nucleation site activity (frequency and size of the produced bubbles). The poster will show analytical functions and comparisons of forecasted and measured particle paths.



Scheme: Production method of PEM plates. First PDMS stamp is coated with PEM, then PEM is printed onto PVA, followed by a evaporation of Pt, dissolution in hot water and letting it run in H₂O₂.

References

1. G. Decher, J. D. Hong, and J. Schmitt, *Thin Solid Films*, 1992, **210-211**, 831–835.
2. R. F. Ismagilov, A. Schwartz, N. Bowden, and G. M. Whitesides, *Angew. Chem. Int. Ed. Engl.*, 2002, **41**, 652–654.

Binding of Amphiphilic and Triphilic Block Copolymers to Lipid Model Membranes and Monolayers: The Role of Perfluorinated Moieties.

Schwieger C, Anja Achilles, Sven Scholz, Jan Ruger, Kirsten Bacia, Kay Saalwaechter, Jorg Kressler, Alfred Blume
Martin Luther University Halle-Wittenberg, Halle, Germany

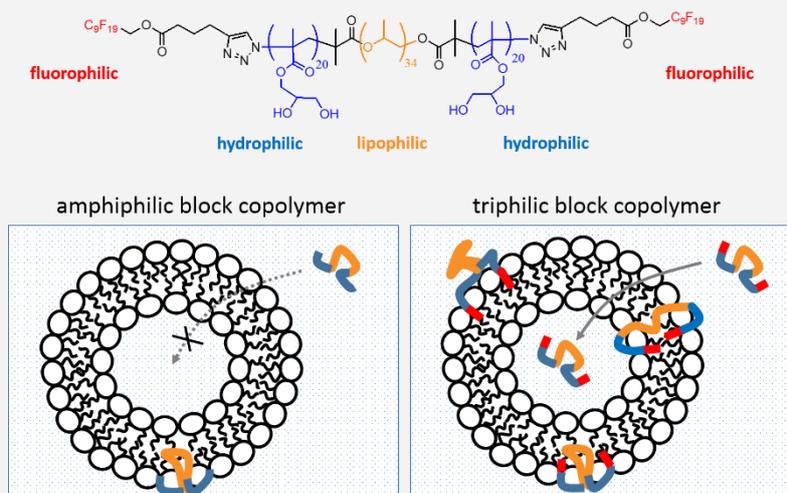
christian.schwieger@chemie.uni-halle.de

A novel class of symmetric amphi- and triphilic (hydrophilic, lipophilic, fluorophilic) block copolymers has been investigated with respect to their interactions with lipid membranes and monolayers. The amphiphilic triblock copolymer has the structure PGMA₂₀-PPO₃₄-PGMA₂₀ (GP). Its triphilic derivative is made by attaching perfluoroalkyl moieties to either end which leads to F₉-PGMA₂₀-PPO₃₄-PGMA₂₀-F₉ (F-GP). The perfluoroalkyl moieties have the tendency to phase segregate in aqueous as well as in an hydrocarbon environment.

By DSC and 2D NMR spectroscopy we could show that PPO and F₉ blocks insert into the hydrophobic part of the membrane concomitantly with PGMA block adsorption to the lipid headgroup layer. The F₉ chains act as additional membrane anchor. By fluorescence microscopy we could show that F-GP binding leads to leakiness of POPC giant unilamellar vesicles (GUVs), allowing the influx of water soluble dyes as well as the translocation of the complete triphilic polymer.

Using monolayer adsorption and compression experiments we show that the perfluorinated moieties enhanced the insertion of the polymers into lipid monolayers. Infrared Reflection Absorption Spectroscopy (IRRAS) shows that end cap fluorination leads to a more stable anchoring of the polymers within lipid monolayers and increases their squeeze out pressures significantly. Also the impact of polymer adsorption on the acyl chain order of lipid monolayers appeared to be higher for F-GP than GP.

In summary, the introduction of a fluorophilic moieties into amphiphilic polymers increases the interaction with lipid membranes and disturbs its barrier function.



Riboflavin bio-inspired amphiphiles: from physico-chemistry to biomedical applications

Nataliia Beztsinna, Axelle Grelard, Fabian Kiessling, Erick Dufourc, Isabelle Bestel

Riboflavin (RF) is an essential vitamin whose derivatives (FMN and FAD) participate in fundamental physiological events. RF also exhibits redox, photosensitizing and fluorescence properties.(1) Moreover, numerous preclinical studies indicate that RF is internalized through RF transporters, which are highly upregulated in prostate, breast cancer cells and neovasculature.(2,3) Taking into account particular physico-chemical properties of RF and its targeting efficacy, we assume that an amphiphilic RF derivative (ARF) could form innovative smart self-assembled nanosystems.

In this study we developed a versatile chemical strategy for the synthesis of ARF and prepared a candidate - RfdiC14. The ability of RfdiC14 to integrate model liposomal formulation was evaluated by NMR, DLS, TEM and Zeta potential measurements. The data indicate that RfdiC14 was easily incorporated into the lipid bilayer of DMPC:DMPG liposomes without significant influence on membrane fluidity, liposome size, charge, morphology or toxicity towards cells. Moreover, internalisation and competitive binding studies by fluorescence microscopy and FACS proved the targeting efficiency of RfdiC14 tagged liposomes towards several types of cancer cells (PC3, A431 and HUVEC). First NMR studies of RfdiC14 self-organization could suggest a hexagonal phase. To confirm these results DLS and cryo-TEM experiments are in progress.

Therefore, RfdiC14, a novel ARF, could be used as a versatile tool for functionalization of any amphiphile-based systems such as micelles, liposomes or lipid nanoparticles to ensure cancer cell targeting. Furthermore, RfdiC14 auto-assemblies could potentially create smart stimuli-responsive (redox or UVA irradiation) fluorescent nanosystems.

1. Northrop-Clewes CA et al. 2012;61(3):224–30.
2. Karande AA et al. Int J Cancer J Int Cancer. 2001 Sep 20;95(5):277–81.
3. Jayapaul J et al. Biomaterials. 2012 Dec;33(34):8822–9.

Presenting author - nataliia.beztsinna@u-bordeaux.fr

Vectorization Dynamics Between Amphiphilic Block Copolymer Micelles and Liposomes

L.M. Bravo-Anaya^{a,b}, J.F.A. Soltero^b, Y. Rharbi^a

^a*Univ. Grenoble Alpes, LRP, F-38000, Grenoble, France*

^b*Departamento de Ingeniería Química, Universidad de Guadalajara, 44430, Guadalajara, Jalisco, México*

monik_ayanami@hotmail.com

Nowadays, the specific delivery of active ingredients, known as vectorization, represents a great challenge in therapeutic research. This process has been used to control the distribution of active ingredients such as proteins, genes for gene therapy and drugs, to a target by associating it with a vector [1]. Molecules for chemotherapy are frequently hydrophobic and require vectorization to be transported to the target cell. Nevertheless, this controlled drug delivery suffers from a phenomenon called “burst release” as the drugs are released before their target [2]. Our main objective is to understand the exchange dynamics between vectors and cells via collective mechanisms, such as fusion/adhesion and exchange/separation. Understanding these dynamics becomes essential for the design and the control of new materials and new processes effective in drug delivery. Our study system is composed by liposomes representing cells, amphiphilic block copolymer micelles modeling the transporting vehicles and highly hydrophobic alkylated pyrene representing the active ingredient introduced into the micelles. Time scan fluorescence technique, which has been previously used to quantify the collective dynamics between amphiphilic block copolymer micelles [3], was used in this work to quantify the vectorization kinetics between micelles and liposomes. We first used different techniques such as dynamic light scattering (DLS) and zeta potential to characterize liposomes and block copolymer micelles and to explore liposome/micelles interactions. Then, we investigated the various parameters that control the collective vectorization dynamics from micelles to liposomes.

[1] G. E. Hildebrand, S. Harnisch, *Mod. Biopharm* **4**, 1361 (2005).

[2] S. D. Allison, *Expert Opin. Drug Deliv.*, **5**(6), 615-628 (2008).

[3] Y. Rharbi, *Macromolecules* **45**, 9823–9826 (2012).

Chitosan Influence in the Vectorization Dynamics Between Amphiphilic Block Copolymer Micelles and Liposomes

L.M. Bravo-Anaya^{a,b}, M. Rinaudo^c, J.F.A. Soltero^b, Y. Rharbi^a

^a*Univ. Grenoble Alpes, LRP, F-38000, Grenoble, France*

^b*Departamento de Ingeniería Química, Universidad de Guadalajara, 44430, Guadalajara, Jalisco, México*

^c*Biomaterials Applications, 6 rue Lesdiguières, 38000 Grenoble, France*

monik_ayanami@hotmail.com

Drug vectorization is a process whereby an active substance is introduced selectively at the location where it will perform the specific therapeutic action. As for chemotherapy, the used molecules are commonly hydrophobic and are transported to the target cell by using vectorization. However, in many of the controlled delivery formulations, an initial amount of drug is released before their target. This phenomenon, called “burst release”, brings negative effects pharmacologically dangerous [1]. Understanding the exchange dynamics between vectors and cells via collective mechanisms, such as fusion/adhesion and exchange/separation is essential for improving the efficiency on the controlled drug release processes. In this work, we used a model composed by liposomes representing cells, amphiphilic block copolymer micelles modeling the transporting vehicles and highly hydrophobic alkylated pyrene as the active ingredient introduced into the micelles. Liposomes were coated with a biocompatible and biodegradable polysaccharide: chitosan [2]. We selected several techniques such as dynamic light scattering (DLS), pH and zeta potential to characterize liposomes and micelles and to identify the chitosan influence on the interactions with them. Then, with a fluorescence technique that has been previously used for studying and quantifying the collective dynamics between different amphiphilic block copolymer micelles [3] we studied the chitosan influence on the vectorization dynamics between amphiphilic block copolymer micelles and liposomes. We performed a fluorescence time-scan study to monitor the monomer and excimer intensities of the alkylated pyrene, used as a fluorescent probe, from which it was possible to quantify the exchange rate of the dynamics and to explore the chitosan influence in controlling the collective mechanism.

[1] X. Huang and C. S. Brazel, *Journal of Controlled Release* **73**, 121–136 (2001).

[2] F. Quemeneur, M. Rinaudo, G. Maret and B. Pépin-Donat, *Soft Matter* **6**, 4471-4481 (2010).

[3] Y. Rharbi, *Macromolecules* **45**, 9823–9826 (2012).

Kappa-Casein: Self- and Mixed Association

Irina Portnaya, Sharon Avni, Ellina Kesselman, Rafail Khalfin, Uri Cogan, Dganit Danino

Milk is a complex colloidal system representing an emulsion of butterfat globules in a water-based solution, which contains the 50-500 nm colloidal assemblies called casein micelles. The micelles are composed of four casein proteins: alpha-s₁, alpha-s₂, beta (βCN) and kappa-casein (κCN) in mole ratio of about 4:1:4:1, respectively. βCN and the two alpha-caseins are embedded within the milk micelle interior, and the majority of the κCN is surface displayed. κCN is the main glycoprotein of cow's milk. It comprises a predominantly hydrophobic block at the N-terminal end, and a hydrophilic block at the C-terminal end. Therefore, like the other milk caseins, κCN is amphiphilic and self-assembles into core-shell micelles. κCN also self-organizes into filaments resembling amyloid fibrils. As was reported earlier [1], βCN is can limit κCN fibrillization. However, the mechanism of this effect is not yet clear. We examined the associative behaviour of κCN and its interactions with βCN as a function of temperature and time, with emphasize on the mechanism by which βCN inhibits κCN fibrillization. Isothermal titration calorimetry, cryogenic-transmission electron microscopy, ζ-potential measurements and small-angle x-ray scattering were employed in the study. Two modes of the κCN/βCN interactions were revealed: mixed micellization and adsorption of βCN species onto the fibrils. Both could result in inhibition of κCN fibrillization. We conclude that the thermodynamics of the mixed micellization is determined by κCN.

Thorn, D. C., et. al., *Biochemistry* **2005**, *44* (51), 17027-36.

portnaya@tx.technion.ac.il

Multicompartmental liposome aggregates: comparison of various methods of liposome aggregation

J. Hanuš, M. Ullrich, J. Haša, M. Živčáková, F. Štěpánek
University of Chemistry and Technology, Prague, Czech Republic

Frantisek.Stepanek@vscht.cz

Individual liposomes are used as encapsulating agents for various drug molecules¹. Their usual mode of action is passive release of the encapsulated substance, although some attempts to control the release have also been made. Our group used concept of alginate microparticles containing both liposomes and magnetic nanoparticles². Quite unexplored however is the possibility to create and use the liposome aggregates as either the encapsulating agent, either as chemical microreactors.

We have tested the effect of high salt concentration to the formation of liposome aggregates. The size and morphology of aggregates was controlled by precise selection of salt concentration, aggregation time and eventual use of wrapping polymer. We can prepare aggregates with sizes varying from hundreds of nanometers to tenths of micrometers.

Another way of liposome aggregation is the use of electrostatic interaction between charged liposomes and polymer with opposite charge³. We used such charged biopolymers as alginate or chitosan and studied encapsulation of model drug to the aggregates.

Last part of the puzzle are the active agents such as iron oxide nanoparticles that can be included in the aggregate and influence the size and morphology of the assembly but above all its functional properties.

- 1) Musacchio, T.; Torchilin, V. P., Recent developments in lipid-based pharmaceutical nanocarriers. *Front. Biosci.* **2011**, 16, 1388-412.
- 2) Hanuš J., Ullrich M., Dohnal J., Singh M., Štěpánek F., Remotely controlled diffusion from magnetic liposome microgels, *Langmuir* **2013**, 29, 4381-4387
- 3) Cametti C., Polyion-induced aggregation of oppositely charged liposomes and charged colloidal particles: the many facets of complex formation in low-density colloidal systems. *Chemistry and physics of lipids*, **2008**, 155.2: 63-73.

Double chain surfactants from arginine: Aggregation behaviour, antimicrobial activity and cytotoxicity

L. Pérez^a, A. Pinazo^a, V. Petrizzelli^a, M. Bustelo^a, R. Pons^a, M.P. Vinardell^b, M. Mitjans^b, A. Manresa^c

^aDepartment of Chemical and Surfactants Technology. IQAC. CSIC. Spain

^bDepartment of Fisiology, Barcelona University. Spain.

^cDepartment of Microbiology, Barcelona University. Spain.

ramon.pons@iqac.csic.es

Cationic double chain surfactants have attracted much interest because they can give rise to cationic vesicles that can be used in biomedical applications. Using a simple and economical synthetic approach, we have synthesized five arginine-based cationic surfactants, one single chain derivative (LAM) and four double chain surfactants with different alkyl chain lengths (LANHC_x) (Figure 1). The critical aggregation concentration of the double chain surfactants is at least one order of magnitude lower than the CMC of LAM and the solutions prepared with the LANHC_x contain stable cationic vesicles. These new arginine derivatives show low hemolytic activity and weaker cytotoxic effects than conventional dialkyl dimethyl ammonium surfactants. In addition, the surfactant with the shortest alkyl chain exhibits good antimicrobial activity against Gram-positive bacteria. The results show that a rational design applied to cationic double chain surfactants might serve as a promising strategy in the development of safe cationic vesicular systems.

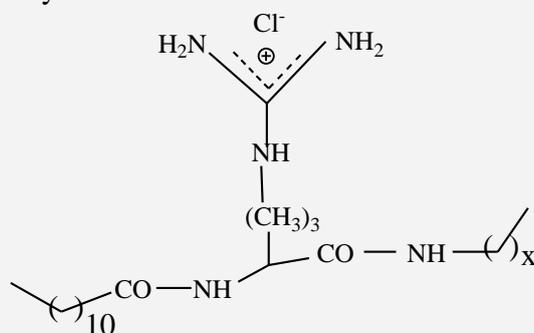


Figure 1. Chemical structure of double chain arginine surfactants LANHC_x (X= 9, 11, 13)

Acknowledgements: Authors acknowledge the financial supports by the National MINECO grants MAT 2012-38047-CO2-02 and CTQ2013-41514-P. Also thanks to Unidad Asociada CSIC-UB "Interacción de tensioactivos con membranas celulares".

Chitosan Hydrogels and Films Formed with Nanoparticles in Self-Assembly Regime

Irina Postnova,^a Yury Shchipunov,^b

^a *Far-East Federal University, 6900950 Vladivostok,*

^b *Russia Institute of Chemistry, Far East Department, Russian Academy of Sciences, 690022 Vladivostok, Russia*

^c *Pusan National University, Busan, Korea*

YAS@ich.dvo.ru

Chitosan as a weak polyelectrolyte can be in the charged/uncharged state that depends on the solution pH. It has been used in our approach for fabrication of its bionanocomposites [1]. Chitosan is dispersed in a solution of nanoparticles at a pH a little larger than its pK_a value at which it is non-charged and insoluble. Polysaccharide is transformed into the charged state by a progressive acidification of solution by addition of gluconolactone. When charging, chitosan is involved in situ in instant electrostatic interactions with oppositely charged nanoparticles. Only gradual pH shift provides the formation of homogeneous material, whereas common mixing of a solution of chitosan in the charged form with another one containing negatively charged counterparts or a sharp pH change causes the heterogeneous precipitation.

Chitosan bionanocomposites were prepared with nanoparticles of various origin and geometry – platelets of clay saponite and oxidized graphene, fibrils of clay sepiolite and oxidized multiwall carbon nanotubes. Both hydrogels and free-standing films were prepared. Their formation caused by the gradually increased interactions of oppositely charged counterparts proceeded in the self-organizing regime. The jellification resulted from an ordered three-dimensional network of various morphology. Fibrillar, plate-like and globular-like nanostructures were found. Films had pronounced stratified layer (nacre-like) structure from stacked nanoparticles and aligned chitosan macromolecules. Bionanocomposites thus prepared were well examined by various physico-chemical techniques including dynamic rheology, dynamic mechanical analysis, scanning and transmission electron microscopy, wide and small-angle X-ray scattering, NMR and FTIR spectroscopy that allowed to suggest a mechanism of self-organization at nanoscopic level.

References

1. Y. Shchipunov, N. Ivanova, V. Silant'ev, *Green Chem.* 2009, 11, 1758

Self-Assembly of Nanotubes Formed by Short Amphiphilic Peptides

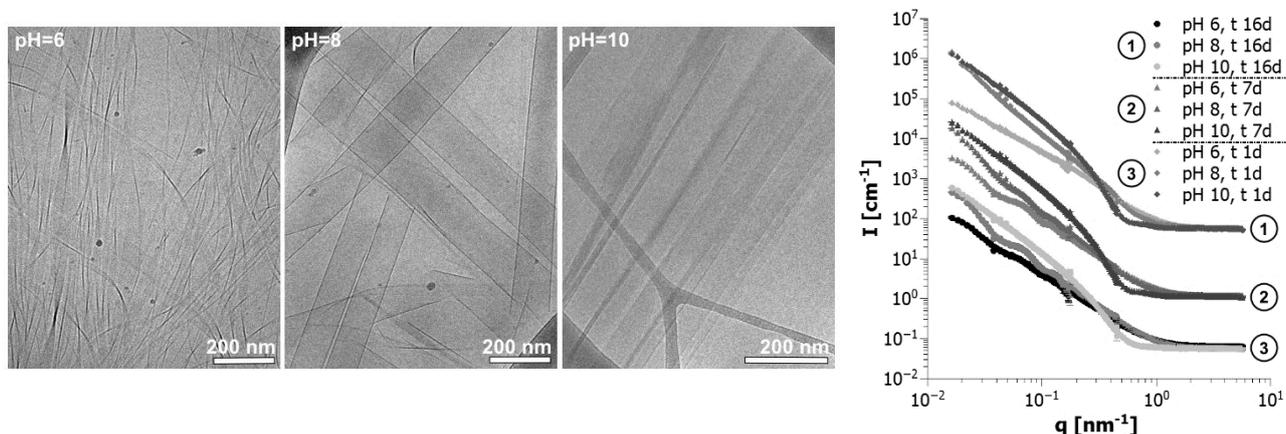
Kathrin Voigtländer^{1,*}, Isabelle Grillo², Luba Kolik³, Michael Gradzielski¹, Dganit Danino³

¹Technische Universität Berlin
Institut für Chemie - Stranski-Laboratorium für Physikalische und Theoretische Chemie
Straße des 17. Juni 124, Sekr. TC 7
10623 Berlin, Germany

²Institute Laue-Langevin
71 Avenue des Martyrs
38000 Grenoble, France

³Technion - Israel Institute of Technology
Department of Biotechnology and Food Engineering
Haifa 32000, Israel

Our goal is to enhance the grasp of the nanotubule self-assembly process by studying the behavior of short synthetic amphiphilic peptides (SAPs, synthesized from amino acids and fatty acids) in aqueous solutions combining different techniques like scattering methods (SLS/DLS, SANS, SAXS), AFM and direct-imaging methods like (cryo-)TEM. So far the self-assembly of the SAP K:C₁₂-β₁₂ (*N*-α-lauryl-lysyl-aminolauryl-lysyl-amide) has been studied to some extent [1]. It self-assembles into stable nanotubes of great length (up to several μm) and a diameter of 70-100 nm by progressing from long thin fibers via twisted and helical ribbons to nanotubes [2]. Recently we have been studying the influence of additives like copolymers (e.g. poloxameres) and the systematic molecular variation of the SAP K:C₁₂-β₁₂ on the self-assembly process and its kinetics in order to determine how this process (formation of nanotubes/ fibrils) can be modulated and controlled in a systematic way. In ongoing studies the effect of different solvent systems as well as changes in pH etc. on the self-assembly of different SAPs and the properties of their self-assembled nanostructures is to be determined.



[1] L. Ziserman, A. Mor, D. Harries, D. Danino, *Phys. Rev. Lett.* 2011, 106, 238105.

[2] L. Ziserman, H.Y. Lee, S.R. Raghavan, A. Mor, D. Danino, *J. Am. Chem. Soc.* 2011, 33, 2511.

*kathrin.voigtlaender@tu-berlin.de

Neutron Scattering Characterization of Micelles of Heptaethylene Glycol Monododecyl Ether C12E7 in Dilute Aqueous Solutions

A. Rajewska^{a,b}

^a*National Centre for Nuclear Research, Swierk-Otwock, Poland*

^b*Joint Institute for Nuclear Research, LNP, Dubna, Russia*

Presenting author's email: zaldona24@hotmail.com

The classic surfactant in aqueous solutions - non-ionic of heptaethylene glycol mono dodecyl ether C₁₂E₇ was investigated by SANS technique for three concentrations (0.17%, 0.5%, and 1%) and temperature range 10^o-35^oC. Measurements have covered Q range from 8x10⁻³ to 0.4 Å⁻¹. For the measurements quartz cells of thickness 2 mm were used. Up to 15 such cells were placed in a sample holder, and the temperature within the cells was kept constant in a range of ± 0.5^oC . For all samples D₂O was used as solvent in order to achieve good contrast conditions. The SANS results were successfully analysed with the package PCG 2.1. It was obtained as the result the size and shape of micelles in aqueous dilute solutions. The shape and size of aggregates depending on surfactant concentration and temperature.

Dynamic Behavior of Hyperbranched Polyelectrolyte/Surfactant Mixtures at Static and Expanding Air/Water Interfaces

Richard A. Campbell,^a Anna Angus-Smyth,^{a,b} Marianna Yanez Arteta,^c Erik Watkins,^d Marc Obiols-Rabasa,^c Karin Schillén,^c Tommy Nylander,^c Imre Varga,^e Colin D. Bain^b

^a*Institut Laue-Langevin, Grenoble, France*

^b*Department of Chemistry, Durham University, Durham, UK*

^c*Division of Physical Chemistry, Lund University, Lund, Sweden*

^d*Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, USA*

^e*Institute of Chemistry, Eötvös-Loránd University, Budapest, Hungary*

campbell@ill.eu

A great effort has been invested over the years to understand the properties of mixed formulations at the air/water interface due to their many applications. Knowledge of the equilibrium (fixed surface area [1]) and dynamic (changing surface area [2]) properties are key to understanding how the products we use every day really behave. An understanding of polyelectrolyte/surfactant (P/S) mixtures at the air/water interface is additionally challenging as various complex processes mean that these systems can be far from equilibrium even when the surface is static [3].

We have studied the dynamic interfacial properties of poly(ethylene imine)/sodium dodecyl sulfate (PEI/SDS) mixtures on an overflowing cylinder [4]. Surprisingly, we found that the delivery of material to the interface can be dominated by the dissociation and spreading of aggregates transported from the bulk as opposed to the diffusion and adsorption of small complexes – which is normally assumed. We went on to study the static interfacial properties of poly(amido amine) dendrimer/SDS (PAMAM/SDS) mixtures and drew clear parallels [5]. Here the bulk phase behavior determined the retention of macroscopic aggregates at the interface versus their dynamic dissociation.

Further work is needed to understand better the static and dynamic properties of the mixtures that control the interfacial behavior of the daily products we use. We have shown that a simple extrapolation of the static interfacial behavior may miss the underlying dynamic behavior completely, and that more involved processes than the diffusion and adsorption of small complexes can control the interfacial properties.

[1] J. Penfold et al. *Langmuir* 2005, 21, 10061.

[2] C. D. Bain. *Adv. Colloid Interface Sci.* 2008, 144, 4.

[3] R. A. Campbell et al. *Langmuir* 2014, 30, 8664.

[4] A. Angus-Smyth et al. *Soft Matter* 2013, 9, 6103.

[5] M. Yanez Arteta et al. *J. Phys. Chem. B* 2014, 118, 11835.

Molecular weight effects on the growth and decay kinetics of Pluronic micelles

A. Arranja*, G. Waton, F. Schosseler, E. Mendes

The dynamics of block copolymer micelles in selective solvent of one block after temperature steps (T-steps) has been the subject of intensive work in the past two decades [1]. In this work, we studied the growth and decay kinetics of dilute Pluronics micelles in brine (2M NaCl) after T-steps by time resolved photon correlation spectroscopy.

Pluronics are commercial $EO_x-PO_y-EO_x$ copolymers (where EO=ethylene oxide and PO=propylene oxide) that form micelles with a PO core in aqueous solutions. Three copolymers with increasing molecular weight and the same EO/PO composition constant (P84, P94 and P104) were selected.

We observed that the growth and decay of the micellar aggregates depended markedly on the molecular weight of the copolymer and followed distinct kinetic pathways.

The smaller P84 copolymer displays a fast adjustment of the average size of the micellar aggregates after T-jumps followed by a much slower equilibration of the number of elongated micelles. This behavior is consistent with a unimer exchange for the first step and a fusion/fission for the second step.

The P94 and P104 copolymers show a continuous growth of the micellar aggregates above a critical temperature. The size and the number of P94 micelles only equilibrate through fusion/fission mechanisms. For P104, the relatively large increase in molecular weight prevents the rearrangement of the PEO shell in the final steps of the fusion/fission processes and only aggregation without elongation is observed.

Upon cooling the solutions down to the spherical micelles regime, the wormlike micelles made from P84 return very rapidly to spherical micelles, while P94 and P104 solutions stay for very long times in their high temperature state.

[1] A.G. Denkova, E. Mendes, M.O. Coppens, *Soft Matter*, 2010, 6:2351–2357.

*Presenting author email: alexandra.arranja@ics-cnrs.unistra.fr

Design of Molecular Organized Media Based on Oligo(Ethylene Oxide) Derivatives of Different Nature

Selivanova N.M.¹, Galyametdinov Y.G.¹

¹*Kazan National Research Technological University, Kazan, Russia
natsel@mail.ru*

Increased interest to lyotropic liquid crystal systems (LLC) is caused by that processes of self-organizing, their underlying formations, are used in nanotechnology and bioengineering. Supramolecular assemblies of metal complexes in anisotropic LLC phases are of great interest and provide new promises in today's materials science. The combination of anisotropic LC properties and electrical, magnetic and optical characteristics of a metal ion suggest great potential for the design of new multifunctional materials. In this work we present data of structure organization and liquid crystal properties lyotropic lanthanide containing (La^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+}) systems based on oligo(ethylene oxide) derivatives several types of compounds: nonionic surfactants with various EO chain lengths $\text{C}_{12}\text{EO}_{10}$, C_{12}EO_4 , amphiphiles oxietheleted calyx[4]arenes CalEO_{10} , CalEO_{16} and cholesteryl oligo(ethylene oxide) amphiphiles CholEO_{10} , CholEO_{17} . Liquid crystal and thermal properties, structure parameters of lanthanide containing LLC were established by methods of POM, DSC and SAXS. Phase diagrams for ternary systems $\text{C}_{12}\text{EO}_n/\text{Ln(III)}/\text{H}_2\text{O}$ were drawn. For design a new lyotropic liquid crystal mesophases the amphiphilic calixarenes oxyethylated at a lower rim have been used. The formation of $\text{CalEO}_n\text{-Ln(III)}$ complexes is probably due to the interaction of the electron donor polyoxyethylene chains located at the lower rim of the cavity with lanthanum cations. The systems on the basis of $\text{CalEO}_{10}/\text{Ln(III)}/\text{H}_2\text{O-C}_2\text{H}_5\text{OH}$ and $\text{CalEO}_{16}/\text{Ln(III)}/\text{H}_2\text{O}$ form hexagonal mesophases in wide concentration and temperature region. Lyotropic liquid crystals based on cholesteryl oligo(ethylene oxide) amphiphiles and Ln(III) ions were synthesized. For binary systems $\text{CholEO}_{10}/\text{Ln}$, $\text{CholEO}_{17}/\text{Ln(III)}$ the smectic phases were obtained. In ternary systems in the present of water the lyotropic polymorphism were observed.

Acknowledgement: N.S. thanks to the grant of RFBR (14-03-00109), Yu.G. thanks to the grant of RSF (14-13-00758).

Microrheological analyses for dairy formulations

R. Ramsch, G. Brambilla, M. Fleury, G. Meunier

Dr. Roland Ramsch, Formulaction, 10 impasse Borde Basse, 31240 L'Union, France

This work presents studies on yoghurt preparation using microrheology. Passive microrheology studies the mobility and displacement of micron sized particles which results from Brownian motion [1]. The motion of particles induces local deformations of the sample, which are directly related to its viscoelastic properties.

Our technique is based on Multi Speckle Diffusing Wave Spectroscopy (MS-DWS), which consists of Dynamic Light Scattering (DLS) extended to an opaque media. With a patented algorithm, the backscattered interfering light can be analysed in terms of Mean Square Displacement (MSD), which is directly related to the viscoelastic properties of a sample. Moreover, the optical method allows to study especially weak gels without any applied shear, which avoids perturbation of the sample.

Nowadays, yogurt formation has caught much attention, as it is a growing market. The choice of proteins and other components are very important. This work shows how passive microrheology can be used to follow up yoghurt preparation and the influence of proteins type and content on the gelation time, and the viscoelastic properties of the yogurt. Gel time was determined by a new rescaling method, namely Time-Cure Superposition (TCS) [2,3]. This data processing determines the gel point according to the Winter-Chambon criterion [4].

[1] D. A. Weitz, D. J. Pine, in: *Dynamic Light Scattering*, W. Brown (Ed.) (Oxford Univ. Press, New York, 1993), Chap. 16

[2] T. H. Larsen, E. M. Furst, *Phys. Rev. Letters*, **2008**, *100*, 14600

[3] K. M. Schultz, E. M. Furst, *Soft Matter*, **2012**, *8*, 6198

[4] H. H. Winter, F. Chambon, *J. Rheology* **1986**, *30*, 364-382

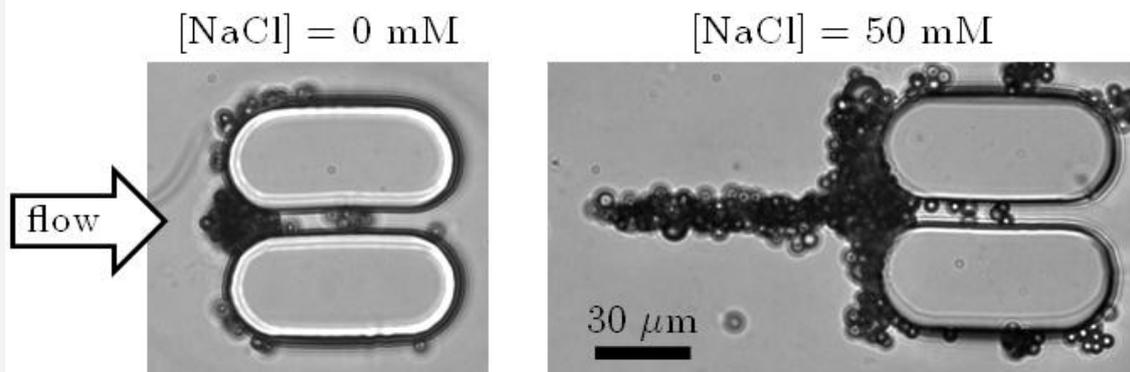
Colloid Accumulation under Confined Flow

M. Robert de Saint Vincent^a and H. Tabuteau^a

^a *Institut de physique de Rennes, UMR 6251, CNRS, Université Rennes 1, Rennes, France*

rdsv.matthieu@gmail.com

Colloidal suspensions are ubiquitous in many natural (geophysical fluids, blood...) and industrial (muds, concrete...) processes. When a flowing suspension is confined, colloidal interactions compete with the hydrodynamic drag, which may thus lead to the formation of aggregates through a jamming-like transition. Using microfluidic tools, we investigate at the pore scale the flow-driven accumulation of colloids on porous solid structures. This accumulation starts with the deposition of particles over the pore walls due to the prevalence of the particle-wall attraction over the interparticle one. This first layer increases the confinement and therefore alters the local hydrodynamics, favouring by this way the deposition of additional particles on the deposited layer. Due to the interplay between cohesive or steric interactions on the one hand, and hydrodynamic drag on the other hand, the dynamics of aggregate growth alternatively follows two regimes: (i) deposition limited by the flow (erosion or spatially selective growth), and (ii) continuous growth. The structure then stabilises to an equilibrium shape according to its growing mode. A rich phase diagram rationalises the observed shapes.



Colloidal aggregates growth onto a porous obstacle. Ionic strength: 0 mM (left), 50 mM (right).

Dynamic Adsorption Behavior of Lung Surfactant Components and Effect of Fibrinogen on the Process

G. Dilli Alp, N. Aydoğan

Hacettepe University, Department of Chemical Engineering, Ankara, Turkey

gdilli@gmail.com

Characterization of dynamic adsorption behavior of various kinds of surfactants and proteins is important in many applications. Respiration, a vital phenomenon for us to sustain our lives, is also a naturally occurring dynamic process. It takes place via the adsorption/desorption of the lung surfactant mixture composed of lipids and proteins [1]. To develop a clear understanding of this mechanism, investigation of the parameters that affect this dynamic process should be done carefully. In this study, short-time and long-time dynamic adsorption behaviors of natural lung surfactant component (DPPC) and a model mixture (Infasurf®) and IPL ($\text{CF}_3(\text{CF}_2)_7\text{SO}_3^- (\text{CH}_2\text{CH}_3)_3\text{N}^+(\text{CH}_2\text{OCH}_2)_{10}(\text{CH}_2)_{15}\text{CH}_3$) are investigated. IPL is a novel lipid synthesized by our group, which can mix with DPPC and mimic the selected properties of lung surfactant protein B. The results show that due to its unique structure, IPL is a fast adsorbing surfactant when compared to model mixture. In addition, the competitive adsorption behaviors of these surfactants in the presence of fibrinogen are studied. Upon the introduction of surfactant and fibrinogen to the same phase simultaneously, surfactant inactivation is investigated. This phenomenon is considered as a model for of Adult Respiratory Distress Syndrome. From the results of these experiments, it is obtained that IPL manages to retard the time necessary for fibrinogen to be active and dominate the interfacial behavior. Whereas the presence of pre-adsorbed DPPC or Infasurf at the interface will not create any retardation effect. The results support that IPL is a powerful candidate that can be used for speeding up the adsorption of lung surfactant lipids and reducing the surfactant inactivation by its ability to resist to fibrinogen adsorption.

[1] Zuo et al., *Biochimica et Biophysica Acta*, 2008.

Rheology of well controlled model flocculated suspensions

J. Fusier^a, J. Goyon^a, F. Toussaint^b, X. Chateau^a
^a*Laboratoire Navier UMR 8205, Champs sur Marne, France*
^b*Lafarge Research Center, Saint Quentin Fallavier, France*

jennifer.fusier@ifsttar.fr

Suspensions of colloidal particles are encountered in many fields from food industry to civil engineering. They are of interests because of their complex behaviour coming from the interplay between attractive, repulsive interactions and particle microscopic properties.

This works aims to understand and describe, at different scales, flocculation process which occurs in fresh cement pastes. As in real system diversity in sizes, shapes, chemical constituents combined with chemical reaction in time make the system hard to control; we chose to work with model suspensions. We use two different particles: micrometric monodisperse spherical silica particles synthesized via Stöber process and crushed silica particles (quartz), both of them suspended in aqueous solution.

In these systems, flocculation is mainly controlled by adjustment of electrostatic repulsive amplitude through salt addition in the aqueous solution (i.e change in ionic strength). We also vary volumic fraction, particle size and since the suspensions are thixotropic we follow structuration for several rest time.

Yield stress and elastic modulus of the suspensions were measured as function of the parameters of the suspensions. We observe that both the yield stress and the elastic modulus are increasing function of the rest time, the particle concentration and the ionic strength. In addition, when plotting elastic modulus against yield stress a single curve is obtained for each kind of material, whatever the volumic fraction, the rest time or the ionic strength.

We also obtain a master curve for different sizes of silica suspensions when rescaling the yield stress with particle size squared and the elastic modulus with particle size.

.

Diffusion of small polyelectrolytes in crowded media

C. Dolce, G. Mériquet

Sorbonne Universités, UPMC Univ Paris 06, UMR 8234, PHENIX, F-75005, Paris, France.

CNRS, UMR 8234, PHENIX, F-75005, Paris, France.

caterina.dolce@upmc.fr

Polyelectrolytes have a widespread use in several formulations and processes. They are present in complex mixtures in industrial, household and personal care products. So far, despite numerous studies on polyelectrolytes (1), there is still a paucity of information on the dynamics of short polyelectrolytes in these complex mixtures. In this work, we focus on the dynamics of such polyelectrolytes in crowded media. The diffusion in crowded media is a phenomenon occurring in various contexts, ranging from dynamics of the complex diffusion behaviour of the DNA to diffusion in crowded cellular environments (2).

Beyond the excluded volume of the obstacles, the pH of the solvent can change the charge properties of the system that alter the electrostatic interactions, hence the hindrance of the obstacles to the diffusion of the polyelectrolytes.

To investigate these effects, an experimental system made of dispersions of short polyelectrolytes (sodium polyacrylate, PAANa) in water solutions and charged nanoparticles (silica) is used (3). Both are negatively charged and the charge is adjusted with the pH. The self-diffusion of the polyelectrolyte was investigated with using nuclear magnetic resonance diffusion experiments (4).

The first results show a significant decrease in the diffusion of the PAANa with the pH and also in the presence of negative charged obstacles. The addition of monovalent salt, at constant pH, causes an increase in the diffusion coefficients at low volume fraction of obstacles. A future step of this work is the comparison of these results with computer simulations (5).

(1) A. Dobrynin et al. *Progr. Polym. Sci.* 2005, 30, 1049.

(2) J. Huang et al. *Polymer.* 2006, 47, 2928.

(3) C. Flood et al. *Langmuir* 2007, 23, 6191.

(4) W. S. Price et al. Cambridge University Press, 2009.

(5) G. G. Putzel et al. *Phys. Rev. Lett.* 2014, 113, 138302.

Simulation of structure and rheology of a chain-forming ferrocolloid

D. Zablotzky,^{a,b} E. Blums,^b H.J. Herrmann,^a ...

^a *Computational Physics for Engineering Materials, IfB, ETH Zurich, Stefano-Franscini-Platz 3, CH-8093 Zurich, Switzerland*

^b *Institute of Physics, University of Latvia, 32 Miera iela, Salaspils, LV-2169 Latvia*

e-mail: dmitrijs.zablockis@gmail.com

The emerging applications of ferromagnetic colloids in biomedicine - in magnetic drug targeting, magnetic hyperthermia or imaging - require the understanding of the rheology of these materials in living tissue, i.e. in permeable structures and membranes, in the conditions of the simultaneous influence of shear flow and magnetic field. It is known from previous studies that the ferrocolloids show strong magnetoviscous effect – the dependence of their viscosity on the magnetic field. The presence of relatively minor amount of magnetic nanoparticles can lead to a dramatic increase of the shear viscosity by up to several orders of magnitude [1-3].

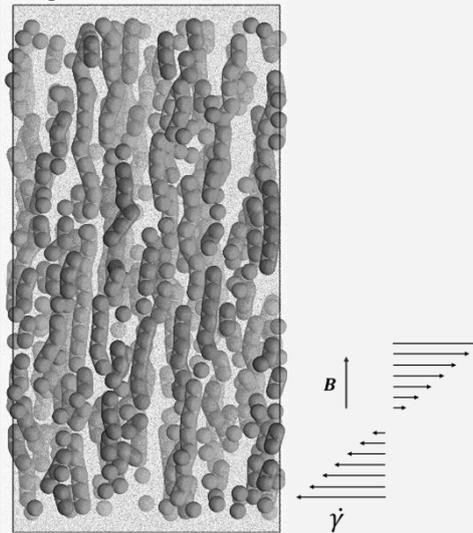


Fig. 1. Simulation snapshot: structure of the ferrocolloid under shear and vertical magnetic field.

We will present the results of numerical simulations of the structure and rheology of ferromagnetic colloids in the presence of magnetic field. Using molecular dynamics and stochastic rotation dynamics we observe the assembly of suspended magnetic nanoparticles in linear chains (Fig. 1) due to strong dipole-dipole interaction and the eventual destruction of chains under shear flow. We determine the shear viscosity of the colloid, which shows significant shear thinning owing to the change of internal structure. Finally, we will present a quantitative comparison of our results with theoretical models and some of the experimental data published by different groups over the previous years.

[1] J. Nowak et al., *JMMM* 354, 98 (2014)

[2] M. T. Lopez-Lopez et al., *Langmuir* 28, 6232 (2012)

[3] D. I. Santiago-Quinonez et al., *Soft Matter* 8, 5327 (2012)

Effect of Microchannel Bottleneck Shape on the Clogging Dynamics in Microfluidic Filters

Z.B. SENDEKIE^{a,b}, P. BACCHIN^{a,b}

^aUniversité de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 118
Route de Narbonne, F-31062 Toulouse, France

^bCNRS, UMR 5503, F-31062 Toulouse, France

Presenting author's email: zenamar23@gmail.com

The pore clogging phenomena is of importance in many fields of science and engineering [1]. This work investigates the pore shape influence on the local interplay between hydrodynamics and colloidal interactions at pore entrance with a real time visualization at pore scale in microfluidic filters designed with different pore entrance geometries. 2.3 and 5 μm monodisperse polystyrene particles are used and the flowrate and the pressure are monitored with time.

The results show that the clogging depends on the pore shape. In all cases, an opening angle at pore entrance favors the clogging transition; this effect being more pronounced for the microparticles dispersed in 0.1 M KCl (where the repulsion are partially screened). These results are discussed at the light of the interplay between colloidal interactions and hydrodynamics. The arches formed at low ionic strength are very robust and dense, and they are reinforced by the opening angle leading to a more rapid decrease in permeability. At high ionic strength, the clogging is controlled by the fragility of the arches that are frequently broken and swept out and the square corners favor this phenomena leading to a clogging retardation. The worst conditions are reached when combining high frequency for arches formation (at high ionic strength when the collision efficiency is higher) and durable arches (with an opening angle increasing the arches robustness). These results will be further analyzed with additional data on the deposit hydraulic resistance and on the deposit relaxation when the flow is stopped.

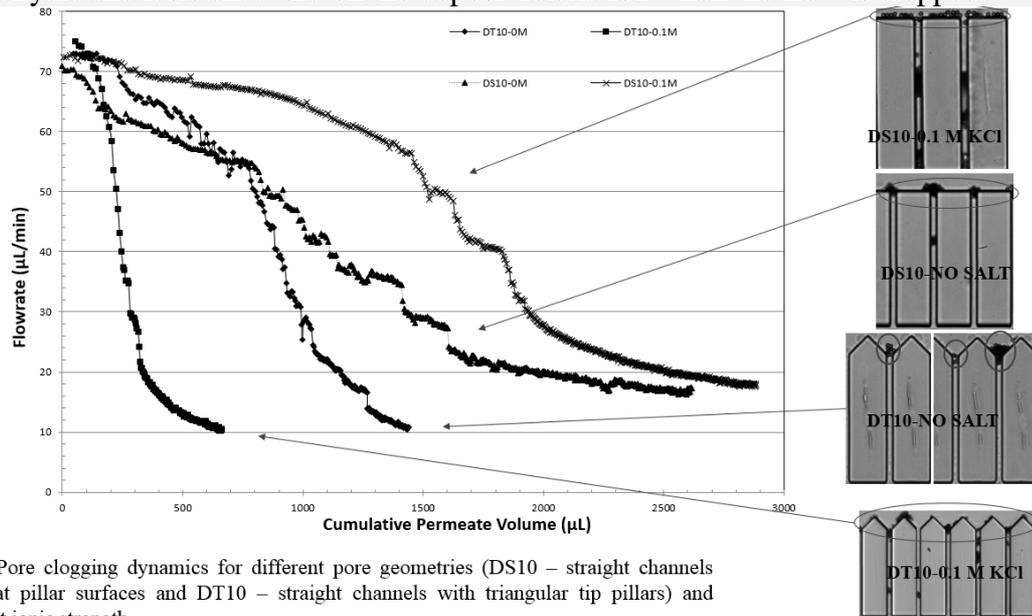


Fig 1: Pore clogging dynamics for different pore geometries (DS10 – straight channels with flat pillar surfaces and DT10 – straight channels with triangular tip pillars) and different ionic strength

[1] Zuriguel, I. et al. Clogging transition of many-particle systems flowing through bottlenecks. *Sci. Rep.* 4, 7324 (2014)

Rheo-SAXS on Colloidal Platelets Probed at the Flow-Gradient Plane

O. Korculanin^a, H. Hirsemann^b, B. Struth^c, G. Portale^d, M. P. Lettinga,^e

^{a,e}*ICS-3, Forschungszentrum Jülich, Jülich, Germany*

^{b,c}*DESY, Hamburg, Germany*

^d*Dubble, ESRF, Grenoble, France*

o.korculanin@fz-juelich.de

Dispersions of colloidal Gibbsite platelets in the nematic phase display a complex response to Large Amplitude Oscillatory Shear flow (LAOS) which strongly depends on the strain amplitude. [1] In this work we applied Large Amplitude Oscillatory Stress to the nematic dispersion and probed the structure with time-resolved SAXS measurements. By using plate-plate and couette geometry, we had access to both the flow-vorticity and flow-gradient plane, respectively.

We show an extreme example where the response of the nematic dispersion becomes highly asymmetric while it remains linear. This in contrast to strain controlled LAOS, which converges to a symmetric but non-linear response.

The couette geometry enables us to identify the underlying microscopic cause of the rheological response, which is the tilting of the director with respect to the gradient direction. By varying the stress amplitude to study the yielding rocking motion of the platelets, we observed that the response becomes more symmetric; however, this strongly depends on the frequency, hence the time necessary for the system to yield.

References

1. M. P. Lettinga, P. Holmqvist, P. Ballesta, S. Rogers, D. Kleshchenok, and B. Struth. Non-linear behavior of colloidal platelets in shear flow. *Phys. Rev. Lett.*(2012) Vol. 109, 246001.

Dynamics of cationic surfactant-DNA complex formation

R. Pons^a, J. Morros^a, J. Caelles^a, I Carrera^a, L. Pérez^a, A. Pinazo^a, A. Mezei,^b
^a*Institut de Química Avanzada de Catalunya IQAC-CSIC, Barcelona, Catalonia*

ramon.pons@iqac.csic.es

When contacting a solution of cationic surfactant with the oppositely charged DNA, precipitation occurs. In the right concentrations, this precipitation can lead to the formation of closed films, forming particles which can reach up to few millimetres. Our objective was to determine the kinetics of formation of such films as well as their microstructure. To investigate the kinetics we formed the precipitate in a planar configuration, that is, we contact the two solutions in a vertical capillary and we will follow the X-ray scattering as a function of height and time. The experiments were performed at the Non Crystalline diffraction beamline at ALBA Synchrotron. We performed experiments changing the surfactant chemical structure (using off the shelf surfactants as well as home synthesized lipopeptide surfactants) as well as by changing control variables like concentration of DNA and surfactants solutions. Results on the kinetics of formation of the precipitate allow comparison with observations performed when preparing DNA-cationic surfactant particles.

Magnetorheology of hybrid colloids measured by spin coating and classical rheometry

R. Aslam¹, J. de Vicente² and W. González-Viñas¹

¹*Dept. of Physics and Appl. Math., University of Navarra, Pamplona, Spain*

²*Department of Applied Physics, University of Granada, Spain*

rmuhammad@alumni.unav.es

Hybrid colloids composed of micron-sized ferromagnetic and diamagnetic particles constitute a promising category of magnetorheological fluids with enhanced field-induced apparent yield stress [1]. However, the physical mechanism explaining this stress enhancement is currently lacking. For the first time, we measure and compare the magnetic field-dependent viscosity of hybrid diluted colloids of carbonyl iron+silica in cyclohexanone using spin-coating [2] and magnetorheometry [3]. In the former technique, a magnetic field is applied during the spin coating of the colloidal suspension involving evaporation of the solvent. The viscosity of the colloidal suspension at applied field can be derived from the surface coverage of the dry spin-coated deposits and from the viscosity of the colloid at zero field. In the latter, we also measure the viscosity of the same suspension with a torsional parallel plate magnetorheometer under uniaxial magnetic fields aligned in the gradient direction of a steady shearing flow. The experimental results under different conditions and the effect of each component on the magnetorheological properties of the resulting colloid will be discussed.

[1] Ulicny, J C et al., *Appl. Phys. Lett.* 2010, 96, 231903

[2] M. Pichumani et al., *Soft Matter*, 2013, 9, 3220-3229

[3] de Vicente *et al.*, *Soft Matter*, 2011, 7, 3701-3710

A comprehensive toolbox for thermodynamic and kinetic analysis of ligand adsorption at colloidal surfaces

W. Lin,^a J. Walter,^a M. Haderlein,^a A. Burger,^b H. Maid,^b A. Hirsch,^b W. Peukert^a,
D. Segets^a

^a*Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU),
Erlangen, Germany*

^b*Institute of Organic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU),
Erlangen, Germany*

Doris.Segets@fau.de

Although being of major importance for various particle-based applications, the creation of colloidal surfaces with tailored properties is a still open and demanding question. Quantitative routines to analyze both, thermodynamics and kinetics of ligand adsorption are largely missing. To address this issue, we established a general approach by means of catechols binding to 4.1 nm ZnO quantum dots. Catechols were chosen due to the fact that they have emerged as promising anchor group for ZnO QDs when they are applied in dye-sensitized solar cells.

For thermodynamic analysis, the heat of adsorption was measured by isothermal titration calorimetry and all relevant parameters, namely association constant, enthalpy, entropy and free energy of ligand binding were extracted. The free energy was cross-validated by mass-based adsorption isotherms and analytical ultracentrifugation. The latter was applied to detect the amount of free, unbound catechol in the supernatant. Finally, Raman and nuclear magnetic resonance spectroscopy were performed to quantify the replaced amount of the original acetate ligand with catechol (65%) and to distinguish chemi- from physisorption.

Finally, adsorption kinetics were analyzed by stopped-flow UV/Vis spectroscopy. No static absorbance feature was used but the recorded spectra were deconvoluted into contributions of bound and free catechol. Noteworthy, no adsorption model needed to be assumed as the concentrations of chemi- and physisorbed catechol were directly obtained.

Our concept is flexible, widely applicable and – due to the careful cross-validation by independent methods – can be realized with much less effort for any future study. Our work gives quantitative access to ligand binding which is of paramount importance for knowledge-based surface design.

[1] V. Lesnyak *et al.*, Chem. Soc. Rev **2013**, 42, 2905-2929

[2] A.J. Morris-Cohen *et al.*, Chem. Mater. **2012**, 25, 1155-1165

[3] D. Segets *et al.*, ACS Nano **2009**, 3, 1703-1710

[4] W. Lin *et al.*, Chem. Mater. **2015**, 27, 358-369

Wet granular matter under shear

Laurent Gilson, Jennifer Wenzl, Günter K. Auernhammer
Max Planck Institute for Polymer Research, Physics at Interfaces, Mainz, Germany
auhammer@mpip-mainz.mpg.de

We will present a detailed experimental study on the shear zone formation in wet granular matter. Here, we focus on the influence of liquid droplets on the trajectories of the particles. We imaged and tracked each individual particle and liquid droplet in a miniature shear cell in 3D during quasi-steady strain controlled shear experiments.

The shear cell is composed of a fixed bottom plate and a flat diamond tip [1], forming a strain-controlled shear cell without lateral walls. Polydisperse spherical silica particles (average diameter 7 μ m) suspended in an index matching liquid were used as a model system. We added immiscible droplets to create a wet granular matter. Position and shape of the droplets, as well as position and size of the particles were recorded simultaneously using a laser scanning confocal microscope [1,2,3]. The sample was imaged continuously in 3D during large amplitude oscillatory shear. Using automatic image analysis, we follow the trajectories of all particles and droplets during the experiment. From our analysis it follows that the particle and droplet motions are strongly correlated. Particles are sticking to the droplet surface. The ensemble that is moving is a droplet-particles cluster. These ensembles are moving and rolling within the shear zone, changing the shear profile, as well as diffusion within the shear zone.

The questions that we discuss in the presentation include: What are the specific characteristics in the trajectories of particles with and without contact to droplets? In how far does the formation of shear zones differ in wet granular matter from mechanisms known from dry granular matter?

[1] Wenzl, J., Seto, R., Roth, M., Butt, H.-J., Auernhammer, G. K., *Granul. Matter*, **15**, 391-400 (2012).

[2] Crocker, J.C., Grier, D.G, *J. Colloid Interface Sci.* **179(1)**, 298-310 (1996).

[3] Roth, M., Schilde, C., Lellig, P., Kwade, A., Auernhammer, G., *Eur. Phys. J. E*, **35(11)**, 124 (2012)

In Situ Observing Platinum Nanoring Assembly in TEM Liquid Cells

Guanhua Lin^a, Utkarsh Anand^a, Qi Liu^a, Jingyu Lu^a, Utkur Mirsaidov^a

^aCentre for BioImaging Sciences, Department of Biological Sciences, National University of Singapore, Science Drive 4, Singapore, 117543.

Linguanhua01@gmail.com

The assembly of nanostructures from nanoparticles in solution is fundamental to “bottom-up” fabrication of functional materials and devices (1-2). However, it remains largely unclear how fluid interfaces facilitate or hinder nanoscale assembly (3). *In-situ* TEM imaging has enabled the direct visualization of nanoscale processes in solutions and revealed that direct inter-particle interactions.

The assembly dynamics of platinum (Pt) nanoparticles around fluid-like ethylenediaminetetraacetic acid (EDTA) nanodroplets in solution had been investigated by using in situ imaging technology. An aqueous precursor solution comprising 2 mM K_2PtCl_4 and 2 mM EDTA (pH=7.3) was prepared and left at room temperature for 24 hours to form nanoparticles and then loaded approximately 400 nL of the solution into liquid cells. It was suggested that Pt nanoparticles assemble into well-defined ring-like structures of different sizes around the EDTA nanodroplets in solution. Nanoparticle assembly into a ring via attachment, which is commonly observed here and all attached nanoparticles stay bounded to the surface of an EDTA nanodroplet throughout the observation time. An alternative path to ring formation by direct attachment of nanoparticles to a nanodroplet is the coalescence of these nanoparticle ring assemblies in solution to form a larger ring. Our study describes nanoparticle assembly into rings around a nanodroplet through: (1) direct attachment to the fluid-fluid interface, and (2) coalescence of assemblies. We believe that the intermediate states in nanoparticle assembly at nanodroplet surface observed here is quite general and apply to other fluid interfaces and fluid-like aggregates in solution used for self-assembly.

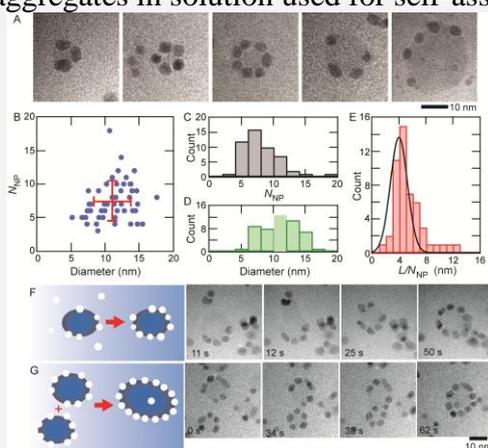


Figure 1. (A) TEM images of Pt nanorings, (B), (C), (D) and E are size distribution of Pt nanorings, (F) dynamic process of Pt nanoparticles bonded into interface of droplets, (G) dynamics coalescence process of two small nanorings into a larger one.

(1) Liu K, *et al. Science*, 2010, 329(5988):197-200.

(2) Henzie J, Grünwald M, Widmer-Cooper A, Geissler PL, & Yang P. *Nat Mater*, 2012, 11(2):131-137.

(3) Zheng H, *et al. Science*, 2009, 324(5932):1309-1312.

Turbulent Aggregation Rates between Oppositely-Charged Particles: Insensitivity to Charge Density

T. Sugimoto,^a M. Kobayashi^b

^aGraduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Japan

^bFaculty of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Japan

s1530265@u.tsukuba.ac.jp

Hetero-coagulation, which is aggregation between dissimilar particles, usually occurs in natural and industrial processes. However, understanding of hetero-coagulation in flow fields is still not sufficient due to the lack of experimental data. Therefore, we measured turbulent hetero-coagulation rate constants between oppositely-charged particles with different charge densities as a function of ionic strength at pH 5. To clarify the effect of charge densities on the hetero-coagulation rates, we employed positively-charged model colloidal particles, namely amidine (AL) and aldehyde amidine (AA) latex particles, and negatively-charged sulfate (SL) and carboxyl (CL) latex particles. These particles bear different charge densities σ in magnitude (Table 1). The obtained turbulent hetero-coagulation rates between oppositely-charged particles are plotted against ionic strength (Fig. 1). Symbols are experimental values, solid and dashed lines are the theoretical values obtained by using the trajectory analysis with a Hamaker constant of 10^{-20} J. The texts in Fig. 1 indicate the combinations of particles by alphabets with particle diameters in μm by decimals. The enhanced coagulation by electrostatic attraction was observed below 1 mM, while the increase of experimental rates beyond 1 mM may indicate the simultaneous occurrence of homo-coagulation between similar particles. We found that the effect of charge density on the enhancement of the rates is not significant, that is, the effect of ionic strength is dominant. The theoretical calculations support this finding qualitatively.

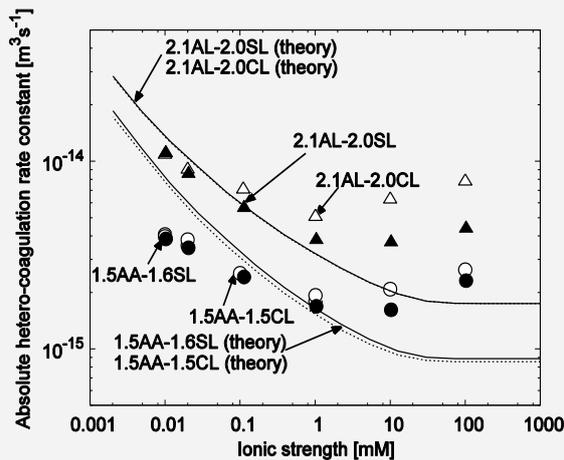


Table 1: Properties of the particles used in this study:
 d particle diameter, σ surface charge density
at 0.01 mM and pH 5.

| | Surface head-groups | d [μm] | σ [mC/m^2] |
|-------|---------------------|-----------------------|-------------------------------------|
| 2.1AL | Amidine | 2.1 | 302 |
| 2.0SL | Sulfate | 2.0 | -84 |
| 2.0CL | Carboxyl | 2.0 | -2.3 |
| 1.5AA | Aldehyde Amidine | 1.5 | 182 |
| 1.6SL | Sulfate | 1.6 | -50 |
| 1.5CL | Carboxyl | 1.5 | -2.0 |

Fig. 1 Turbulent hetero-coagulation rates as a function of ionic strength for four different combinations: Symbols are experimental data, solid and dashed lines are the theoretical values calculated by using the trajectory analysis with a Hamaker constant of 10^{-20} J

Electric birefringence spectroscopy of planar clay particles

M.L. Jiménez, P. Arenas-Guerrero, G.R. Iglesias, A.V. Delgado
University of Granada, Granada, Spain

jimenez@ugr.es

Upon application of an external electric field, dispersed non-spherical nanoparticles can orient giving rise to a macroscopic optical anisotropy known as electric birefringence [1]. Such an orientation is due to the coupling of the particle's dipole to the external electric field and therefore the analysis of the frequency dependence of the birefringence can provide insightful information about the polarization mechanisms of the particles in suspension [2].

With this motivation, in this work we have studied the birefringence spectrum of sodium montmorillonite. Particularly, we have analyzed the effect of the pH, since the heterogeneous charge distribution of this material is pH-dependent. The measured spectra (Fig. 1) show very interesting features among which we can underline the presence of a sign reversal of the birefringence in the low frequency range. This effect corresponds to a shift of the axis of alignment of the particles at a characteristic frequency that seems to be pH-independent.

Although sign inversions of the birefringence have already been reported for this material [3], this anomalous phenomenology has not been fully studied and a satisfactory explanation is still to be achieved.

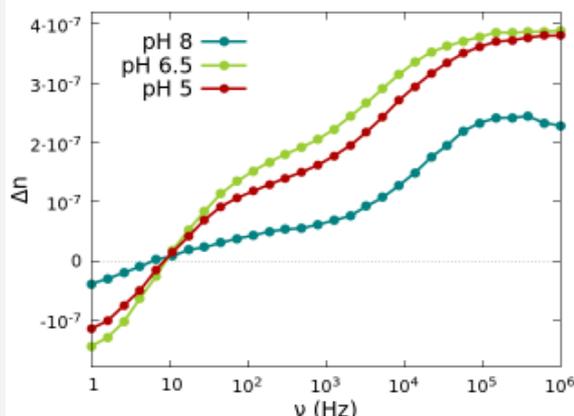


Fig. 1: Electric birefringence (Δn) of a sample of sodium montmorillonite (1 g/L, 0,3 mM NaCl) as a function of the frequency (ν) for 3 different values of the pH.

1. E. Frederiq, C. Houssier. *Electric Dichroism and Electric Birefringence*. Clarendon: Oxford (1973).
2. Curr. Opi. Coll. Int. Sci. 15, 131–144 (2010).
3. K. Yamaoka, R. Sasai. *J. Colloidal and Interface Sci.*, 209 (2), 408-420 (1999).

Acknowledgements: This work was partially supported by PE2012-0694 (Junta de Andalucía, Spain); FIS2013-47666-C3-1-R (MINECO, Spain); COST CM1101 and the FPU 2014 Program (MEC, Spain).

NMR Relaxometry Study of Laponite Tactoids Exfoliation in Aqueous Suspensions

A.L. Karpovich^a, V.S. Sukharev^a, M.F. Vlasova^a, N.I. Sapronova^a, V.V. Ivanov^a
^a *Moscow Institute of Physics and Technology, Dolgoprudny, Russian Federation*

nascar.by@gmail.com

Many experimental methods have been employed to study processes that proceed in aqueous laponite suspensions after preparation. However, at the moment there is no agreement if laponite tactoids totally disperse in water. Some experimental techniques give evidence that laponite particles exist in water as independent disks¹, other techniques reveal presence of oligomers². We propose to investigate laponite tactoids dispersion rate by NMR relaxometry method. This method enables to measure wetted particle surfaces, allowing detection of oligomers in unmodified suspension (without dilution or drying). We have found that significant number of tactoids are present in suspension just after preparation and exfoliation takes a long time. We estimated the characteristic time of tactoids delamination for a wide range of particle concentrations. Moreover, we demonstrated a new approach of estimation of sizes of nonspherical particles in liquids by the example of laponite. We measured specific surface area of laponite in aqueous medium by NMR relaxometry, determined particles equivalent spherical diameter by dynamic light scattering, and then calculated radius and thickness of disk-like laponite particles. This approach of size determination was proposed as an alternative to known method³, which is not suitable for swelling clays because surface area is measured in dry state.

Acknowledgement.

The authors gratefully acknowledge financial support from the Ministry of Education and Science of the Russian Federation (agreement number RFMEFI57514X0091)

- (1) Morvan, M., Espinat, D., Lambard, J., and Zemb, T., *Colloids Surf. A: Physiochem. Eng. Aspects* **82**, 193 (1994).
- (2) Balnois, E., Durand-Vidal, S., and Levitz, P., *Langmuir* **19**, 6633 (2003).
- (3) Ali, S., and Bandyopadhyay, R., *Langmuir* **29**, 12663 (2013).

Shear induced breakage of liposomes

Ankush Pal, P. Sunthar and D. V. Khakhar

Department of Chemical Engineering

Indian Institute of Technology Bombay

Powai, Mumbai 400076, India

Liposomes are nanometer to micron sized spherical lipid vesicles, which can encapsulate drugs and find wide application in targeted drug delivery. In this work the breakage of micron sized lipid vesicles, known as giant unilamellar vesicles, is studied in a simple shear flow. Giant unilamellar vesicles of SOPC lipid are prepared by the electroformation method. The vesicles are sheared inside a double gap Couette geometry using a rheometer, over a wide range of shear rate (500 s^{-1} to 3000 s^{-1}). The images of vesicles are captured before and after shearing using optical microscopy and are analyzed to obtain size distribution vesicles, counting about 60,000 vesicles for each distribution. The average size of vesicles is found to be reduced significantly after the application of shear at the high shear rates (2000 s^{-1}) and the size distribution curve also shifts to small diameters. However, below a shear rate of 500 s^{-1} the size distributions remain the same before and after shearing, indicating that there is no significant breakage of vesicles or shear induced coalescence. The results are analyzed using a population balance model.

A new approach to predict the dynamic interactions between an air bubble/drop and a flat solid surface

M. Shahalami^a

^a *University of Alberta, Edmonton, Canada*

shahalam@ualberta.ca

In this paper the Generic Stokes-Reynolds Young-Laplace model (GSRYL model) is proposed to predict the dynamic interaction forces acting between an air bubble and a flat solid surface when they are in relative axisymmetric motion in a Newtonian liquid. In the Generic SRYL model, which is basically similar to the alternative SRYL model, the Stokes-Reynolds equation is combined with the non-linearized second order form of the augmented Young Laplace equation to relate the mean curvature of the fluid interface to the pressure difference across the interface. The non-linearized second order form of the augmented Young Laplace equation built in the GSRYL model, leads to the appearance of the capillary number in the scaled equations.

This new theoretical framework has two important advantages over the alternative SRYL model. First, this model offers an accurate perspective of the bubble geometry at the initial separation and eliminates the approximation of the elliptical bubble geometry used as the initial separation in the alternative SRYL model. The second advantage of this model is that in spite of the SRYL model in which the scaled equations of system have a universal nature which predicts the bubble behaves nearly in a universal way over all ranges of capillary numbers, the scaled equations of the GSRYL model do not have a universal nature and depend on the physical parameters of system via capillary number.

The accuracy of this model is tested with the recent experimental data reported in the literature and confirms that this model can be successfully applied to predict the non-equilibrium interactions between an air bubble and a flat solid surface. This new model is worth further investigation, as we can take into account the bubble deformation, the original shape of the bubble at initial separation and all the physical parameters of system for this prediction.

Measurement for a size of Ovalbumin soluble aggregate using ultrasound spectroscopy and effect of propylene glycol addition on the rheological properties

Naoko Yuno-Ohta^a and Chinami Yoshita^b
^{a, b} Food and Nutrition, Junior College of Nihon University
2-31-145 Bunkyou-cho Mishima Shizuoka, Japan.

^a NaokoOHTA@aol.com

We measured the changes in size of ovalbumin (OVA) soluble aggregates accompanied with heat-treatment using the ultrasound spectroscopy equipped with particle sizing software. This analysis was based on the ultrasonic attenuation values. Furthermore, we investigated that the effect of propylene glycol addition on the rheological properties of OVA using a dynamic viscoelastic measurement and the ultrasound spectroscopy.

The OVA of 2.5 % (w/v) solution had 230 nm diameters before heat-treatment, and then the size became to decrease up to 70 nm in the heating process from 25 °C to 90 °C. In the cooling process from 90 °C to 25 °C, the diameter increased gradually up to 725 nm. This result implies that cooling treatment is important for the development of aggregates. In other words, hydrogen bonding plays roles to form the network of OVA. The effect of propylene glycol which is known as an enhancer of the hydrogen bonding on the 10 % OVA solution under heating and cooling treatment was investigated using ultrasound velocity measurements. The results show that the velocities of OVA solution containing 20 % or 40 % propylene glycol were remarkably decreased with increasing temperature, indicating that the compressibility of the OVA-propylene glycol mixed system increased. It is known that increase in compressibility means the fluid system come to gelation. These results were coincident to the rheological behavior using dynamic viscoelastic measurement.

Email: NaokoOHTA@aol.com

A new robust biodegradable platform for the engineering of macromolecules for consumer and biomedical applications

H.Ye^a, C.Owh^b

^a *Institute of Materials Research and Engineering, Singapore, Singapore*

^b *National University of Singapore, Singapore, Singapore*

yehy@imre.a-star.edu.sg

Polyglycerol sebacate (PGS) is a biodegradable elastomer that has been widely explored for applications such as drug delivery, biocompatible coating on implantable biomedical devices and tissue engineering (such as cardiac, vascular and nervous tissues). Using PGS as a biocompatible and biodegradable base material, we have developed a series of new materials for consumer and biomedical applications such as biodegradable plastics, antimicrobial polymers and biodegradable and injectable hydrogels for delivery of active ingredients. This novel approach of PGS modification is robust and easily tunable, giving PGS new properties. We are looking forward to expanding this platform and broaden the diversity of its applications.

Effect of low-temperature plasma modification on PEEK polymer characteristics

A.E. Wiacek*, M. Jurak, K. Terpiłowski, M. Worzakowska
Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

*a.wiacek@poczta.umcs.lublin.pl

The investigations of modified polymers are of great importance. PEEK (polyetheretherketone) is a colourless organic semicrystalline thermoplastic polymer in the PAEK family (polyaryletherketones). It is highly resistant to thermal degradation as well as attack by both organic and aqueous environments. PEEK is one of the few plastics compatible with ultra-high vacuum applications extensively used in many engineering industries: the aerospace, automotive, chemical process, medical implants. Such materials can be modified to obtain altered wettability and biocompatibility properties. For example, mechanical activation enabled shape memory behaviour in PEEK to be applied in the orthopedic surgery. One of the modification techniques is the usage of low-temperature plasma. Chitosan and/or plasma treatment with air or N₂ gases has a two-fold effect on the polymer surface, the wettability and biocompatibility increase, chitosan improves also antibacterial properties. Contact angles of the probe liquids (water, formamide and diiodomethane) on the PEEK and PEEK/CH surfaces were measured using a contact angle meter GBX (France). After plasma treatment a weak hydrophilic character of polymer was changed to larger (or even strong) hydrophilic. Before and after plasma modification the polymer was characterized by the same values of melting point, hardness according to Brinell, tensile strength and glass transition temperature. However, there are small differences in flexural modulus at bending, flexural strength and elongation due to the change of cross-link density and higher elasticity of sample after plasma modification. In addition, significant differences in thermal stability are clearly observed. The profilometer images show different values of roughness for the modified surface. The effect is more visible for N₂ than air plasma. Plasma treated surfaces have a good adhesive function, but the effect depends on the time of exposure and the gas used.

Support from Marie Curie Initial Training Network “Complex Wetting Phenomena” (Project number 607861) is highly appreciated.

Phase Separation of Polymer Mixtures upon Solvent Evaporation

C. Schaefer,^{a,b} P. van der Schoot,^b J.J. Michels^c

^aDutch Polymer Institute, Eindhoven, the Netherlands

^bEindhoven University of Technology, Eindhoven, the Netherlands

^cMax Planck Institute for Polymer Research, Mainz, Germany

c.schaefer@tue.nl

Phase-separated morphologies of binary polymer mixtures are used as photo-active material in thin-film organic solar cells. These 100 nm thin blend layers are usually spin-coated from solution, where solvent evaporation drives liquid-liquid phase separation. The fact that the mean composition of the mixture is time dependent gives rise to a coupling between the kinetics of evaporation and demixing. From theoretically studying a generalized diffusion equation with a description for evaporation, we find¹ that evaporation influences the early-stage emergence of the dominant spinodal length scale, as well as the kinetics of late-stage coarsening. Consequently, for both regimes a clear difference is observed compared to thermally quenched blends. In the early stages of demixing the typical structural length scale of the emerging morphology *decreases* with one over the square root of time, whereas in the late stages the rate of coarsening does *not* obey the classical Lifshitz-Slyozov-Wagner power law. The length scale at the cross-over from early to late stage dynamics itself exhibits a one-sixth power-law behavior with the evaporation rate that is set by the spin speed of the spin-coating process, see figure.

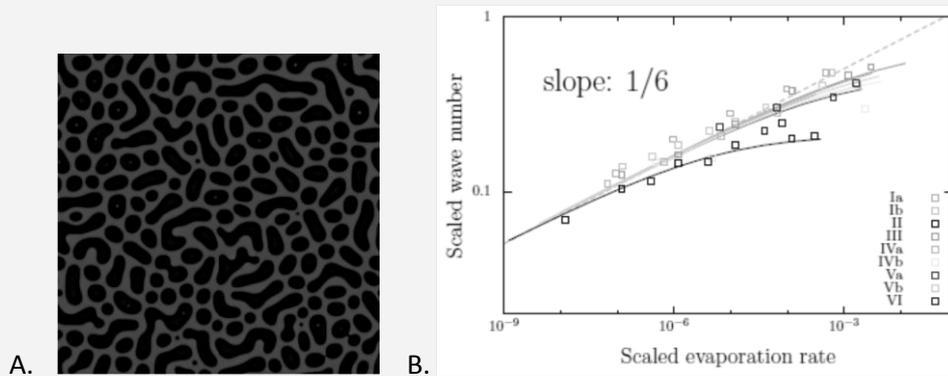


Figure: (A) Example of a calculated dry-layer phase-separated morphology. (B) Dependence of the wave number prior to coarsening on the evaporation rate, as obtained from calculations for sets of various parameter values such as interaction parameters and degrees of polymerization. Solid lines: analytical predictions; Squares: numerical results; For slow evaporation the data collapses onto the dashed line.

¹C.Schaefer, P. van der Schoot, J.J. Michels, *Phys. Rev. E* **91**, 022602 (2015)

Designing peptide-based biomaterials: structure and related properties

M. Daniele,^a S. Sennato,^b L.Chronopoulou,^c F. Domenici^a, C. Palocci^c, S. Lupi^a,
F. Bordi^a

^a Physics Dept. La Sapienza University of Rome, Rome, Italy

^b CNR-ISC Institute for Complex Systems, Rome, Italy

^c Chemistry Dept. La Sapienza University of Rome, Rome, Italy

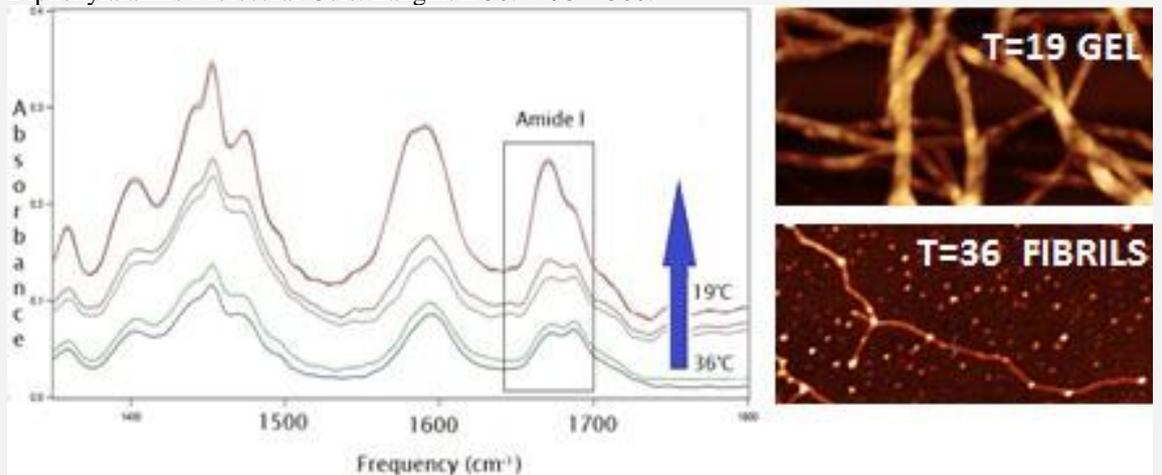
simona.sennato@roma1.infn.it

Recently, scientific as well as technological interest in the synthesis of novel peptide-based hydrogel materials have grown dramatically. Applications of such materials mostly concern the biomedical field with examples covering diverse sectors such as drug delivery, tissue engineering and production of scaffolds for cell growth, thanks to their biocompatibility and biodegradability (1).

In this framework, we have explored the phase diagram of molecular gels produced from a solution of the aromatic polypeptide derivative fluorenyl-methoxycarbonyl(poly)phenylalanine (Fmoc-polyPhe) (2). Our experiments indicate the importance of phenylalanine in the gel formation, suggesting that different combinations of Fmoc-polyPhe promote the formation of gels with different strength and fluidity. Furthermore, we have characterized the kinetic of gelation demonstrating its reversibility. By combining Dynamic Light Scattering and Fourier Transform Infrared Spectroscopy techniques we have revealed that the gel structural details strongly depends on temperature suggesting a specific mechanisms of formation. The complex self-assembled networks formed by nanofibers has been investigated by Atomic Force Microscopy investigation on hydrogels deposited on mica, and the structural details of the nanofibers have been determined.

These information can be used for a rational optimization of the design and of the applications of novel hydrogels.

1. H. J. Chung, T. G. Park 2009. Self-assembled and nanostructured hydrogels for drug delivery and tissue engineering. *Nano Today* 4: 429-437.
2. N.A. Dudukovic and C. F. Zukoski 2014. Mechanical Properties of Self-Assembled Fmoc-Diphenylalanine Molecular Gels. *Langmuir* 30: 4493-4500.



Chitosan-Based Sensitive Coatings for NH₃ and H₂S Optical Detection

A. Mironenko^a, A. Sergeev^b, S. Voznesenskiy^b, S. Bratskaya^a
^a*Institute of Chemistry of FEB RAS, Vladivostok, Russia*
^b*Institute for Automation and Control Processes, Vladivostok, Russia*

sbratska@ich.dvo.ru

Among numerous detection methods, fast response time and high electromagnetic interference immunity of optical sensors [1] make them very promising area of research in the recent years [2-5]. Polymer materials are frequently used as matrices for sensitive additives in optical sensors. Due to high availability, low cost, and good film-forming properties, some of the natural polymers can be considered as an alternative to synthetic polymers for optoelectronic applications. Here we demonstrate the possibility to use natural polysaccharide chitosan for optical gas sensing application.

Two different approaches have been implemented to fabricate ammonia and hydrogen sulphide sensors. An evanescent wave ammonia sensor was obtained by deposition of chemochromic cladding on the surface of a planar waveguide via layer-by-layer (LbL) self-assembly of oppositely charged polysaccharides (chitosan and λ -carrageenan) followed by doping with pH-sensitive dye bromothymol blue (BTB). The correlation between polymer layer thickness, dye content and sensitivity to ammonia was found. We have shown that such sensor exhibits a linear optical response to the ammonia presence in the range of 1-300 ppm with the response time less than 1 second and high reversibility.

Deposition of 100 nm thick chitosan film on the surface of a planar waveguide via the spin-coating technique followed by doping polymer layers with Ag⁺ ions and “*in situ*” reduction and formation of Ag nanoparticles allowed producing a planar waveguide with the Ag/chitosan composite sensing layer. Ag nanoparticles in chitosan matrix demonstrate ultimate sensitivity toward H₂S gas. It has been shown that composite Ag/chitosan-based waveguide film allows detection of H₂S at ppb level.

References

- [1] J.M. Corres, F.J. Arregui and I.R. Matias, *Sensor. Actuat. B.* 122, 442 (2007)
- [2] J. Courbat, D. Briand, J. Damon-Lacoste, J. Wollenstein and N.F. de Rooij, *Sensor. Actuat. B.* 143, 62 (2009)
- [3] Y. Yang, Y. Ma and W. Yang, *Polym. Advan. Technol.* 22, 1042 (2011)
- [4] A. Yimit, K. Itoh and M. Murabayashi, *Sensor. Actuat. B.* 88, 239 (2003)
- [5] Y. Shang, X. Wang, E. Xu, C. Tong and J. Wu, *Anal. Chim. Acta.* 685, 58 (2011)

Acknowledgements

Financial support from Russian Foundation of Basic Research (project 14-03-31434 mol_a) is gratefully acknowledged.

Gold-Microgel Hybrids and their Volume Phase Transition

M. Lehmann,^a S.T. Turner,^a L. Kuhrts,^a R.v. Klitzing^a
^aTU Berlin, Applied Physical Chemistry, Berlin, Germany

maren.lehmann@campus.tu-berlin.de

Microgels are attractive for application such as sensoric and drug delivery systems due to their ability to reversibly response to external stimuli. This external stimuli are often associated with a change in temperature or pH-value and causes the microgel to undergo a volume phase transition (VPT) from the swollen to the collapsed state. However, non-invasive excitations through light may also be used to induce a VPT since it can be focused into areas of interest and quickly switched [1]. Our approach includes gold nanoparticles, which serve as adsorption centers of the laser light with a wavelength matching the one of the plasmon resonance bands. The local temperature changes and may provide enough heat to induce the VPT. The influence of the gold nanoparticle concentration on the swelling and shrinking behavior of the gold-microgel particles are investigated via dynamic light scattering (DLS). Furthermore, the internal structure of the microgel may play a role in the incorporation of gold nanoparticles into the microgel network. It is well known that the common batch surfactant-free polymerization used to synthesize microgels provides a highly cross-linked core and looser shell structure [2] [3]. We synthesized poly(N-isopropylacrylamide) (PNIPAM) microgel particles of various cross-linking density and studied the distribution and loading of the gold nanoparticles via electron transmission microscopy (TEM). The change in the plasmon resonance of the gold nanoparticles in the hybrid system is examined by temperature-controlled UV-vis adsorption spectroscopy.

[1] A. Garcia et al. *Langmuir* **23** (2007)

[2] X. Wu et al. *Coll. Polym. Sci.* **272** (1994)

[3] K. Gawlitza et al. *Phys. Chem. Chem. Phys.* **15** (2013)

BULK AND INTERFACIAL RHEOLOGICAL CHARACTERISTICS OF AQUEOUS SOLUTIONS OF PNIPAM-g-PEO COPOLYMERS AND NSAID

Elena Mileva,^a Dimi Arabadzhieva,^a Roumiana Kotsilkova,^b Viktoria Michailova,^c

^a*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

^b*Institute of Mechanics, Bulgarian Academy of Sciences, Sofia, Bulgaria*

^c*Faculty of Pharmacy, Medical University, Sofia, Bulgaria*

mileva@ipc.bas.bg

Nanoparticles from thermally-responsive biocompatible PNIPAM-g-PEO copolymers with low grafting density can incorporate hydrophobic NSAID indomethacin at room temperature and release the drug under controlled conditions at 37 °C. This polymer-drug system is the basic constituent of a formulation whose composition may be optimized in view of possible pharmaceutical applications. The aim of the present investigation is to clarify the mechanisms of drug inclusion and discharge processes.

The performance of the system is particularly sensitive to temperature, the concentration of ethanol and other low-molecular additives which are the necessary components of such formulations. Extensive studies are performed on the dynamic, equilibrium and rheological properties of the adsorption layer of the polymer solutions at the air/solution interface, with varying the ethanol quantity, in wide temperature range, with and without added NSAID. The results of the detailed studies of the bulk oscillatory rheograms with variation of the system's composition are also presented. The rheological data are juxtaposed to those obtained in previous studies using other scientific instrumentations (microscopic thin liquid film techniques, TEM, etc.).

The combined bulk and interfacial rheological results provide new information about the the entrapment and the release mechanisms of the NSAID indomethacin by PNIPAM-g-PEO nanoparticles. The basic outcome is the possibility to elaborate an efficient protocol for the procedure of fine-tuning the incorporation and the discharge of hydrophobic drugs by the polymer nanoparticles.

Acknowledgements:

The studies are performed under the umbrella of COST Action MP1106 "Smart and green interfaces – from single bubbles and drops to industrial, environmental and biomedical applications" (SGI).

STUDYING ON THE EFFECT OF PH ON VOLUME PHASE TRANSITION FOR COMPOSITE HYDROGEL USING BY FLUORESCENCE TECHNIQUE

Demet Kaya Aktas¹

¹ *Istanbul Technical University, Department of Physics, Maslak 34469 Istanbul - Turkey
demet@itu.edu.tr*

Keywords: Composite hydrogel, Swelling, pH, Fluorescence

Hydrogels can be defined as three-dimensional networks of polymers which can swell several hundred times in relation to their dry network mass when in contact with water or aqueous solutions [1]. Hydrogel properties depend strongly on their degree of crosslinking, the chemical composition of the polymer chains, as well as chemical and physical properties of the surrounding materials they are exposed to which vary the interactions between the network and surrounding liquids. Especially, on the basis of their dramatic swelling and shrinking behaviours, pH-sensitive hydrogels are being utilized for new potential applications [2]. In this work, we studied the effect of pH on the swelling of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) composite gels using by Steady-state fluorescence (SSF) technique. Disc shaped composite gels were prepared by free-radical crosslinking copolymerization of P(AAm-co-AAc). N, N'- methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Pyranine 4 was introduced as a fluorescence probe. P(AAm-co-AAc) composite gels were dried before being used for swelling experiments. The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer. All measurements were made at vertical position and slit widths were kept at 5 nm. Disc-shaped gel samples were placed on the walls of 1x1 quartz cells filled with different pH solutions for the swelling experiments. Fluorescence intensity of pyranine 4 was monitored during *in situ* swelling processes of composite gels. Emission and scattered intensity of P(AAm-co-AAc) composite gel samples were monitored during the swelling processes in different pH solutions. It can be seen that as the water uptake is increased, fluorescence intensity, I_{em} decreased and the scattered light intensity, I_{sc} increased. Since the increase in I_{sc} corresponds to increase in turbidity of the swelling gel, then we have defined corrected fluorescence intensity, "I" as I_{em}/I_{sc} . It was observed that fluorescence intensity values decreased as swelling progressed. Li-Tanaka equation [3] was used to determine the swelling time constants, τ_c and cooperative diffusion coefficients, D_c for the swelling processes. Results were shown that swelling time constants, τ decreased and diffusion coefficients, D increased as the pH values increased.

In conclusion these results have shown that the direct fluorescence method can be used for real-time monitoring of P(AAm-co-AAc) composite hydrogel swelling process. In this method in situ fluorescence experiments are easy to perform and provide us with quite sensitive results to measure the swelling parameters.

[1] Almdal, K., et al., "What is a gel?", Macromolecular Symposia, 76, 1993, pp. 49-51.

[2] Peppas, N.A., et al., "Analysis of drug release behaviour from swellable polymer carriers using the dimensionality index", Journal of Controlled Release, 45, 1997, pp. 35-40.

[3] Li, Y., et al., "Kinetics of swelling and shrinking of gels", J. Chem. Phys. 92, 1990, pp. 1365-1371.

Thin films of water-based biopolymers for protection of reactive surfaces

C. Fernández-Solis, M. Rohwerder, A. Erbe
Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

c.fernandez-solis@mpie.de

Corrosion of metals is a natural occurring electrochemical phenomenon that constitutes a ubiquitous problem in modern society, especially for infrastructure and industry. Polysaccharides and polypeptides compounds represent two of the most abundant polymer groups in nature, with interesting properties. Both classes of polymers can take up water. We explore using such water-soluble biomacromolecules to create thin films on metals as an alternative to advance towards greener functional materials for protection of reactive surfaces.

Thin films were deposited on zinc substrate, utilising solutions of alginate, chitosan and gelatine. The coatings were characterised using infrared spectroscopy (IR), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Scanning Kelvin probe (SKP) measurements were performed to study the delamination kinetics of the system after creation of an artificial defect. Additionally, water uptake and ion permeability of the layer were analysed using electrochemical impedance spectroscopy (EIS).

AFM and SEM of coated substrate showed a complete, homogeneous coverage of the surface. SKP measurements recorded an apparent delamination front. The variation of potentials can be attributed to effects of Donnan potential in the coating. Potentials constantly remain above the corrosion potential expected for freely corroding zinc. EIS data recorded over 400 min showed water uptake, where alginate-based coating incorporates a significantly higher amount of water compared to chitosan and gelatine. The final capacitances of all coatings are very similar. However, no secondary processes were observed for any of these films, but water diffusion into the protective layer. Complementary linear polarisation resistance measurements showed a decrease of corrosion current about 1/50 compared to bare substrate. The water-based biopolymers coatings studied in this work exhibited charge transfer resistance values comparable to that of hydrophobic coatings. However, corrosion is delayed by retention of corrosive ions within the coating layer.

The biomaterial hyaluronic acid as pharmaceutical excipient for buccal delivery

F. Laffleur,^a

^a *University of Innsbruck, Department of Pharmaceutical Technology, Innsbruck, Austria*

Flavia.Laffleur@uibk.ac.at

Objective: Novel biomaterial was tested for its potential for buccal drug delivery.

Background: Polysaccharide hyaluronic acid (HA) was chemically modified with cysteine ethyl ether (CYS). By immobilization of the thiol bearing ligand on the polymeric backbone the thiolated bioconjugate HA-CYS was obtained.

Methods: Mucoadhesive, permeation enhancing and stability potential as well as mechanical, physicochemical properties further mucoadhesive strength, swelling index and residence time were investigated. The developed thiolated bioconjugate displayed enhanced mucoadhesiveness on buccal mucosa as well as permeation behavior and polymer stability. The near neutral pH and negative cytotoxicity studies indicated their non-irritability and biocompatible nature with biological tissues. Further, the model drug sulforhodamine 101 was incorporated to determine its drug release profiles.

Results: The synthesized thiomers showed no toxicity. The mucoadhesion of thiolated hyaluronic acid on buccal mucosa was significantly improved in comparison to unmodified one. The biomaterial showed 2.5-fold higher stability in polymer structure. The release of sulforhodamine in presence of thiolated hyaluronic acid was 2.3-fold increased compared to hyaluronic acid.

Conclusion: Thus, the promising results encourage further investigations and exploitation of this versatile polysaccharide. So far, hyaluronic acid was not evaluated for buccal drug delivery.

Colloidal Poly(melamine-formaldehyde) Dispersions as Precursor for Mesoporous Polymer Xerogels

D. Schwarz,^{a, b} and J. Weber,^b

^aMax Planck Institute of Colloids and Interfaces, Science Park Potsdam-Golm, Germany

^bUniversity of Applied Science Zittau/Goerlitz, Zittau, Germany

d.schwarz@hszg.de

Highly porous and cross-linked organic polymers have attracted a wide range of applications due to their properties e.g. high thermal stability, good pH resistivity in aqueous solution and high porosity. Poly(melamine-formaldehyde) (PMF) consists of a highly cross-linked polymer network with a high amount of secondary amine functionalities, resulting in a material with promising adsorption properties.[1] In this work, we designed a stable dispersion of PMF colloids with coexisting silica nanoparticles in aqueous phase. The silica nanoparticles act as a template and framework material for further processing of the dispersion into xerogels, but are not relevant for the stability of the dispersion.[2]

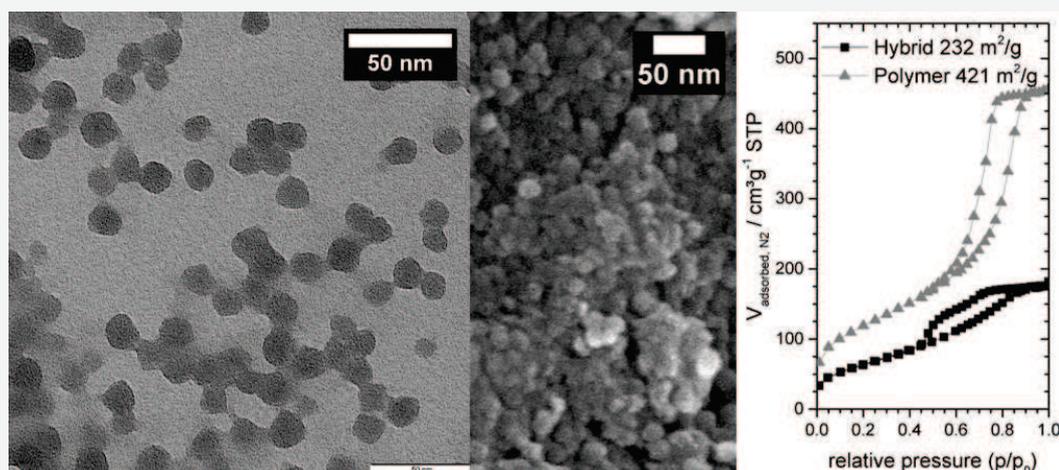


Figure 1. Transmission electron microscopy image of the hybrid dispersion (*left-hand-side*), high resolution scanning electron microscopy image of compacted hybrid xerogel (*middle*) and nitrogen adsorption isotherms with specific surface area (*right-hand-side*) [2]

The dispersion can be easily converted into a mesoporous xerogel with specific surface areas of about 400 m²/g after removal of the template. The dispersion was analysed with several analytical methods (e.g. AUC, DLS, SAXS, microscopy, zetapotential), to get an understanding of the particle size and the interplay between coexisting PMF colloids and silica template.

Finally, first results towards the direct application of the stable dispersion as coating material for membrane modification will be presented as well as the efficiency of the membrane as an adsorber material for oxyanions (e.g. arsenate, selenate, nitrate, phosphate, sulfate).

[1] D. Schwarz and J. Weber, *Macromol. Mater. Eng.* **2015** *in press*, DOI: 10.1002/mame.201400330.

[2] D. Schwarz and J. Weber, *Langmuir* **2015** *in revision*

Renovated Microscopic Insights into the Critical Behavior of Poly(*N*-isopropylacrylamide) Studied by Small- and Wide-angle X-ray Scattering and Dielectric Relaxation Spectroscopy

K. Yanase,^a R. Buchner,^c D. Suzuki,^b and T. Sato^b

^a Graduate School of Textile Science and Technology, ^b Division of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Japan

^c Institut für Physikalische and Theoretische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

15st304a@shinshu-u.ac.jp

Poly(*N*-isopropylacrylamide) (pNIPAm) exhibits a well-defined lower critical solution temperature (LCST) in aqueous media. At a critical temperature, $T_C \approx 32\text{-}34^\circ\text{C}$, these polymer chains undergo a coil-to-globule transition. Significant efforts have been devoted not only to fundamental research into the critical behavior of pNIPAm, but to developments of a wide range of applications of pNIPAm-based hydrogels [1-4].

Here, we studied temperature-induced structural and dynamical modification of semi-dilute pNIPAm in H₂O and D₂O by means of simultaneous small- and wide-angle X-ray scattering (SWAXS) in the extended q -range of $0.072\text{-}20\text{ nm}^{-1}$ and dielectric relaxation spectroscopy (DRS) in H₂O in the frequency range of $0.2 \leq \nu / \text{GHz} \leq 89$ by use of a vector network analyzer and a waveguide interferometer.

We report solvent deuterium isotope effects on T_C as well as the critical exponents of pNIPAm characterizing the divergence of the density fluctuation caused by the polymer network. Then, we discuss our renovated understanding of the microscopic insights into such critical behavior, demonstrating how the formation of polymer-rich and water-rich domains are closely related with strongly temperature-dependent backbone-backbone interactions and dehydration of pNIPAm chains mediated by hydrophobic interaction; i.e., exclusion of hydration water molecules from vicinity of nonpolar side-chain groups.

REFERENCES

- [1] M. Shibayama, T. Tanaka, and C. C. Han, *J. Chem. Phys.* **97**, 6829 (1992).
- [2] A. Meier-Koll, *et al.*, *Langmuir*, **28**, 8791 (2012).
- [3] Y. Ono, and T. Shikata, *J. Am. Chem. Soc.*, **128**, 10030 (2006).
- [4] M. Füllbrandt, *et al.*, *J. Phys. Chem. B*, **118**, 3750 (2014).

Highly hydrophilic gels based on semi-interpenetrating polymer networks for cleaning delicate Cultural Heritage artefacts

Joana A. L. Domingues,^{a,b} Nicole Bonelli,^b Emiliano Carretti,^b Michele Baglioni,^b
Emiliano Fratini,^b David Chelazzi,^b Rodorico Giorgi,^b Piero Baglioni^b

^a*Procter & Gamble, BIC, Strombeek-Bever, Belgium*

^b*University of Florence, Department of Chemistry and CSGI, Sesto Fiorentino, Italy*

domingues.j.1@pg.com

The restoration of Cultural Heritage artefacts involves interfacial interactions between different materials, where the original materials constituting the work of art must remain as unaltered as possible. Traditional methods used in the cleaning of artefacts (e.g. the removal of discoloured varnishes) include the use of organic solvents embedded in cotton-swabs or in viscous materials (solvent gel), which can cause paint binder swelling, re-deposition of the dissolved materials or residues from the gelling agent employed in for the solvent gel. Chemical gels overcome these issues.^{1,2} In particular, chemical hydrogels are nanocontainers able to efficiently avoid liquid penetration and reduce mechanical abrasion of the painted surface, while water-based nanostructured fluids are low-toxic cleaning tools with enhanced detergency with respect to neat organic solvents. We report on a chemical hydrogel that can be loaded with water-in-oil microemulsions and micellar solutions, specifically designed for the cleaning of water-sensitive artefacts. It is constituted by a cross-linked poly(hydroxyethyl methacrylate) network with an interpenetrated poly(vinylpyrrolidone), i.e. a semi-interpenetrating polymer network (SIPN) with high hydrophilicity. The investigated gel formulations have an equilibrium water content up to 87wt%, from which 72-77% is free water. The SIPNs are classified as gels from a rheological point of view and can be tuned in mechanical behaviour by varying cross-linking density and polymer concentration. Hydrogels structure was characterized by Small Angle X-ray Scattering and porosity was observed by Scanning Electron Microscopy. Some case studies are reported on the use of the investigated hydrogels for the removal of hydrophilic and hydrophobic materials from artefacts.

References

- 1) Baglioni, P.; Carretti, E.; Chelazzi, D. Nanomaterials in art conservation. *Nature Nanotechnology* 10, 287-290, 2015.
- 2) Baglioni, P.; Berti, D.; Bonini, M.; Carretti, E.; Dei, L.; Fratini, E.; Giorgi, R. Micelle, Microemulsions, and Gels for the Conservation of Cultural Heritage. *Adv. Colloid Interface Sci.* 2014, 205, 361–371.

* No kinship among the authors

On the release of a cargo from poly(N-isopropylacrylamide) brushes

Celine Mercier, Eric Tyrode, David Johnson and Colin Bain

The controlled release of cargo molecules by a polymer film has potential to deliver the required components in lubrication, anti-fouling, drug-delivery and other clean tech applications. The aim of this work is to monitor the release of cargo molecules by changes in temperature, pH and/or ionic strength. The thermoresponsive polymer, poly(N-isopropylacrylamide) (pNIPAm) was chosen as an example system as its bulk properties in aqueous solution are well known. Its conformation at the surface is, however, less well understood. pNIPAm films are grown on a solid (fused silica) substrate, following an atom-transfer radical-polymerization (ATRP) protocol [1] to produce films of varying surface densities. Molecular structure changes during the phase transition, as well as the uptake and release of a cargo molecule were investigated in situ using the surface-selective technique, total internal reflection (TIR) Raman spectroscopy. Changes in molecular interactions and orientations were recorded with 1 second time resolution. The method is not limited to pNIPAm and could be used for studying the interaction between other combinations of polymer - cargo molecules

[1] *Macromolecules*, 2010, 43 (23), pp 9945–9956

Nanocarbon composites based on aqueous polymer matrices: phase, aggregative and nonlinear optical properties

I.M. Kislyakov,^a A.Yu. Vlasov,^b A.L. Nikolaeva,^b A.V. Sokolov,^b S.A. Povarov,^a
A.V. Volkova^b

^a *Saint-Petersburg National Research University of Information Technologies, Mechanics, and Optics, St.Petersburg, Russia*

^b *Institute of Chemistry, Saint-Petersburg State University, St.Petersburg, Russia*

iv.kis@mail.ru

Fluid systems containing nano-carbon are anticipated to feature as materials for laser-connected applications: optical filters, limiters, switchers etc. Such systems should procure high resistance regarding femto- to nano-second intense pulse-periodic irradiation of high repetition rate. Although a number of the said materials show up promising, they 1) have poor performance at high repetition rates because they are bleaching and/or blurring 2) are less germane to the practical use as compared to a solid state.

As to the first issue, we have shown that introduction of a polyvinyl alcohol (PVA) in an aqueous carbon black suspension (CBS) stabilized by sodium dodecylbenzenesulfonate (SDBS) can retroact bleaching relating to optical power limiting (OPL) due to modulation of the fluid matrix viscosity. Herein we give a correlation of functional properties of an optical CBS composite vs. aggregative characteristics of SDBS (CMCs, aggregation numbers, degrees of counter-ion binding) in aqueous PVA solutions, solution viscosity and SDBS Krafft boundaries in such solvents.

We also tackled another type of nano-carbon composite, *viz.*, the aqueous suspension of single-wall carbon nanotubes (SWCNT) stabilized by an amphiphile polymer pluronic F127. This system can organize the hydro-gel at certain polymer concentrations and temperatures. We give phase boundaries of the pristine and SWCNTs-containing hydro-gel phase in juxtaposition with OPL parameters of the micellar solution and the hydro-gel. Although the system does not provide bleaching reduction, it procures healing of optical damages caused by irradiation of the gel. The effect is due to thermoreversible phase transition of the matrix into fluid phase.

We show that functional performance of nano-carbon nonlinear optical materials may well be optimized by controlled content of polymer moieties in the system.

Authors acknowledge support of Russian Foundation for Basic Research (grants #14-02-00851 and #13-03-01111). They were further supported by the Government of Russian Federation (grant #074-U01).

Adhesion and self-adhesion of hydrogels filled by nanoparticles

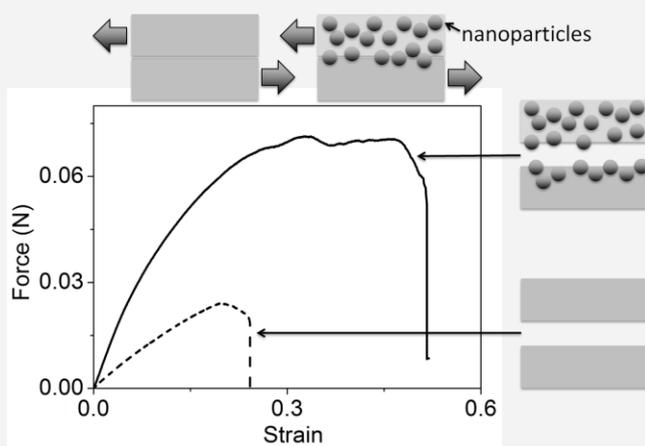
M. Gracia,^a A. Marcellan,^b L. Leibler^c

^{a,c}*Matière Molle & Chimie, ESPCI ParisTech, France*

^b*Sciences et Ingénierie de la Matière Molle, ESPCI ParisTech, France*

marie.gracia@espci.fr

Dispersing nanoparticles into hydrogel matrices is known to greatly enhance the stiffness and toughness of hydrogels. The reinforcement and toughening in these nanocomposite gels are related to the adsorption/desorption processes of gel strands onto nanoparticles, which then act as additional physical cross-links. The same principle of chain adsorption on nanoparticle surfaces was recently used to glue together two pieces of gel.¹ Here, we investigate how this mechanism is involved in the adhesive properties of nanocomposite gels. Model nanocomposite hydrogels were prepared by dispersing silica nanoparticles into covalently cross-linked Poly(*N,N* dimethylacrylamide) (PDMA) hydrogel. The adhesive properties were quantified using a lap-shear experiment by pulling apart two ribbons of gel that were previously pressed together along a given length. For nanocomposite PDMA gels containing 0.2 volume fraction of silica nanoparticles, the adhesion energy to peel the ribbons is much higher than for unfilled PDMA gels. Measurements at various speed show that viscoelastic losses due to bulk rearrangement is a significant part of this energy. The interfacial contribution of adhesion is explored using a mixed geometry where a ribbon of nanocomposite gel is pressed onto a ribbon of unfilled gel. We find that adhesion significantly increases with contact time. Moreover, post-mortem observations of the peeled areas by scanning electron microscopy show that silica nanoparticles remained embedded into the unfilled gel. These results demonstrate that adhesion comes from a progressive reorganization of particles at the interface through dynamic adsorption/desorption processes and for high speed amplified by visco-elastic dissipation in bulk of nanocomposite gels.



- (1) Rose, S.; Prevotau, A.; Elzière, P.; Hourdet, D.; Marcellan, A.; Leibler, L. *Nature* **2013**, 505 (7483), 382–385.

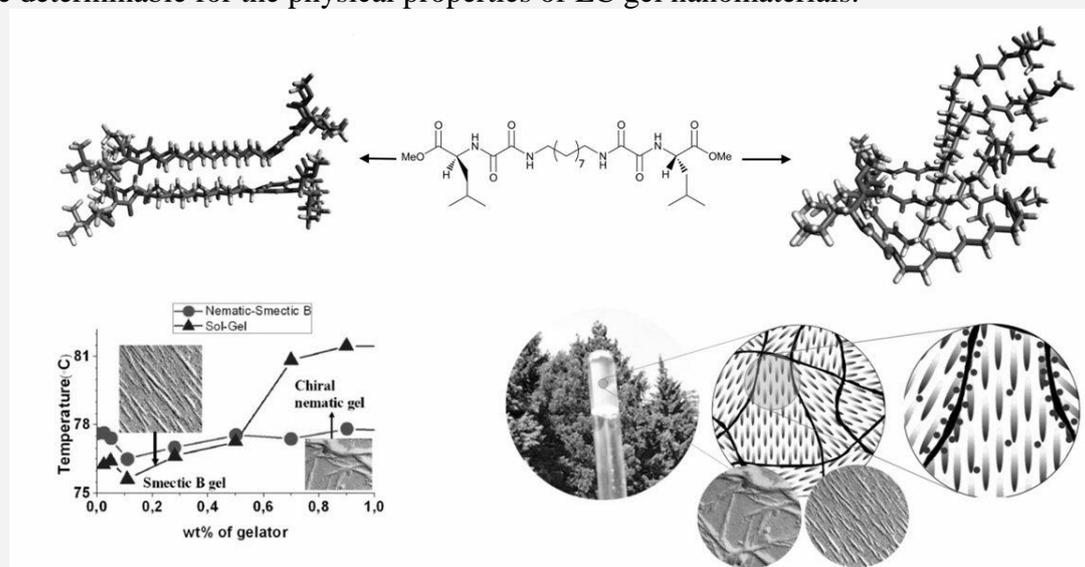
Controlled Self-Assembly of Chiral Bisoxalamide Gelator Molecules Induced by Liquid Crystalline Phase Transition

N. Šijaković Vujičić,^a M. Žinić,^a M. Kveder^a
^aRuđer Bošković Institute, Zagreb, Croatia

nsijakov@irb.hr

Liquid crystalline (LC) physical gels represent a new type of soft materials that possess induced or enhanced electro-optical, photochemical and electronic properties. The latter represent systems of phase segregated structures consisting of a mesogen as a solvent and gelator molecules, each capable of giving a different type of noncovalent supramolecular organization at a specific temperature. The conformationally flexible chiral oxalamide compounds are capable of forming diverse supramolecular gel aggregates of chiral and achiral morphologies. [1] Chiral bisoxalamide gelators show remarkable gelling capacity of the nematic and smectic B liquid-crystalline phases of *trans*-4-heptylcyclohexanecarboxylic acid (**HCCA**). Chiral nematic gel was formed if the gelator is present in amounts higher than 0.55 wt% containing helical fiber bundles. With lower amounts of gelator, no nematic gel forms, however, nematic to smectic B phase transition triggers instantaneous self-assembly of gelator molecules into aligned fibers. [2] The latter liquid crystalline gel system represents an example of controlled self-assembly induced by liquid crystalline phase transition.

The ESR spectra revealed that the gelator network confines the **HCCA** into the domains within the bulk crystalline matrix where the local molecular dynamics is not frozen. [3] It is proposed that nano scale inhomogeneity of molecular organization in LC gels can be determinable for the physical properties of LC gel nanomaterials.



- 1) N. Šijaković Vujičić, Z. Glasovac, N. Zweep, J. H. van Esch, M. Vinković, J. Popović, M. Žinić, *Chemistry A European Journal*, **2013**, 19, 26, 8558-8572.
- 2) Šijaković Vujičić, N., Šepelj, M., Lesac, A., Žinić, M. *Tetrahedron Letters* **2009**, 50, 31, 4430-4434.
- 3) M. Andreis, D. Carić, N. Šijaković Vujičić, M. Jokić, M. Žinić, M. Kveder, *Chemical Physics*, **2012**, 403, 81-88.

Fluorescence Quenching Study of Counterion Condensation on Naphthalene-Tagged Polyelectrolytes

J. Škvarla^a, M. Štěpánek^a, F. Uhlík^a, P. Košovan^a, M. Janata^a

^a*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, 128 40 Prague 2, Czech Republic*

^b*Institute of Macromolecular Chemistry AS CR, v.v.i., Heyrovského nam. 2, 162 06 Prague 6, Czech Republic*

juraj.skvarla@natur.cuni.cz

The aim of the study was to investigate counterion condensation on the polyelectrolyte chain by means of fluorescence quenching. Two samples of naphthalene-tagged poly(methacrylic acid) (one of them tagged at the end of the chain and the other in the middle) were quenched by Cs⁺ ions in aqueous solutions at different pH and ionic strength. Steady-state as well as time-resolved fluorescence measurements were performed. The electrostatic effect which governs quenching efficiency at high pH was found to be much stronger for the polymer labelled in the middle of the chain than for that labelled at the end of the chain.

Time-resolved fluorescence measurements proved the presence of two distinct lifetime distributions of the naphthyl fluorescence. While the short component with mean lifetime of ca. 5 ns corresponds to the quenching by the condensed Cs⁺ ions, the long component with the mean lifetime of ca. 28 ns corresponds to the collisional quenching by Cs⁺ in the bulk solution. At higher ionic strengths, the fractional contribution of the short component is much less significant, which suggests that at the high ionic strengths no counterion condensation occurs. In the case of quenching by I⁻ ions which exhibit no condensation on the PMAA chain, only the collisionally quenched population is present.

Living PDMS vitrimers

F. Angot^a

^a *Matière Molle et Chimie, UMR 7167 ESPCI-CNRS, Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris ESPCI ParisTech, 10 rue Vauquelin, 75005 Paris, France*

fanny.angot@espci.fr

Commercially available silicone adhesives are obtained by platinum-catalyzed cross-linking of vinyl- and hydrogenosiloxanes (hydrosilylation). Nevertheless, such siloxane networks can also be proceeded by the potassium silanolate-initiated ring-opening copolymerization of methylcyclosiloxanes D_n (n, the number of -Si(Me)₂-O- units) and bis(methylcyclosiloxanyl)-ethane (bis-D_n).

As active silanolates remain, these are “living” networks and have been demonstrated to be self-healing. Moreover these materials could be vitrimers. Indeed, vitrimers are defined as covalent networks that are able to rearrange their topology by catalyzed exchange reactions without altering the number of links between their atoms. Thus, at high temperature, exchange reactions are fast and materials flow like thermoplastics, whereas at low temperature, they behave like thermosets. This property was tacitly observed in 1954 when Osthoff *et al.* related the stress relaxation behavior of siloxane elastomers to the *trans-siloxanation*, a catalyzed chain exchange reaction.

Ring-opening polymerization of siloxanes leads, at the equilibrium, to 15% of free small rings. If the exchange reaction takes place at high temperature, rings evaporate and the equilibrium is displaced. Yet, as the *trans-siloxanation* may also be an intramolecular process, forming new small rings can restore the equilibrium. Therefore, any equilibrium displacement would lead to the depolymerization of the siloxane network: it is no longer vitrimer...

To obtain an efficient rate of the exchange reaction beneath the depolymerization temperature, we investigated parameters such as the concentration of silanolates and the nature of their counter ions. By varying the basic initiator, we showed that the looser the silanolate/cation ion pair is, the faster the exchange reaction is. Adding compounds breaking the ion pairs (DMSO, crown-ethers) considerably diminish the exchange rate, cations templating the *trans-siloxanation*. Best results were obtained with carbonate salts, which both help the dissociation of ion pairs and template the *trans-siloxanation*.

Micro-Mechanical Investigation of Core-Shell Microgels with Switchable Elasticity and Constant Surface Chemistry

M. Seuss,^a W. Schmolke,^b S. Seiffert,^b A. Fery^a ...

^aUniversität Bayreuth, Bayreuth, Germany

^bFreie Universität Berlin, Berlin, Germany

maximilian.seuss@uni-bayreuth.de

Hydrogels based on poly(*N*-isopropylacrylamide) (pNIPAAm) exhibit a reversible volume phase transition from swollen to deswollen states as the temperature exceeds the lower critical solution temperature (LCST) at 33.6 °C. Accompanying this change of the hydrogel volume, also the elastic modulus and the surface chemistry of the hydrogel change.

To decouple these effects from one another, we present a class of sub-millimeter sized hydrogel particles that consist of a thermo-sensitive pNIPAAm core wrapped by a chemically related, non-thermo-sensitive polyacrylamide (pAAm) shell. These particles are templated by droplet-based microfluidics.^[1] They can be fabricated with either topologically connected or non-connected core and shell. The state of interconnection introduces markedly different mechanical properties of the shell with varying temperature.

Using colloidal probe atomic force microscopy experiments,^[2] we observed an increasing shell elastic modulus with increasing temperature, if the core and the shell are interconnected. This stiffening is attributed to the densification of pAAm hydrogel due to contraction caused by the shrinking of the core. In contrast, without interconnection, the shell further swells into the redundant space of the core upon temperature increase. This results in a decreasing elastic modulus. However, the surface chemical properties of the outer pAAm shell are mainly independent around the LCST. As a result, these core-shell microgel particles can serve as a promising platform for the assembly of soft materials with rationally and independently tunable mechanics, and constant surface chemistry.

[1] S. Seiffert, J. Thiele, A. R. Abate, D. A. Weitz, *J. Am. Chem. Soc.* **2010**, *132*, 168

[2] S. Schmidt, M. Zeiser, T. Hellweg, C. Duschl, A. Fery, H. Möhwald, *Adv. Funct. Mater.* **2010**, *20*, 3235

Study of nucleation kinetics and particle growth of active substance from an oversaturated solution in a gel layer

Modern active pharmaceutical ingredients (API) despite their increased effectiveness often suffer from poor solubility. Common way to counter this is to embed the API in a polymer matrix to increase the specific surface area, increase the wettability of the API and stabilize the amorphous form of the API. However, during the dissolution the concentration of the API can locally become oversaturated and precipitation can occur in the medium which is uncalled for.

To better understand this process we are developing a method for observing nucleation kinetics and particle growth from an oversaturated API solution in a concentrated polymer solution, effectively simulating a wetted gel layer of a dissolving tablet. For this a transparent glass measurement cell was designed and assembled. It consists of several isolated compartments for parallel observation. Each is equipped with a feed line to introduce API at the same time into the gel polymer layer of different concentrations located inside the compartments. The compartments are then monitored via an optical microscope for signs of precipitation (colour change of the API). Effect of different polymers and their concentration on the API dissolution and stability in solution were observed and a computational model for computer simulation of this process will be created from the obtained data.

Marek.soltys@vscht.cz

Investigations of adhesion of biologically active substances to a polymer support treated or untreated with plasma

E. Chibowski^{*}, A.E. Wiącek, M. Jurak, K. Terpiłowski

*Maria Curie-Sklodowska University, Faculty of Chemistry, Department of Physical Chemistry-
Interfacial Phenomena, 20-031 Lublin, Poland*

email: emil.chibowski@umcs.pl

Solid-supported lipid layers are suitable models of biological membranes. But investigations of layers prepared from substances of pharmaceutical importance (e.g. bacteriostatic or antibacterial) are rare. Characteristic of mixed lipid layers with antibacterial chitosan or alkyl gallate can be useful for application where biocompatibility is important. From a medical point of view essential polymer is polyether ether ketone (PEEK), which is used as implant thanks to its excellent properties such as high strength, stiffness, good fracture toughness, resistance to corrosion and density comparable to human tissue. Its relatively low adhesion to the bone tissue has limited its more common application. However, adhesion of biomolecules to polymer can increase its biocompatibility, and simultaneously can facilitate introduction of the active substance bonded to the polymer carrier into the human body, where it is gradually released. In our studies low-temperature plasma obtained from air, oxygen, argon, nitrogen or mixed gas systems was used to enhance PEEK adhesive properties and as “pre-deposition” before the main process which was deposition of layers of biologically active substances, e.g. phospholipid, chitosan, lauryl gallate and mixed layers, by means of solution spreading or Langmuir-Blodgett techniques. The contact angles of chosen liquids were measured on such thin films covering the surface of the polymeric support, non-activated and activated by plasma. Then the surface free energy was evaluated, and finally topography of the examined surfaces was determined. Depending on the kind of plasma, biological layer and technique of its preparation, significant changes of wettability and surface roughness were observed. It is believed that plasma treatment will be a source of new information about shape-memory polymer surface mostly in the field of biomaterial engineering, adhesion of biomolecules as far as biocompatibility.

Acknowledgements: Financial support of this project from Marie Curie Action FP7-PEOPLE-2013, Initial Training Network: “Complex Wetting Phenomena” (Project No: 607861) is highly appreciated.

Development and Characterization of Cellulose-Based Hydrogels for Probiotic Bacteria Delivery

P. Singh ^a, B. Medronho ^b, M.G. Miguel ^{a,c}, B. Lindman ^{c,d,e}

^a *University of Coimbra, Department of Chemistry, 3004-535 Coimbra, Portugal*

^b *Faculty of Sciences and Technology, Centre for Mediterranean Bioresources and Food, Ed. 8, University of Algarve, Campus de Gambelas, 8005-139 Faro, Portugal*

^c *Nanyang Technol Univ, Sch Mat Sci & Engn, Singapore 639798, Singapore*

^d *Lund Univ, Phys Chem, S-22100 Lund, Sweden*

^e *Mid Sweden Univ, Fibre Sci & Commun Network, Sundsvall, Sweden*

Email: poonamsingh.singh34@gmail.com

Cellulose is abundantly found in nature with unique properties such as biocompatibility and biodegradability. It is an amphiphilic polysaccharide so when it forms hydrogels, it can undergo swelling and de-swelling with tuned pore size, depending on the environment characteristics. Moreover, the non-toxic profile is thus appealing to be used as a bio-carrier. Among the vast range of possible species to be encapsulated and delivered (e.g. ions, molecules, microorganisms, etc), probiotics emerge as very interesting class receiving a lot of attention nowadays.

In this work, different polymer mixtures were developed and characterized regarding their phase behavior and rheology. Additionally, the gels were further studied by FTIR spectroscopy, thermal gravimetric analysis, X-ray scattering and scanning electron microscopy. The equilibrium swelling and release properties were also evaluated.

Multiscale rheology of bronchial mucus

D. Donnarumma^a, C. Blanc^a, M. K. Khelloufi^b, I. Vachier^c, A. Bourdin^c, P. Chanez^d, A. Viallat^b & G. Massiera^a

^aLaboratoire Charles Coulomb, Université de Montpellier UMR 5221, Montpellier, France

^bAix Marseille Université, CNRS LAI, UMR7333, Inserm UMR 1067, Marseille, France

^cInserm U1046, UM1, UM2, Respiratory Disease, CHU Montpellier, Montpellier, France

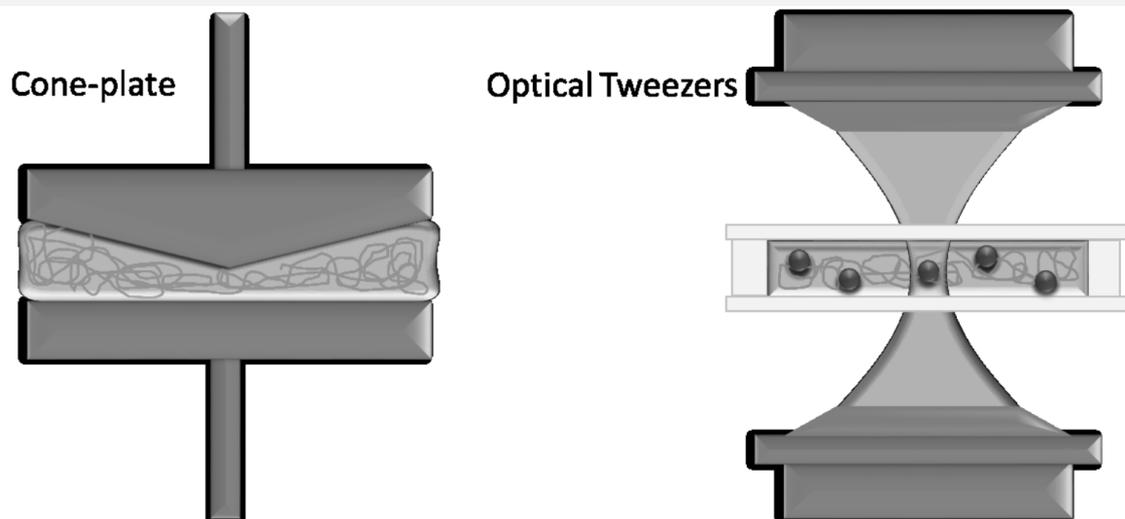
^dAP-HM, Inserm U1067 UMR 6212, Aix Marseille University, Marseille, France

dario.donnarumma@univ-montp2.fr

Severe chronic bronchial diseases affect 120 millions of people worldwide. These respiratory diseases are often associated with mucus hypersecretion in the airways, but the distinctive roles of cilia beating and mucus properties and hypersecretion are still to be determined. The project is focused on the physical aspects of mucociliary clearance, and more specifically on the rheological properties of healthy and pathological mucus. This preliminary study will help to better understand how cilia beating is coupled to the viscoelastic properties of the mucus, to generate mucus transport in lungs.

Mucus is a gel with a complex viscoelastic behaviour; entangled long chains of mucin and inorganic salts suspended in water mainly compose this biological “slimy” material.

The mucus samples were obtained from bronchial epithelium culture. Classical cone/plate rheometry experiments will be compared to microrheology experiments to characterize the heterogeneity of mucus and the different scales of its complex structure. Classic cone-plate frequency sweep provides quantitative measurements of the shear-dependent elastic moduli in the frequency range corresponding to cilia beating. Optical tweezers were used to analyze mucus in a passive or oscillating optical trap. During a passive tracking experiment, a bead is held in place by the trap, and the Brownian motion is recorded. In an active experiment, an oscillating mode is used to simulate the cilia beating. These results will be compared to passive microrheology deduced from a population of beads embedded in the mucus.



Drug Delivery Systems regarding the Treatment of Chronic Inflammation: The Application of Functionalized Layer-by-Layer Microcarriers

M. Fichtner^a, M. Göse^a, U. Reibetanz^a

^aInstitute for Medical Physics and Biophysics, Faculty of Medicine, University of Leipzig, Leipzig, Germany

uta.reibetanz@medizin.uni-leipzig.de

The modular construction of Layer-by-Layer (LbL) polyelectrolyte-coated microcarriers offers new and promising transport options in drug delivery. Active agents can be integrated into various positions of multilayer and core in different amounts and different release kinetics. Additional modifications can be made to meet the special requirements of drug delivery systems: reduced opsonization in blood stream, protection of the agents from early degradation, specific cell addressing, intracellular carrier transport into specific target compartments and subsequent controlled release.

Here, the development of a specific design addressing immune cells in inflammatory regions is described. The focus is on the inhibition of excessive degradative enzymes (e.g., elastase) produced and secreted by polymorphonuclear leukocytes (PMNs). The application of LbL-microcarriers to transport its antagonist α 1-antitrypsin (AT) is intended to provide enhanced inhibitory effects by dual efficacy: in a single design, AT-functionalized carriers have to address both, intracellular and extracellular elastase.

Several aspects have been investigated: LbL-carriers were constructed from a biopolymer multilayer with fast disassembly properties in phagolysosomes, the target compartment of PMNs^[1]. AT was successfully assembled into the biopolymer multilayer in defined amounts; once released, a selective intracellular elastase inhibition occurs. In parallel, extracellularly remaining AT-carriers immobilize already released elastase^[2]. Beside inhibitory properties, the carriers themselves do not affect immune cells regarding apoptosis, necrosis or pro-inflammatory signaling, neither in PMNs nor in macrophages^[3-4].

This application proves the suitability of multifunctional LbL-microcarriers regarding the treatment of inflammation.

[1] S. Rathmann et. al. *Cytom. Part A* (79A): 979–989, 2011.

[2] U. Reibetanz et al. *ACS Nano* (6): 6325–6336, 2012.

[3] M. Fichtner et. al. *Macromol. Biosci.* DOI: 10.1002/mabi.201400405, 2015.

[4] J. Leßig et. al. *Biomacromolecules* (12): 105–115, 2011.

The development and application of some interfacial methods for animal milk diagnostics are important for physical-colloid chemistry and biomedical sciences. Recently the powerful techniques of the dynamic surface tension (DST) measurements has been developed and successfully applied for biological liquids. The DST investigations (especially, their dependences on a physiological condition of an animal and a biochemical compounds in biological liquids) can give valuable information for an early estimation of the physiological-biochemical status of the animal organism.

The main aims of the present work are the following: to study the dynamic surface tension and the biochemical parameters of the animal's milk; to obtain the relationship between DST parameters and fat or protein content of cow's milk in order to prove the availability of such method for animal milk diagnostics. The milk samples from the healthy cattle were examined. All animals in this study were considered as analogies (the same breed, genetic line, one direction of use, etc.). All procedures were carried out with the approval of the Animal Care Committee of the Moscow State Academy of Veterinary Medicine and Biotechnology. All milk samples were analyzed using spectrophotometer «Bentley 150» (USA) and tensiometer «BPA-1P» («Sinterface», Germany). For studied milk samples with fat content of 1.5-2.5%; 2.5-4.0%; 4.0-6.0% the maximum DST values of 56.61 ± 0.63 ; 57.15 ± 1.83 ; 61.62 ± 0.95 mN/m were obtained, respectively. Analyzing such data the correlation coefficients between the DST and biochemical parameters were calculated. The obtained relationships between milk biochemical parameters and corresponding dynamic surface tension values have high importance both for fundamental studies and bioapplications.

The author is thankful to I.V.Milaeva, N.A.Dovshenko for technical assistance. This work was supported by the Russian Scientific Foundation (grant 14-16-00046).

Studies of Arenediazonium Ions Reaction with Gallates in the β -Cyclodextrine Solution

Marta Szymula^{a*}, Andrzej Sienkiewicz^a, Jolanta Narkiewicz-Michalek^a, Carlos Bravo-Diaz^b

^aMaria Curie-Skłodowska University, Faculty of Chemistry, 20-031 Lublin, Poland

^bDepartamento de Química-Física, Universidad de Vigo, 36-200 Vigo, Spain

Email:szymula@hektor.umcs.

Arenediazonium compounds, ArN_2^+ , are strong oxidizing agents that can easily undergo homolytic fragmentation to produce aryl radicals upon reacting with certain electron donors via one-electron transfer processes. The basic aspects of the electrochemical reduction processes of arenediazonium ions in aqueous solutions and in some binary systems are known [1,2], and new trends and applications are appear.

In this paper, we have explored the effect of β -CD on the electrochemical behaviour of p-substituted arenediazonium ions by employing differential pulse polarography. Polarograms reflect all reduction steps of arenediazonium ions, and provide valuable information on the effects of CDs on the substrate electroactivity.

Five para-substituted benzenediazonium salts: benzenediazonium (BD), 4 – methylobenzenediazonium (4MBD), 4 – metoxybenzenediazonium (4MOXBD), 4 – bromobenzenediazonium (4BrBD) and 4 – nitrobenzenediazonium (4NOBD) tetrafluoroborate were investigated. It was found that the addition of β -cyclodextrin (β -CD) to the aqueous acidic solution substantially changes the peak potentials, E_p , and peak currents, I_p , of the investigated arenediazonium ions and that these changes depend on the type of substituent. Either the decrease in I_p , or the shift of E_{app} can be interpreted in terms of the formation of the inclusion complex 1:1 between β -CD and an arenediazonium ion.

The presence of β -CD influences also the reaction between arenediazonium ions and nucleophiles such as e.g. alkyl gallates which are well known synthetic antioxidants.

1. E. Gonzalez-Romero, B. Fernandez-Calvar, C. Bravo-Diaz, *Progr. Colloid Polym. Sci.* **123**(2004)131.
2. E. Gonzalez-Romero, B. Malvido-Hermelo, C. Bravo-Diaz, *Langmuir* **18**(2002)46.

Flocculating Properties of an Extracellular Substance Produced by Bacterial Strain *Rhodococcus Opacus*

Lucyna Holysz^a, Aleksandra Szczes^a, Magdalena Czemińska^b, Anna Jarosz-Wilkolazka^b

^a*Department of Physical Chemistry-Interfacial Phenomena, M. Curie-Sklodowska University, 20-031 Lublin, Poland*

^b*Department of Biochemistry, M. Curie-Sklodowska University, 20-031 Lublin, Poland*

E-mail: lucyna.holysz@umcs.pl

Flocculation is an essential phenomenon used in different industrial processes such as wastewater treatment, drinking water purification and downstream processes in biotechnology. Some microorganisms, including algae, bacteria, actinomycetes and fungi, have been reported to produce extracellular biopolymers containing glycoproteins, polysaccharides, proteins, lipids, glycolipid and nucleic acid with flocculation activity. Compared with conventional synthetic organic flocculants these natural occurring ones are environment-friendly, biodegradable, nontoxic and non carcinogenic [1,2].

The mechanisms of flocculation in biological systems has been extensively investigated, however are not fully understand. In general, bioflocculants cause aggregation of cells and particles by bridging and charge neutralization. Most bioflocculants and suspended particles are negatively charged. Hence, cations can neutralize negatively charged functional groups of both bioflocculant molecules and suspended particles, which increased the adsorption of biopolymer on suspended particles and may mediate bridging between solid particles and the bioflocculant molecules [3,4].

The influence of extracellular substance produced by bacterial strain belonging to family Nocardiaceae on the behavior of kaolin dispersions was studied in the presence of Na⁺, Ca²⁺, Mg²⁺ and Fe²⁺ ions at different pH, temperature and ions concentrations. Kaolin suspension acted as a model to explore the flocculating mechanism. Flocculating activity was investigated by means of zeta potential, mean diameter and light transmittance measurements.

This project was financed by The National Science Centre based on the decision number DEC-2012/07/B/ST5/01799.

References

1. J. Bao-jun, Y. Jiang-mei, *Phys. Procedia* 21 (2012) 425.
2. S.A. Zaki, M.F. Elkady, S. Farag, D. Abd-El-Haleem, *J. Environ. Biol.* 34 (2013) 31.
3. H. Salehizadeh, S.A. Shojaosadati, *Biotechnol. Adv.* 19 (2001) 371.
4. J.-Y. Wu, H.-F. Ye, *Process Biochem.* 42 (2007) 1114.

Ultrasmall fluorescent gold nanoclusters for biomedical applications

E. Csapó, D. Ungor, I. Dékány

*MTA-SZTE Supramolecular and Nanostructured Materials Research Group, University of Szeged,
Department of Medical Chemistry, Faculty of Medicine, H-6720 Szeged, Hungary*

Nanoparticles (NPs), especially of plasmonic gold and silver NPs, are of particular interest due to their size-, shape- and composition-dependent optical, electric and magnetic properties. The utilization of Au NPs, especially in the field of biomedical applications, (*e.g.* diagnostic, in vivo and in vitro imaging, therapeutic techniques *etc.*) requires biocompatible preparation routes. In this case only one (bio)ligand (*e.g.* peptide or protein) acts the part of both reductant and stabilizing agent. BSA, lysozyme, pepsin, trypsin, insulin *etc.* have been used to synthesize different protein-protected gold nano-objects. Different nanostructures (NPs or nanoclusters/nanodots) can be synthesized depending on the molar ratio of gold precursor and the protein as reductant. Small ligand/protein excess results in the formation of plasmonic NPs with diameters larger than 2 nm, while in case of high protein excess sub-nanometer sized particles (nanoclusters (NCs)/nanodots) are formed ($d < 2$ nm). In contrast to the bulk materials and AuNPs, these ultra-small NCs show unique physical and chemical properties such as well-defined molecular structure, discrete electronic transitions and characteristic size-dependent photoluminescence. Based on these above mentioned outstanding properties, Au NCs have been used to develop optical probes for bio-sensing, bio-labelling and bio-imaging applications.

In our work different biomolecules (amino acids, dipeptide and large protein) have been used to synthesize fluorescent gold NCs. The size and the structure of the prepared NCs have been characterized by UV-Vis and fluorescence spectroscopy, and HRTEM, XRD, DLS, XPS and MS techniques have been applied for detailed characterization. Based on the applied bioligands as reductant the photoluminescent properties of AuNCs can be tuned.

Properties of fibrinogen monolayers on mica – electrokinetic and colloid deposition studies

M. Wasilewska, Z. Adamczyk, M. Nattich-Rak
J. Haber Institute of Catalysis and Surface Chemistry, PAS, Cracow, Poland

ncwasile@cyf-kr.edu.pl

Fibrinogen is a thrombin-coagulable multifunctional glycoprotein occurring in the blood of vertebrates and exhibits a strong tendency to adsorb on various surfaces under broad range of conditions. Fibrinogen adsorption at biomaterial surfaces plays an important role in mediating cellular interactions that are key event in determining biocompatibility of these materials.

Therefore the main objective was to reveal conformational state of fibrinogen monolayers on mica at different pHs of 3.5 and 7.4. Two methods were used in our investigations: the streaming potential which offers a unique possibility of direct, *in situ* determination of the electric properties of particle and protein monolayers and the colloid deposition method useful for determining fibrinogen molecule orientation.

It was established that at pH 3.5 fibrinogen adsorption is irreversible for ionic strength range 3×10^{-4} to 0.15 M. On the other hand, for pH 7.4, a partial desorption of fibrinogen was observed for ionic strength below 10^{-2} M. Additionally it was confirmed that fibrinogen monolayers formed at both pHs are characterized by the presence of the side-on and end-on oriented molecules. At pH 3.5 the population of the side-on adsorbed molecules is rather small and the end-on adsorbed molecules assume extended conformations. On the other hand, at pH of 7.4 the population of the side-on molecules adsorbed with the side A α chains located underneath and levitating above the negatively charged surface is larger. Accordingly the thickness of the fibrinogen monolayers equals to 70 and 25 nm at pH of 3.5 and 7.4, respectively, as received by the colloid deposition method.

Nattich-Rak, M., Adamczyk, Z., Wasilewska, M., Sadowska, M. J. Collod. Interface Sci. 2015, 449, 62-71

Application of an EPS produced by Bacterial Strain *Rhodococcus* for Removal of Pb (II), Cd (II) and Ni (II) Ions from Aqueous Solutions

A. Szczes,^a R. Dobrowolski,^a M. Czemińska,^b A. Jarosz-Wilkolazka^b

^aFaculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

^bFaculty of Biology and Biotechnology, Maria Curie-Skłodowska University, Lublin, Poland

aszczes@poczta.umcs.lublin.pl

Heavy metal pollution is one of the most important environmental problems today, especially in relation to water contamination. Hence, the metal binding capacity of different bacteria seems to be a promising, eco-friendly and economically attractive technique for treating metal contaminated waters. Biosorption as a method that involves the use of biological materials that form complexes with metal ions is considered as a potential instrument for the removal of metals from waste solutions and for precious metals recovery, and becomes alternative to the conventional processes, such as those based on ion exchange, or adsorption on activated carbon. In this process a chemical link between functional groups on the biosorbent and the metal ions present in the solution or an ion-exchange reaction due to the high ion-exchange capacity of the biosorbent may occur. Bioremediation of heavy metals employ living or non-living microbial biomass or isolated biopolymers. Extracellular polymeric substances (EPS) are a complex mixture of macromolecules such as polysaccharides, proteins, nucleic acids, uronic acids, lipids produced by prokaryotic and eukaryotic microorganisms [1,2].

The heavy metal binding capacity of extracellular polymeric substances (EPS) produced by bacterial strains *Rhodococcus opacus* and *Rhodococcus rhodochrous* was investigated by adsorption from synthetic metal solution. The metal concentration was analyzed using atomic absorption spectroscopy (AAS) technique. Metal uptake capacity has been evaluated using sorption isotherm curves derived from equilibrium batch sorption experiments.

Acknowledgements: This project was financed by The National Science Centre based on the decision number DEC-2012/07/B/ST5/01799.

References

1. J. Bao-jun, Y. Jiang-mei, *Phys. Procedia* 24 (2012) 425.
2. A. Pal, A.K. Paul, *Indian J. Microbiol.* 48 (2008) 49.

The uptake of a hydrophobe by a phospholipid bilayer: a connection between pheromone and anaesthetic action

P. Lo Nostro,^a N. Peruzzi,^a S. Macchi,^b B. W. Ninham,^c S. Borsacchi,^b M. Geppi,^b
E. Fratini,^a P. Baglioni^a

^a *Dept. Chemistry & CSGI, University of Florence, 50019 Sesto Fiorentino (Firenze) – Italy*

^b *Dept. Chemistry and Industrial Chemistry, University of Pisa, 56124 Pisa - Italy*

^c *Research School of Physical Sciences and Engineering, Canberra, ACT0200 – Australia*

PLN@csgi.unifi.it

The phase behavior of mixtures of a typical insect pheromone (“olean”) and phospholipids is extensively explored through NMR, SAXS and DSC. The results mimic those for mixtures of anaesthetic molecules and phospholipids. They also mimic the behavior and microstructure of ternary mixtures of membrane mimetic, bilayer-forming double chained surfactants, oils and water. Taken together with recent models for conduction of the nervous impulse, all hint at lipid involvement and underline unity in mechanisms of pheromone, anaesthetic and hydrophobic drugs.

Shearing of Red Blood Cells Aggregates Induced by Rod-Like Colloids

O. Korculanin and M. P. Lettinga
ICS-3, Forschungszentrum Jülich, Jülich, Germany

o.korculanin@fz-juelich.de

Blood is a shear thinning fluid with a complex response that strongly depends on the Red Blood Cells (RBC) ability to form aggregates in the form of stacks, called rouleaux. [1] In turn, the formation of rouleaux is influenced by the buffer in which the red blood cells are dispersed as well as the flow they are subjected to.

Depletion has long been believed to play a role in rouleaux formation, namely the presence of macromolecules such as fibrinogen in blood plasma. However, despite numerous investigations, microscopic understanding of the formation and break up of RBC aggregates has not been fully elucidated. To that end, we combined a home-build counter-rotating cone-plate shear cell with ultra-fast confocal microscope enabling visualization of the structures while shearing. For fine-tuning the interaction forces between the cells we used the rod-like fd virus, a very efficient colloidal depletant with high length-to-diameter ratio. [2] We present a phase diagram for mixtures of Red Blood Cells at low haematocrit and fd virus.

References

1. Fedosov, D. A., Pan, W., Caswell, B., Gompper, G., & Karniadakis, G. E. (2011). Predicting human blood viscosity in silico. *Proceedings of the National Academy of Sciences of the United States of America*, 108(29), 11772–11777. doi:10.1073/pnas.1101210108
2. D. Guu, J.K.G. Dhont, G.A. Vliegthart, M.P. Lettinga, Depletion induced clustering in mixtures of colloidal spheres and fd-virus, *Journal of Physics-Condensed Matter*, 24 (2012).

A general approach to the immobilization of glyco-enzymes acting in cascade inside calcium alginate beads.

A. Mallardi,^a V. Angarano,^b G. Palazzo,*^b...

^a *CNR - IPCF, Istituto per i Processi Chimico-Fisici, Bari, Italy*

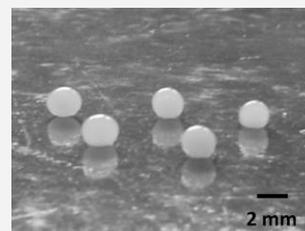
^b *Dipartimento di Chimica, Università di Bari, Bari, Italy*

gerardo.palazzo@uniba.it

The present study proposes a general enzyme encapsulation approach, based on the use of calcium alginate hydrogels. Alginate is an anionic polymer whose gelation can be obtained by ionic cross-linking with multivalent cations¹. When an “external gelation” occurs, beads with a diameter of few millimeters can be obtained (see figure).

These beads are biocompatible and low cost and can provide a good matrix for the entrapment of sensitive biomolecules.

The entrapment of enzymes in alginate beads suffers some disadvantages, like as low enzyme loading efficiency with reduction of the immobilization yields and reusability, related to the enzyme leakage from the large beads pores (cut off of about 100 kDa).



We have entrapped in alginate beads, as model system, three glycoenzymes (trehalase, glucose oxidase and horseradish peroxidase) acting in series. Leakage of entrapped enzymes after gelation has been avoided using the biospecific complexation between concanavalin A (Con A) and sugar residues of glycoenzymes as the driving force for the formation of large enzyme networks, that cannot go through beads pores. After enzyme immobilization in beads the trehalase activity of the system has been used for the optical determination of trehalose sugar and the analytical performances of this biosensor have been examined.

References

J. P. Paques, E. van der Linden, C. J.M. van Rijn, L. M.C. Sagis, *Advances in Colloid and Interface Science* 209 (2014) 163.

Study of the wettability and absorptivity of mucoadhesive polymers by simulated biological fluids

M. Rojewska^a, M. Olejniczak–Rabinek^b, A. Bartkowiak^a,
K. Prochaska^a, J. Lulek^b

^aUniversity of Technology, Institute of Chemical Technology and Engineering, ul. Berdychowo 4,
60-965 Poznan, Poland

^bPoznan University of Medical Sciences, Department of Pharmaceutical Technology,
Grunwaldzka 6, 60-780 Poznan, Poland

monika.rojewska@put.poznan.pl

The improve and enhance of the bioavailability of potential drugs is the main issue in the formulation science. In recent years, increasing interest in mucoadhesive polymers have been observed because the formulation with the participation of these polymers can provide prolonging the residence time of the dosage form on the adsorbing membrane as well as localizing drugs in a particular region. The rate at which a solid oral drug delivery system dissolves depends on many parameters, and occurs in a series of steps: wetting, solvent penetration, disintegration, swelling (if applicable) and dissolution of components.

The contact surface between the surface of mucoadhesive polymers and biological fluids has crucial meaning from the perspective of biomedical applications. The aim of our work was estimated the influence of the composition of the mixture of polymers and type of biological fluids on the wetting properties and absorptivity of mucoadhesive polymers (Kollidon VA 64, Hydroxyethylcellulose, Polycarbophil AA–1 and Carbopol 974P NF). New formulations were prepared by mixing the selected mucoadhesive polymers in two forms: powders and tablets. The individual polymers were mixed in a various ratios.

Measurements of advancing contact angle of simulated biological fluids on the polymeric matrix tablets were carried out using the sessile drop method (Tracker I.T.Concept, Theta KSV Optical tensiometer). The wetting of mucoadhesive polymers powders was measured by Washburn method (Sigma 701, KSV). Additionally, the swelling index of the polymeric matrix tablets tested in biological fluids was determined. SEM images were made in order to make a qualitative evaluation of polymeric surfaces of tablets and determination of morphology of powders of mucoadhesive polymers.

The results obtained indicated that the composition of the mucoadhesive polymer mixtures and the type of biological fluids have a significant importance for the absorptivity and wettability of the considered materials. In the case of some tested polymer blends has been observed a distinct synergism in the wetting properties.

Acknowledgement

The research was financially supported by 03/32/DS-PB/0501 and by 502–01–033–14–429–03439 PUMS.

Protein Phase Behavior: Linking Experiments to Colloidal Interaction Models

F. Platten, D. Wagner, J. Hansen, S.U. Egelhaaf
Heinrich Heine University, Duesseldorf, Germany

Florian.Platten@hhu.de

Although interactions in protein solution are frequently tuned by additives, quantitative information on the related protein-protein interaction potential is scarce.

We studied the phase behavior of lysozyme in the presence of NaCl and guanidine hydrochloride (GuHCl) [1]. From the metastable liquid-liquid phase separation, we analyze the concurrent effects of the two salts on the interactions between lysozyme molecules. In particular, we disentangle electrostatic and guanidine-specific contributions to the interaction potential. Remarkably, in mixtures of high salt concentrations, the contributions of both salts appear to be additive.

Colloidal interactions can be characterized by a global parameter, the second virial coefficient. Based on colloidal interaction models, we present two approaches how to infer the second virial coefficient from the phase behavior: (i) on the basis of modified DLVO theory and light scattering data for a reference state and (ii) based on the extended law of corresponding states (ELCS) for protein solutions [2]. Furthermore, we show that, for a number of different solution conditions, the binodal phase boundaries of protein solutions fall on top of each other if the second virial coefficient is used instead of temperature and repulsive interactions are accounted for by an effective particle size.

[1] F. Platten, J. Hansen, D. Wagner, J. Milius, S.U. Egelhaaf, in preparation.

[2] F. Platten, N.E. Valadez-Perez, R. Castaneda-Priego, S.U. Egelhaaf, submitted to J. Chem. Phys; arXiv:1503.00790.

Analytical Ultracentrifugation of charged proteins

D.M.E. Thies-Weesie, J. van Rijssel, and A.P. Philipse

Van 't Hoff laboratory for Physical and Colloid Chemistry, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, the Netherlands

d.m.e.thies@uu.nl

Analytical ultracentrifugation (AUC) is one of the classical methods for the characterization of proteins in dilute solutions. It can reveal the molar mass, the gross shape and the heterogeneity of the sample, as well as information on self- and hetero associating properties¹.

The determination of molecular masses from barometric sedimentation profiles is thought to be quantitatively correct for non-interacting particles. However, strongly inflated sedimentation profiles were observed for dilute dispersions of charged particles^{2,3}. Theory⁴ and simulations⁵ proposed that these strongly non-barometric profiles were caused by an internal macroscopic electric field that, even for non-interacting particles, significantly decreases the buoyant particle mass. This has been confirmed experimentally by Raşa and Philipse⁶ for charged silica spheres at low ionic strength.

Proteins are usually studied under salt concentrations to suppress charge effects. Work by Raşa and Philipse justifies this approach. However, their work also clearly shows that an excess of salt suppresses important information on the electrical properties of macromolecules. Centrifugal analysis of proteins at low salt concentration still provides the molecular mass, but in principle also yields its valency.

In this work the results of Raşa and Philipse are extended to proteins and obtained sedimentation diffusion profiles are compared with results obtained with a membrane osmometer.

¹ Scott, D.J., Harding, S.E., and Rowe, A.J. (eds) Analytical ultracentrifugation, Techniques and methods, (Royal Society of Chemistry, Cambridge 1995).

² Piazza, R., Bellini, T., and Degiorgio, V., Phys. Rev. Lett. **71**, 4267-4270 (1993).

³ Philipse, A.P., and Koenderink, G.H., Adv. Colloid Interface Sci. **100-102**, 613-639 (2003).

⁴ Roij, R. van, J. Phys.: Condens. Matter **15**, S3569-S3580, 2003.

⁵ Hynninen, A.P., Roij, R. van, Dijkstra, M., Europhys. Lett. **65**, 719-725, 2004.

⁶ Raşa, M., and Philipse, A.P., Nature **429**, 857-860, 2004.

Acacia gum: a good candidate for emulsification through coalescence-limited mechanisms.

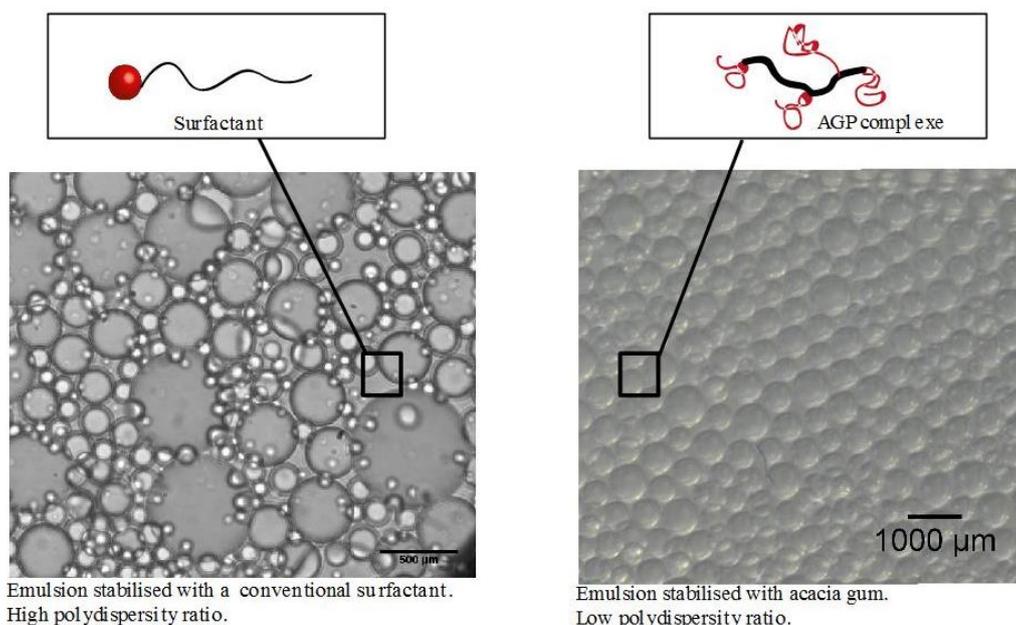
*M. Atgié, O. Masbernat, K. Roger
Laboratoire de Génie Chimique, INP, Toulouse, FR

* marina.atgie@ensiacet.fr

Acacia gum is known to possess outstanding emulsion stabilization properties. It is composed of polysaccharides (Arabinogalactan AG ~93%), proteins (~2%) and of polysaccharides-proteins conjugates (Arabinogalactan-proteinaceous AGP ~5%), which are known to be the emulsifying agents in the gum [1]. Herein the objective is to study the ability of acacia gum to produce stable and narrow-size distributed emulsions. It is expected that similar to mineral particles, AGP would spontaneously adsorb at oil/water interfaces and, through a coalescence-limited mechanism, form Pickering-type emulsions [2].

Interfacial tension measurements first show that AGP exhibits higher energies of adsorption than small amphiphilic molecules but the adsorption at an oil/water interface is quite sensitive to the pH. However once adsorbed, emulsions stability is no longer subject to the pH or the salinity of the bulk. Steric repulsions resulting from the barrier formed by the branched polysaccharides are responsible of the emulsion stability.

Then it is shown that a range of operating parameters exists within which o/w emulsions can be produced through a coalescence-limited mechanism. Due to the insoluble monolayer-type behavior, the rate of coverage of the interface by AGP results from successive coalescence events. Thus stable micrometric emulsions with low polydispersity ratios are obtained (see figure below).



[1] D. Renard et al., *Carbohydrate Polymer*, 90, 322-332 (2012)

[2] S. Arditty et al., *Eur. Phys. J. E11*, 273-281 (2003)

Blood's sol-gel transition

F. Caton,^a E. Ghiringhelli,^a B. Polack,^b ...

^a*Laboratoire rhéologie et et procédés, UMR CNRS 5520 Université Grenoble-Alpes, Grenoble, France*

^b*Hématologie Biologique CHU de Grenoble ; TIMC-TheREx UMR 5525, Université Grenoble Alpes, Grenoble, France*

catonf@ujf-grenoble.fr

Since the very beginning of blood mechanical behaviour studies (~1950), there has been a debate on blood eventual yield stress (e.g. [1]), i.e. whether it is solid or liquid at small deformations. As recent results show that blood flow is plug-like, blood is probably submitted in average to much lower shear rates in the circulation than previously thought. In particular, aggregates endure in the circulation since they are submitted only to the small deformations present in the plug ([2]). Unfortunately, proper measurements of the yield stress on a low viscosity fluid, highly concentrated in heavy colloids and packed with proteins are very difficult, accentuated by blood's large biological variability.

In order to decrease this variability, we used model blood consisting in washed erythrocytes resuspended in buffer supplemented with the main plasma proteins (fibrinogen, albumin, immunoglobulins). We used oscillatory measurements which provide a direct determination of the liquid or solid state of the material, while avoiding the shear-induced wall depletion effect. To decrease the influence of erythrocytes sedimentation, we used Optimal Fourier Rheometry [3] which is the fastest possible viscoelastic measurement technique.

Results show that the elastic modulus of blood depends on both volume fraction and fibrinogen concentrations and can be larger than the viscous modulus. Using the Winter and Chambon criterion [4], a sol-gel transition in blood's phase diagram is found at values slightly above normal physiological values. The origin of this transition both in terms of protein content and microstructure is analysed. Finally, we discuss the implications of this finding on the (micro)circulation of blood and its potential influence on pathophysiology.

Refs.

1. Dufaux et al. *Determination of rheological properties of red blood cells by Couette viscometry* 1980, Vol. 15, pp. 1367-1374; Picart et al. *Human blood shear yield stress and its hematocrit dependence.* 1, 1998, J. Rheol., Vol. 42.
2. Ghiringhelli et al. *Optimal Fourier Rheometry.* 5, 2012, Vol. 51, pp. 413-420.
3. Winter HH *Can the gel point of a cross-linking polymer be detected by the G' - G'' crossover?*, Polym. Eng. Sci., vol. 27, no. 22, pp. 1698-1702, 1987.
4. M. Brust et al., *The plasma protein fibrinogen stabilizes clusters of red blood cells in microcapillary flows.*, Sci. Rep., vol. 4, p. 4348, Jan. 2014.

Silver-Enhancement Protocol for TEM imaging of Antibody Nanoparticles Conjugates adsorbed on SBA-15 Mesoporous Silica

Maura Monduzzi,^a Marco Piludu,^b Luca Medda,^a Francesca Cugia,^a and Andrea Salis^a

^aDepartment of Chemical and Geological Sciences, CSGI and CNBS, ^bDepartment of Biomedical Science, University of Cagliari, Cittadella Universitaria, S.S. 554 bivio Sestu, 09042- Monserrato (CA), Italy.; E-mail: monduzzi@unica.it

Nanomedicine has become one of the most exciting challenges of the present century. Biomacromolecules are being coupled with inorganic nanomaterials for targeted drug delivery, imaging and therapeutics. Among biomacromolecules, antibodies are large Y-shaped proteins produced by the immune system in response to specific antigens. Besides as drug themselves, antibodies can also be used for the targeting of specific drugs or metallic nanoparticles. Ordered Mesoporous materials¹ are receiving great attention as possible carriers for therapeutic agents, and biomacromolecules. In previous work we used Immune Gold Staining to prove the location of lysozyme adsorbed inside SBA-15 pores.² Here we immobilised an antibody fragment F(ab')₂GAMIgG (diameter 3 nm) conjugated with ultra-small gold nanoparticles, GNPs (diameter 0.8 nm) into the mesopores of amino functionalised SBA-15 mesoporous silica. These nano-bioconjugates are being studied for either cancer therapies and imaging purposes. The aim of this work is the visualisation of the conjugates adsorbed on SBA-15 with conventional transmission electronic microscopy (TEM). Due to the ultra-small size of GNPs, we use the silver enhancement procedure³ to amplify their size. In this method, the GNPs act as the nuclei for the deposition of metallic Ag atoms obtained by the reduction of Ag⁺ ions. The silver-enhanced GNPs are visible at conventional TEM thus allowing for an unequivocal imaging of the location of the antibody fragment-GNPs conjugates, in particular in the inner channels of SBA-15.

1) L. Medda, M. F. Casula, M. Monduzzi and A. Salis, *Langmuir*, 2014, **43**, 12996–13004.

2) M. Piras, A. Salis, M. Piludu, D. Steri and M. Monduzzi, *Chem. Commun.*, 2011, **47**, 7338–40.

3) M. Piludu, M. S. Lantini, M. Cossu, M. Piras, F. G. Oppenheim, E. J. Helmerhorst, W. Siqueira and A. R. Hand, *Arch. Oral Biol.*, 2006, **51**, 967–73.

The molecular motion of BSA protein under physiological conditions is ion specific

Andrea Salis, Luca Medda, and Maura Monduzzi

^aDepartment of Chemical and Geological Sciences, CSGI and CNBS, ^bDepartment of Biomedical Science, University of Cagliari, Cittadella Universitaria, S.S. 554 bivio Sestu, 09042- Monserrato (CA), Italy.;
E-mail: asalis@unica.it

There is at present an extraordinary interest toward ion specific ‘Hofmeister’ phenomena [1–3]. In this work we investigated the specific effect of salts on the Brownian molecular motion of a concentrated solution of a model protein (bovine serum albumin, BSA) by measuring the diffusion coefficient (D_c) through dynamic light scattering (DLS). At a physiological concentration of BSA (40 mg/mL) and physiological conditions ($T=37^\circ\text{C}$, pH 7 and 0.1 M salt) the D_c values display a marked ion specific dependence. A monotonic Hofmeister series for anions ($\text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$) and a bell shaped series for cations ($\text{Rb}^+ \sim \text{K}^+ > \text{Na}^+ > \text{Cs}^+ \sim \text{Li}^+$) are obtained. These data allow to obtain useful insights about the electrolytes' effects on the molecular motion of proteins under physiological conditions, and on the molecular mechanisms which address the widely debated Hofmeister effect.

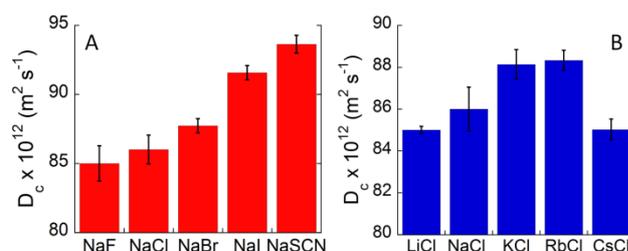


Fig. 1 Specific ion effects on the diffusion coefficient of BSA (40 mg/mL) in 10 mM phosphate buffer solutions at pH 7, and 100 mM salt concentration. (A) Effect of anions on D_c values at 37°C. (B) Effect of cations on D_c values at 37°C.

References

- 1) P. Jungwirth and P. S. Cremer, *Nat. Chem.*, 2014, **6**, 261–263.
- 2) A. Salis and B. W. Ninham, *Chem. Soc. Rev.*, 2014, **43**, 7358–7377.
- 3) P. Lo Nostro and B. W. Ninham, *Chem. Rev.*, 2012, **112**, 2286–2322.

Formulation, Characterization and Colloid Stability of Nanostructured Lipid Carriers for Delivery of Myricetin and Bioimaging Markers

A. Pucek^a, J. Kulbacka^b, A. Lewińska^c, K.A. Wilk^a

^aDepartment of Organic and Pharmaceutical Technology, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

^bDepartment of Medical Biochemistry, Medical University, Chałubińskiego 10, 50-368 Wrocław, Poland

^cFaculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

agata.pucek@pwr.edu.pl

Recent advances in nanotechnology have contributed to the development of multifunctional nanoparticles which are designed for bioimaging or theranostic applications. Nanostructured lipid carriers (NLCs) are an outstanding type of delivery system offering improved performance in terms of drug loading and long-term stability with the ability to form highly concentrated dispersions. NLC matrix is composed of a mixture of spatially different lipid molecules, normally mixture of solid and liquid lipid, which makes more imperfection in the matrix to accommodate more drug molecules.

In our study we provide properties of nanostructured lipid carriers loaded with multifunctional hydrophobic cargoes: natural occurring flavonoid – myricetin and sensitizer IR-780 compared to core–shell CdSe/ZnS quantum dots (QDs). QDs have been applied as efficient fluorescent probes for bioimaging of cancer cells as an alternative to traditional organic fluorophores (IR-780) because of opportunities for using them as imaging agents within the so-called “biological transmission window” (650-1000 nm). The NLC formulations were obtained via solvent-diffusion method and offer low costs, low energy consumption and simplicity. The obtained NLCs were physicochemically characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), atomic force microscopy (AFM) and differential scanning calorimetry (DSC). The delivery efficiency *in vitro* was evaluated with two human colon cancer cell lines: doxorubicin sensitive LoVo and doxorubicin resistant LoVo/DX. Confocal laser scanning microscopy (CLSM) was applied for intracellular distribution of QDs and IR-780. Simultaneously mitochondria and nuclei were stained. Cytotoxicity was evaluated by MTT assay. The encapsulation of myricetin and the selected biolabels (i.e., IR-780, core–shell CdSe/ZnS QDs) leads to custom-designed products designated for the bioimaging purposes. This work was supported by the National Science Center (Poland) under Grant No. 2012/05/B/ST4/00095.

Folate-Functionalized Biocompatible Polymeric Micelles for Tumor Targeted Delivery of Zinc (II) Phthalocyanine

K. A. Wilk^a, Ł. Lamch^a, J. Kulbacka^b, M. Dubińska-Magiera^c

^a Department of Organic and Pharmaceutical Technology, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

^b Department of Medical Biochemistry, Wrocław Medical University, Chałubińskiego 10, 50-368 Wrocław, Poland

^c Department of General Zoology, Zoological Institute, University of Wrocław, Sienkiewicza 21, 50-335 Wrocław, Poland

kazimiera.wilk@pwr.edu.pl

Targeted drug delivery is becoming increasingly attractive in cancer therapy since it can both improve drug efficacy and reduce the side effects of drugs on normal tissues. The targeting can be achieved via the enhanced permeability and retention effect (into the areas with the compromised vasculature) as well as by attaching specific targeting ligand molecules to the micelle surface.

Therefore, in our studies, we entrapped a 2nd generation photosensitizer (zinc (II) phthalocyanine – ZnPc) in the folate functionalized micelles of biocompatible, FDA-approved for biomedical applications diblock copolymer methoxypoly(ethylene oxide)-b-poly(L-lactide) (mPEG-b-PLLA) and its derivative with folate attached to the end of PEG chain (FA-PEG-b-PLLA). The folate conjugated copolymer was synthesized by PEG-ylated folic acid attachment to poly(L-lactide) through esterification under Steglich conditions. Functionalized polymeric micelles systems were prepared by dropwise adding of mPEG-b-PLLA and/or FA-PEG-b-PLLA and ZnPc solution in DMSO, followed by organic solvent removal. The potential of the obtained micelles was evaluated in cyto- and photocytotoxicity studies as well as in imaging of intracellular localization, accumulation and distribution of photosensitizer delivered to ovarian carcinoma (SKOV3) and metastatic melanoma (Me45) cell lines, as well as normal human keratinocytes (HaCaT). Analysis of reactive oxygen species (ROS) generation and apoptotic marker PARP-1 (poly(ADP-ribose)polymerase) expression in cells confirmed enhanced efficiency of encapsulated ZnPc in comparison to the free photosensitizer. DLS measurements confirmed the micelles diameter below 150 nm, low polydispersity index and good colloid stability of the studied nanocarriers, while AFM was used to investigate their morphology. Our results prove that the obtained functionalized polymeric micelles are promising nanocarriers for PDT procedures. This work was supported by the Wrocław Research Center EIT+ under the project “Biotechnologies and advanced medical technologies” - BioMed (POIG 01.01.02-02-003/08-00) financed from the European Regional Development Fund Operational Programme Innovative Economy, 1.1.2.

Formation of spatially-patterned patches of lipids

A.Simon^{1,2}, C. Faure²

¹ Université Lyon 1, University of Lyon, 43 Bd du 11 Nov. 1918, F-69622 Villeurbanne cedex, France. ² CBMN UMR CNRS 5248, Université de Bordeaux, Allée Geoffroy Saint Hilaire, Bat. 14B, Pessac, France

We recently developed a new patterning process, called electro-colloidal lithography (ECL) which only requires electric fields and colloidal particles.¹ ECL is used here to design holed metallic film on which lipids are deposited by vesicles fusion.² This results in producing lipids patterned in an hexagonal array format (Figure 1). Fluorescent microscopy revealed 5 μm -sized lipid domains. This challenging approach could contribute to mimic many properties of native cell membranes and also to further develop membrane protein sensing platforms.

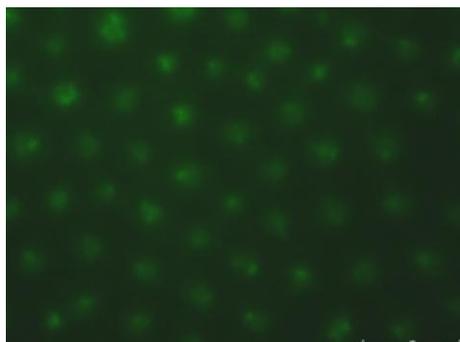


Figure 1. Fluorescent image of an array containing addressed fluorescently-labelled lipid.

Image scale: 224 μm x 167 μm .

1. Bazin D., Faure C. *Soft Matter*, 2012, 8, 3053.

2. Reviakine I., Simon A., Brisson A. *Langmuir*, 2000, 16(4), 1473.

Pressure Distribution under Bio-Inspired Adhesive Microstructures

Jens W. Neubauer,^a Longjian Xue,^b Johann Erath,^a Dirk-M. Drotlef,^b
Aránzazu del Campo,^b Andreas Fery^a

^aUniversity of Bayreuth, Physical Chemistry II, Bayreuth, Germany

^bMax-Planck-Institute for Polymer Research, Dynamic Biointerfaces, Mainz, Germany

Jens.Neubauer@uni-bayreuth.de

Animals and plants have evolved fibrillar hierarchical structures to gain adhesion even on smooth surfaces. Mimicking these structures, adhesives with micropillars of various shapes can be produced. [1] They excel in regards of adhesion or friction, depending on the shape of the micropillars. [2] Therefore, the pressure distribution at the contact area is of particular interest.

We use a mechano-responsive polyelectrolyte brush to sense pressures down to 10 kPa with a spatial resolution better than human skin (1 μm). [3] The polyelectrolyte brush is labeled with a fluorescent dye, and sensitive to local pressures. Soft colloidal probe AFM [4] is combined with confocal microscopy to correlate the local pressure with the local fluorescence intensity.

After calibration, the local pressure under the micropillars of the adhesives can be read out from the fluorescence intensity. For this purpose, the contact formation is controlled with a commercial setup (PVM-A, GeSiM) and observed with confocal microscopy.

- [1] del Campo, Greiner, Arzt *Langmuir* **2007**, 23, 10235.
- [2] Xue, Iturri, Kappl, Butt, del Campo *Langmuir* **2014**, 30, 11175.
- [3] Bünsow, Erath, Biesheuvel, Fery, Huck *Angew. Chem. Int. Ed.* **2011**, 50, 9629.
- [4] Erath, Schmidt, Fery *Soft Matter* **2010**, 6, 1432.

Microencapsulation by complex coacervation of whey protein and acacia gum

Delphine Ach,^a Stéphanie Briançon,^a Yves Chevalier,^a Guy Broze^b

^a *University of Lyon 1, LAGEP, Villeurbanne, France*

^b *Prayon SA, Engis, Belgium*

ach@lagep.univ-lyon1.fr

Complex coacervation is the phase separation of two oppositely charged hydrocolloids from the mixture of their solutions. The deposition of the newly-formed coacervate phase around droplets of active ingredient suspended or emulsified result in their encapsulation, yielding microcapsules [1, 2].

The objective was to identify the critical parameters of the microencapsulation process in order to control the formation and characteristics of microcapsules prepared by complex coacervation of whey protein and acacia gum.

Firstly, complex coacervation between whey proteins isolate (WPI) and acacia gum was investigated in order to disclose the roles and the contributions of each component of WPI to the formation of the complex coacervate. The major components of whey protein (β -lactoglobulin and α -lactalbumin) and the acacia gum were quantified in the coacervate. Coacervate composition was influenced by the protein/polysaccharide ratio and pH.

Then, in line observations in the stirred reactor using a video probe was used to study the microencapsulation process [3]. This experimental set-up enabled us to identify four successive steps induced by lowering the pH and leading to the formation of microcapsules. The influence of various parameters on the formation of microcapsules was also studied by using the *in situ* video probe.

[1] Gouin S. (2004). Microencapsulation: industrial appraisal of existing technologies and trends. *Trends Food Sci. Technol.* 15 (7-8), 330-347.

[2] Zhang K. et al. (2012). Synthesis and release studies of microalgal oil-containing microcapsules prepared by complex coacervation. *Colloids Surfaces B: Biointerfaces* 89, 61-66.

[3] Ach D., Briançon S., Broze G., Puel F., Rivoire A., Galvan J.-M., Chevalier Y. (2015). Formation of microcapsules by complex coacervation. *Can. J. Chem. Eng.* 93, 183-192.

Colloid particle adhesion to cells in 3D perfusion tissue engineering constructs

N. Sarvasova,^a M. Majerska,^a A. Karasova,^a J. Dvorak,^a V. Kral,^b F. Stepanek^a

^a Department of Chemical Engineering, Institute of Chemical Technology, Prague, Technická 3, 166 28 Prague 6, Czech Republic, Tel.: +420 220 443 048

^b Laboratory of Structural Biology, Institute of Molecular Genetics, Academy of Sciences of the Czech Republic, v.v.i., Vídeňská 1083, Prague 4, 142 20, Czech Republic

Nina.Sarvasova@vscht.cz

In every development of functional particles, there is an important part consisting of the study of their behaviour in conditions simulating their end use. In the case of colloidal drug delivery carriers, this involves the study of biodistribution and deposition in biological tissues. For both ethical and economic reasons, there is a drive to reduce the use of laboratory animals for *in vivo* studies, and instead use *in vitro* systems that would still be bio-relevant. Three-dimensional (3D) tissue engineering constructs can act as such models. Under perfusion conditions, the hydrodynamic shear forces can be adjusted to values characteristic of the physiological flows. Additionally, magnetic Resonance Imaging (MRI) can be used as non-destructive, non-invasive method that provides an opportunity to observe the adhesion of drug delivery particles within the 3D cell culture in a “*real-time*” arrangement.

This work is focused on the design and development of a measuring protocol for the study of adhesive and bio-adhesive properties of particle systems capable of bio-specific targeting. For such purposes, silica-based particles modified by IgG-M75 antibody, which is specific for carbonic anhydrase IX antigen on HT-29 cancer cells, were used. The perfusion cell itself was designed especially for such purposes. The adhesion study was performed using different polymer-based media (Polydimethylsiloxane PDMS, Poly-L-Lactic acid PLA and Acrylonitrile butadiene styrene ABS). 3D scaffolds for the bio-specific adhesion in the form of lattices were printed by a 3D printer using biocompatible polymer PLA. The growth of two cell lines, HT-29 colon cancer cells and NIH-3T3 mouse fibroblasts, was studied on these 3D structures. Both cell lines were able to grow on the 3D structures, overgrowing their whole surface. Such 3D tissue model was used for studying the adhesion of antibody-modified nanoparticles under the conditions simulating interstitial fluid flow velocities in normal and tumor tissues. Character of flow in the cell (flow rates from 1 ml/min to 22 ml/min) was studied using MRI and CFD (Computational Fluid Dynamics) techniques.

Interaction of lyotropic liquid crystalline dispersions with the complement system and strategies to bypass complement activation

Peter P. Wibroe, Anan Yaghmur, S. Moein Moghimi

The use of nanoparticles for efficient targeting and delivery of drugs to various sites in the body has become a well-established field. Following intravenous injection, many synthetic surfaces are quickly recognized by the complement system, which is a major player of the innate immune system. Complement activation can prime nanoparticles for clearance by phagocytic cells, but inadvertent complement activation may induce adverse reactions. This presentation will highlight recent advances in understanding the interaction between complement pattern recognition molecules and particle surface morphology with particular focus on a set of lyotropic liquid crystalline dispersions. Novel surface engineering approaches in overcoming nanoparticle-mediated complement activation will be presented.

Bioactive helical Nanomaterials and their Influence on Stem Cell Differentiation

Gregor Kemper, Laurent Plawinski, Emilie Pouget, Shawn Wettig, Reiko Oda, Marie-Christine Durrieu

Elucidation of the cues that control fate decisions of stem cells is critical in the understanding of normal development and repair, and can be utilized in tissue engineering and regeneration applications.

In this study, we focus on how MSC adhesion and differentiation are influenced by nanohelices with the same periodicity as Collagen I, functionalized or not with RGD and BMP-2 mimetic peptides and grafted onto glass surfaces. Nanohelices presenting different lengths are used in this work.

Chiral structures with nanometric periodicity are synthesized by silica transcription of organic precursors made by self-assembly of gemini surfactant tartrate and functionalized or not with cell adhesion promoting peptide (RGD peptides) or/and BMP-2 mimetic peptides. Human mesenchymal stem cells are cultivated on these substrates and examined using scanning electron and fluorescence microscopy. Materials without peptide and/or helices act as reference surfaces.

Different surfaces were characterized using AFM, XPS, fluorescent microscopy using fluorescent peptides and SEM to validate our grafting process.

Ongoing work focusses on the behaviour of MSC seeded on nanohelices presenting different lengths (functionalized or not with RGD and BMP-2 mimetic peptides) and grafted onto glass surfaces.

Email: gregor.kemper@gmail.com



New Efficient Pickering Emulsifiers: Framboidal Triblock Copolymer Vesicles of Controllable Surface Roughness

S. P. Armes^a

^a*Department of Chemistry, The University of Sheffield, Sheffield, UK.*

S.P.Armes@sheffield.ac.uk

Pickering emulsions offer important advantages over conventional surfactant-stabilised emulsions, including enhanced long-term stability, more reproducible formulations and reduced foaming problems. The recent development of polymerisation-induced self-assembly (PISA)¹ offers broad scope for the design of a wide range of block copolymer nanoparticles with variable surface wettability that can serve as bespoke Pickering emulsifiers. In the present study, we use PISA to design *framboidal* (raspberry-like) triblock copolymer vesicles with exquisitely tunable surface roughness.² More specifically, a poly(glycerol monomethacrylate) (PGMA) chain transfer agent was first prepared by RAFT solution polymerisation and then chain-extended using 2-hydroxypropyl methacrylate (HPMA) using a RAFT aqueous dispersion polymerisation formulation to produce PGMA-HPMA diblock copolymer vesicles.³ These precursor vesicles were then used as a 'seed' for the RAFT aqueous emulsion polymerisation of benzyl methacrylate (BzMA). This water-insoluble monomer polymerises within the hydrophobic PHPMA membrane, leading to nanoscale phase separation between the enthalpically incompatible PHPMA and PBzMA blocks and the protrusion of globules of 20-50 nm diameter from the membrane surface. Small-angle X-ray scattering (SAXS) and transmission electron microscopy were used to characterise the framboidal morphology of the resulting framboidal vesicles, which were subsequently used as Pickering emulsifiers to stabilise *n*-dodecane emulsion droplets in water. The adsorption efficiency was determined as a function of surface roughness using a turbidimetry assay to monitor the concentration of non-adsorbed vesicles in the aqueous continuous phase. A strong correlation between surface roughness and adsorption efficiency was observed, with the latter increasing from 36 % up to 94 %. This is significantly higher than that reported previously for vesicles with smooth surfaces.⁴ In summary, framboidal vesicles with appreciable surface roughness are highly effective Pickering emulsifiers; this parameter can be fine-tuned using an efficient PISA formulation that offers considerable potential for industrial scale-up.⁵

1. N. J. Warren and S. P. Armes, *J. Am. Chem. Soc.*, **2014**, *136*, 10174.
2. P. Chambon, S. P. Armes et al., *Macromolecules*, **2012**, *45*, 5081.
3. A. Blanazs, S. P. Armes et al., *J. Am. Chem. Soc.*, **2011**, *133*, 16581.
4. K. L. Thompson, S. P. Armes et al., *J. Am. Chem. Soc.*, **2012**, *134*, 12450.
5. C. J. Mable, O. O. Mykhaylyk, S. P. Armes et al., **2015**, manuscript in preparation.

Have titania, it will pattern! Direct and remote photolithography: an innovative approach for polymer brushes micropatterning.

G. Soliveri^a, G. Panzarasa^b, K. Sparnacci^b, S. Ardizzone^a

^aDipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

^bDipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale
"Amedeo Avogadro", Alessandria, Italy

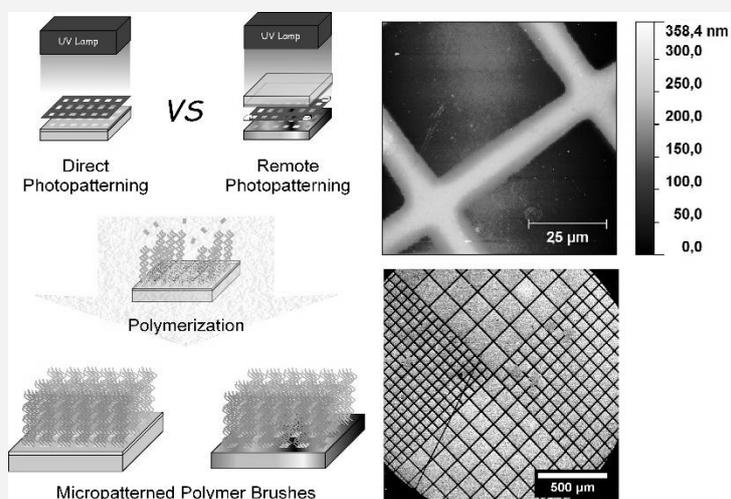
guido.soliveri@unimi.it

Photocatalytic lithography is a well established technique to achieve micro- and nanopatterning at a solid interface [1]. Such approach overcomes the drawbacks of ordinary lithographic means (*i.e.* dedicated devices, high-energy light sources, use of photoresists) simply exploiting the formation of oxidative species on a titanium dioxide photoactive surface irradiated in near-UV. However, no reports are available on the use of such a powerful technique for the patterning of polymer brushes. Polymer brushes, stretched arrays of polymer chains chemically attached at a surface, are compelling tools for surface engineering with applications ranging from biochemistry to electronics [2]. We implemented, for the first time, photocatalytic lithography to the patterning of polymer brushes [3]. In the "grafting-from" approach, a surface-immobilized initiator allows the growth of polymer brushes directly from the surface: if the initiator layer is patterned, patterned brushes will be obtained. We functionalized with a suitable initiator both titanium dioxide and silicon surfaces which were exposed, respectively, to near-UV light directly through a photomask (direct approach) or through a transparent photoactive TiO₂ film (remote approach). Initiator patterns were then amplified as polymer brushes with surface-initiated atom transfer radical polymerization (SI-ATRP). Features down to 10 μm can be simply obtained using cheap equipment.

[1] Y. Paz, *Beilstein J. Nanotechnol.* **2011**, 2, 845.

[2] R. Barbey *et al.*, *Chem. Rev.* **2009**, 109, 5437.

[3] G. Panzarasa *et al.*, *Chem. Commun.* **2015**, Advance Article, DOI: 10.1039/C5CC00255A



Stabilization Of Silver Nanowires Transparent Electrodes Against Oxidation

J. Idier^a, R. Backov^a, P. Poulin^a

^aCentre de Recherche Paul Pascal, UPR 8641, PESSAC, France

idier@crpp-bordeaux.cnrs.fr

Silver nanowires (AgNWs) are promising candidates to replace Indium Tin Oxide (ITO) as material for flexible transparent electrodes. Their one-dimensional structure plays an important role in electrode performances as the percolation threshold can be reached for low concentration of materials. Unfortunately, AgNWs suffer from oxidation when exposed in air. As a consequence, both their conductive and transmittance performances decrease with time.

Polymer coatings and encapsulation technologies have been proposed to slow down oxidation of silver nanowires^{1,2}. Nevertheless, these solutions are not fully satisfactory since they tend to reduce the electrodes performances.

Here we report the effect of triphenylphosphine (PPh₃), which allows efficient stabilization of silver nanowires at zero-valent state against oxidation without sacrificing their transparency and conductivity during time³. The achieved electrodes exhibit constant resistance/transmittance performances of 12 Ω/square and 80% transmittance over three months in ambient atmosphere. Stability is also demonstrated under severe oxidative atmosphere such as nitric acid. After 75 minutes in nitric acid oxidative conditions, the Figure of Merit σ_{dc}/σ_{op} decreases from 110 to 68 for the AgNWs/PPh₃-based films (relative loss of 38%) while it decreases from 85 to 25 (relative loss of 71%) for the conventional AgNWs-based films free of PPh₃.

REFERENCES :

- 1: Y. Ahn, Y. Jeong, Y. Lee, Improved thermal oxidation stability of solution-processable silver nanowire transparent electrode by reduced graphene oxide, *Applied Materials and Interfaces* **2012**, *4*, 6410-6414.
- 2: R. Chen, S. R. Das, C. Jeong, M. R. Khan, D. B. Janes, M. A. Alam, Co-percolating graphene-wrapped silver nanowires network for high performance, highly stable, transparent conducting electrodes, *Advanced Functional Materials* **2013**, *23*, 5150-5158.
- 3: P. Poulin, R. Backov, J. Idier, Method for the preparation of a transparent and conductive auto-supported silver nanowire film and applications thereof, patent PP000516WO, 2014

ORIGIN OF BEES AT BITUMEN AIR-INTERFACE: THE ROLE OF ASPHALTENES HEAT CAPACITY

M Mercé^a, H Saadaoui^a, F Dole^a, LBuisson^a, A Bentaleb^a, D Ruggi^a, V Schmitt^a and R Backov^a
^a *Bordeaux University, CNRS, CRPP, UPR 8641, F-33600 Pessac, France*
merce@crpp-bordeaux.cnrs.fr

Bitumens are the heaviest fraction of petroleum obtained after refining. They are commonly used in the road industry where they are mixed with mineral aggregates to form asphalt concrete pavements.

Nowadays, the crude oil resources are becoming heavier since light ones were easier to extract and have been mostly consumed. Heavy crude oils are more concentrated in asphaltenes, in this point of view bitumens are hence looking like heavy crude oils and are then good models to get better understanding of the properties of heavy petroleum fractions. Indeed, issues encountered in heavy oil extraction and bitumen manufacture are to some extent similar.

In this study, we separate bitumen into two fractions: asphaltenes and maltenes using n-heptane as a precipitant and we perform the separation at different temperatures. Using this protocol we obtain different compositions which allow us to study the contribution of each fraction to the well known “bee structures” observed on bitumen surface (see figure below).

Using multi-scale investigations coupling AFM, DSC analyses, SAXS and optical microscopy, we propose an interpretation for the origin, the composition and formation kinetics of those bees. Finally, the proposed scenario is discussed in light of recent models describing bitumen colloidal structure.

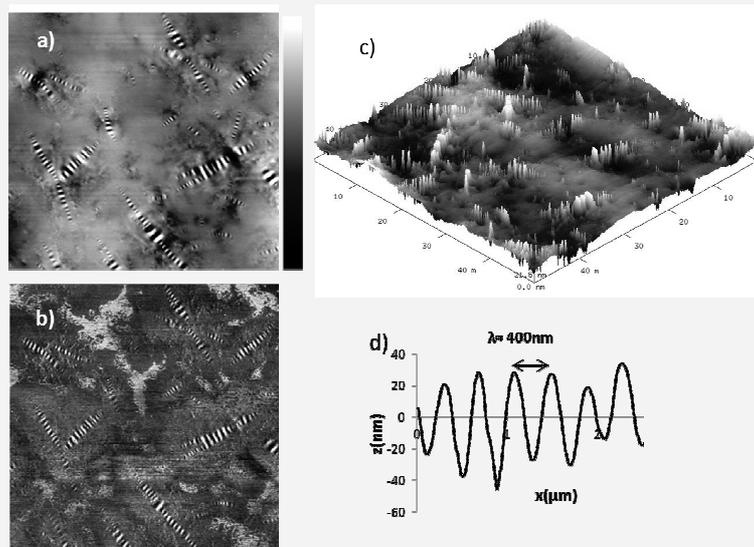


Figure: Typical bitumen/air interface imaged by AFM, the size is $30\ \mu\text{m} \times 30\ \mu\text{m}$, a) Topographic image (differential height is 60nm), b) Phase Detection Microscopy (PDM) image c) corresponding 3D view, d) cross section along the long axis of a « bee ».

Bitumen rheology: link with asphaltenes microstructuration

Manuel MERCE, Rénal BACKOV and Véronique SCHMITT*

Université de Bordeaux, CNRS, CRPP, UPR 8641, F-33600 Pessac, France

*schmitt@crpp-bordeaux.cnrs.fr

Bitumen is the heaviest fraction of petroleum obtained after refining. They are commonly used in the road industry where they are mixed with mineral aggregates to form asphalt concrete pavements.

Nowadays, crude oil resources are becoming heavier since light ones were easier to extract and have been mostly consumed. Heavy crude oils are more concentrated in asphaltenes. Bitumen may then be considered as a dispersion of structured colloids and appear thereby as good models to trigger better understanding of complex suspensions. We prepared bitumen samples with different asphaltene concentrations and study the impact of this fraction over the overall bitumen properties.

In this presentation, we will show results about the bitumen rheology both in flowing and oscillating modes and discuss them in light of new studies concerning bitumen microstructure. Finally some parallels will be made with well know phenomenon in polymers and micelles rheology.

Liquid crystal phase of the colloidal nanosheets derived from layered perovskites with tunable layer thickness

N. Miyamoto,^{a,b} S. Yamamoto,^a Y. Ebina,^c T. Sasaki^c

^aDepartment of Life, Environment, and Materials Science, Fukuoka Institute of Technology (FIT), Fukuoka, Japan.

^bInstitute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan

^cWorld Premier International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan.

miyamoto@fit.ac.jp

Colloids of inorganic nanosheets obtained by exfoliation of layered materials have been highlighted as new-type liquid crystal (LC) material.¹⁾ The formation mechanism of the LC phase is explained based basically on Onsager's theory, and the factors such as average lateral size D and concentration ϕ of the nanosheets affects the structure and structural regularity. However, the factors and mechanism is still to be investigated in detail for further fundamental understanding and optimization and design of the materials for applications. Here we investigated the nanosheet LC system with tunable layer thickness n . The series of the samples were synthesized by exfoliation of the layered perovskites²⁾ $\text{KCa}_2\text{Na}_{3-n}\text{Nb}_n\text{O}_{3n+1}$ ($n = 3, 4$ and 5), and the effect of the thickness and other factors were investigated.

The formation of fully exfoliated nanosheets with the average lateral size $D = \text{ca. } 1.4 \mu\text{m}$ was confirmed by atomic force microscopy. The nanosheet colloids with $\phi > 0.2 \text{ vol}\%$ showed birefringence due to LC phase as observed by polarized optical microscopy.

Small X-ray scattering at the synchrotron X-ray facility, SAGA-LS, clarified the swollen lamellar structure formed in the LC colloid. The as-prepared sample ($n=4$, $\phi=1.7 \text{ vol}\%$) containing excess exfoliating agent, tetrabutylammonium hydroxide (TBAOH), showed highly ordered lamellar structure with the basal spacing $d=7.5 \text{ nm}$, while d increased to up to 122 nm as the TBAOH was washed out. The d value was found to increase as the thickness n increases if compared at the same TBAOH concentration and ϕ . While the difference in the number density of the nanosheets at different n can cause this trend, the difference in the elasticity for the nanosheets with different n can be also the important factor to explain this trend.

Finally, in the optimized sample, the highly ordered lamellar phase with the basal spacing more than 200 nm was obtained. In these cases, the structural colors from blue to red were confirmed by naked eye under white illumination and by reflectance spectra.

Acknowledgements: This research was supported by KAKENHI (#24104005 and #15K05657), Canon Foundation, and Network Joint Research center for Materials and Devices.

References:

- 1) N. Miyamoto, T. Nakato, *Adv. Mater.* **2002**, *14*, 1267.
- 2) N. Miyamoto, S. Yamamoto, K. Shimasaki, Y. Yamauchi, *Chem. Asian, J.*, **6** (2011) 2936.

Filler network formation induced by electric field and physical properties of nanodiamond/polymer composites

S. Akasaka, D. Abe, M. Miwa, K. Morita and S. Asai

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo, Japan

Presenting author's email : akasaka.s.aa@m.titech.ac.jp

Nanodiamond (ND) is nano-sized carbon having diamond crystal structure. It has been attracted attention as a new filler of composites, because it shows the intrinsic characteristics of diamond, such as high hardness, high heat conductivity, high wear resistance etc., and the high surface effect due to nano-sized filler. In order to develop the higher filler-addition effect on physical properties with less loading, we performed a rearrangement of ND in a polymer matrix by applying with an electric field. Figure 1 and 2 show the photographs of the upper surface and SEM images of a cross section of ND/polymer composites unapplied (a) and applied (b) with an electric field respectively. The applied sample formed ND network in vicinity of the positive surface. It was found that its structure was caused by the EHD convection and electrostatic attractive force from the observation during the electric field application. Compared with unapplied sample, applied sample showed lower surface resistivity and higher surface thermal conductivity by ND network.

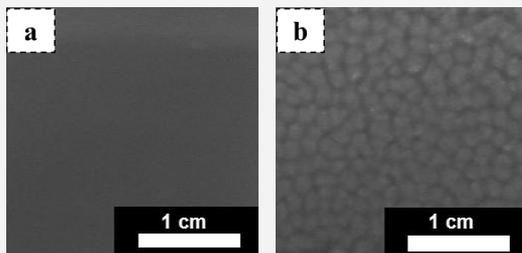


Figure 1 Photographs of the upper surface of ND composite (ND content is 1 wt%); (a) unapplied and (b) applied with an electric field of 250 V/mm.

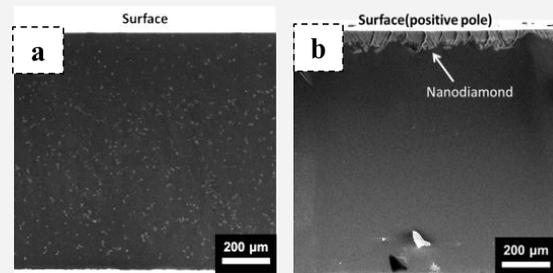


Figure 2 SEM images of a cross section of ND composite (ND content is 1 wt%); (a) unapplied and (b) applied with an electric field of 250 V/mm.

Dispersions of nano-carbon in fluid matrices: temporal stability and non-linear optical properties

A.V.Venediktova^{a,b}, A.Yu.Vlasov^a, D.A. Videnichev^{b,c}, A.V.Volkova, I.M.Kislyakov^{b,c},

^a*Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia*

^b*St. Petersburg National Research University of Information Technologies, Mechanics, and Optic., St. Petersburg, Russia*

^c*Vavilov State Optical Institute, St. Petersburg, Russia*

vened@inbox.ru

Colloidal systems containing carbon nano-species tantalize researchers owing to several potential applications, i.a. photodynamic therapy and nonlinear optical power limiting (OPL) for eye protection against laser irradiation. We address two types of nanocarbon systems. 1) The solvent-controlled aggregation of fullerenes C₆₀ results in the dispersion of particles with sizes ranging from about 1 to 100 nm. The aggregation of fullerenes in various media affects their metastable triplet state T₁ quantum yield and lifetime, both factors determining photodynamic ability of systems on their platform with respect to reverse saturable absorption and singlet oxygen photo-sensibilization. We give data on correlation between stability of the aggregated suspensions of fullerenes and their photo-dynamic properties. 2) We consider suspensions of single wall carbon nanotubes (SWCNTs) non-covalently functionalized by several amphiphiles. The aggregative properties of the latter substances in mixed solvents and phase behavior of their micellar solutions are correlated with temporal and thermal stability of SWCNT suspensions functionalized by these surfactants in the chosen media given controlled degree of nano-particle association. These data are complemented with luminescent, Raman and optical absorption spectra of suspensions alongside their OPL characteristics. The latter depend on the efficacy of converting intense laser irradiation into heat, which causes formation of the solvent bubbles scattering light. Varying amphiphile micro-environment was also employed for a study of relative significance of the optical energy conversion channels.

The results show viability of nonlinear optical filters and singlet-oxygen generators on the platform of variously aggregated carbon nanoparticles.

The authors acknowledge support by RFBR (grants #13-03-01111, #14-02-00851 and #15-03-09316) and by the Government of Russian Federation (grant # 074-U01); A.V.V. was further supported by a Grant of St.Petersburg State University #12.50.1559.2013.

Poster: Calcium carbonate growth tuned by complementary polyelectrolytes as complex templates

Simona Schwarz¹, Florica Doroftei,² Marcela Mihai,² Bogdan C. Simionescu²

¹Leibniz-Institut für Polymerforschung Dresden e. V., Hohe Strasse 6, 01069 Dresden, Germany

²"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Grigore Ghica Voda Alley 41A, 700487 Iasi, Romania

Email: simsch@ipfdd.de

The architectural control of nano- and microcrystals with well-defined shapes is a significant goal of modern materials chemistry. The mineralization process in the biological system has attracted many scientists to biomimetically synthesize inorganic/organic materials [1-3]. In this paper, the characteristics of calcium carbonate microparticles formed in supersaturated aqueous solutions, mediated by *in-situ* mixed complementary polyelectrolytes or preformed nonstoichiometric polyelectrolyte complexes have been investigated comparative with polyanions [4]. For this purpose three polyanions – polyacrylic acid sodium salt, poly(sodium 4-styrenesulfonate) and poly(sodium vinylsulfonate) – and poly(diallyl-dimethylammonium chloride) as polycation were used. The molar ratio between complementary polyelectrolytes used in CaCO₃ composite synthesis varied between 0 (just polyanions) up to 0.95 (close to the equimolar ratio between ionic charges of complementary polyelectrolytes). The polymer presence into the composite particles, as a function of polyanion structure and the preparation mode, was evidenced by energy dispersive X-ray diffraction and particle charge detection in supernatant fraction. Scanning electron microscopy was used to provide the particles morphology, and FTIR-ATR spectroscopy to determine the polymorphs content ratio. The enhanced CaCO₃/polyanion/polycation microparticles stability in EDTA has been also evidenced comparative with CaCO₃/polyanion microparticles as a function of molar ratio between complementary polyelectrolytes and the method of introducing the polycation in the crystallogenesis system.

[1] B. Bhushan, *Phil. Trans. R. Soc. A* **2009**, 367, 1445–1486.

[2] A. W. Decho, *Ecological Eng.* **2010**, 36, 137–144.

[3] D. Ren, Q. Feng, X. Bourrat, *Micron* **2011**, 42, 228–245

[4] M. Mihai, S. Schwarz, F. Doroftei, B. C. Simionescu, *Cryst. Growth Des.* **2014**, 14, 6073 –6083

Interaction of Gold Nanoparticles with biologically relevant interfaces: a multiscale perspective

C. Montis,^a D. Maiolo,^b G. Boccalini,^c I. Alessandri,^d D. Bani,^c P. Bergese,^d D. Berti^a

^a*Department of Chemistry, University of Florence and CSGI, Florence, Italy*

^b*CEN foundation, Department of Chemistry, Material and Chemical Engineering, Milan Italian Polytechnic, Milan, Italy*

^c*Department of Experimental and Clinical Medicine, University of Florence, Florence, Italy*

^d*Chemistry for Technologies Laboratory and INSTM, Department of Mechanical and Industrial Engineering, University of Brescia, Brescia, Italy*

montis@csgi.unifi.it

Gold nanoparticles (AuNPs) are among the most promising nanosystems for applications in nanomedicine, both for therapeutics and diagnostics. In this view, in parallel with the design of AuNPs-based nanodevices, there is an increasing necessity to evaluate the interaction of AuNPs with biological systems. Indeed, a deep comprehension of the connections between the physicochemical features of the NPs and their interaction with biological interfaces and biologically relevant media would allow the design of biomedical nanodevices with improved biocompatibility and efficiency.

We present a Confocal Microscopy (LSCM) and Fluorescence Correlation Spectroscopy (FCS) study on the interaction of gold nanoparticles (AuNPs) with Giant Unilamellar Vesicles (GUVs) and Supported Lipid Bilayers (SLBs), taken as cell membrane model systems of different curvature and composition.

Different morphological effects on the lipid membrane models were highlighted upon incubation with AuNPs of different shape, coating and surface charge. These effects could be systematically rationalized considering the shape anisotropy of AuNPs, the surface energy of "naked" nanoparticles with respect to surface passivated AuNPs and their surface charge as main factors in the interaction with lipid bilayers.

The experimental data obtained on membrane models were compared with LSCM experiments and toxicity assays carried out on macrophage cells incubated with the same NPs, allowing to establish clear connections between the physicochemical features of the considered nanoparticles, their interaction pathway with simple membrane models and their effect on real cells.

Moreover, we found that AuNPs, "naked" or passivated by a protein corona incubated with GUVs determine different or similar effects on the lipid membrane, in terms of bilayer morphology, permeability or fluidity, depending on the observation lengthscale, from the micrometric to the molecular one, allowing to rationalize the interaction pathway between AuNPs and lipid membrane as a multiscale phenomenon.

Montis et al., *Nanoscale*, 2014,6, 6452-6457

Fluorohectorite Nanosheet Colloid With Structural Color and Liquid Crystal Phase

Shinya YAMAMOTO^a, and Nobuyoshi MIYAMOTO^a

^aDepartment of Life, Environment, and Materials Science, Graduate school of Fukuoka Institute of Technology, Fukuoka, Japan
miyamoto@fit.ac.jp

Liquid crystalline nanosheets colloids are obtained by exfoliation of layered materials^{1,2,3}. Among them, clay mineral is distinguished due to its low toxicity, chemical stability and low environmental impact. We recently reported the formation of liquid crystallinity phases in the inorganic nanosheet colloids obtained by exfoliation of a layered clay mineral fluorohectorite³ (Figure 1).

Here we found that this system show a structural colors which is tunable over whole the wavelength range of visible

light by optimizing the conditions such as nanosheets lateral size and nanosheets concentration. The liquid crystalline nanosheets colloids with the structural color of red, green and blue o showed the peak at 650 and 527 and 411 nm, respectively, in the visible reflectance spectrum. These colloids were found to have swollen lamellar structure with the basal spacings of 133 nm, 129 mm and 90nm, repectively, as confirmed by small angle X-ray scattering.

1)N. Miyamoto, T. Nakato, *Adv. Mater.* **2002**, *14*, 1267.

2)J.-C. P. Gabriel, F. Camerel, B. J. Lemaire, H. Desvaux, P. Davidson, P. Batail *Nature*,413 **2001** 504.

3)Miyamoto, N.; Iijima, H.; Ohkubo, H.; Yamauchi, Y. *Chem. Commun.* **2010**, *46*, 4166-41684

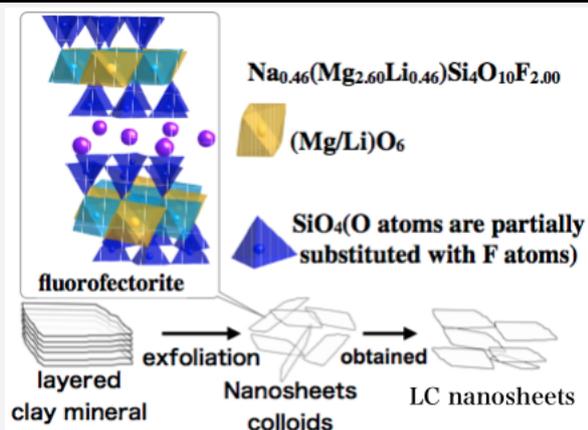


Figure 1. Schematic models for the formation of LC nanosheets of fluorohectorite

Silver nanoparticle deposition on PAH and fibrinogen monolayers

Katarzyna Kubiak, Zbigniew Adamczyk, Monika Wasilewska, Magdalena Oćwieja

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences,
Cracow, Poland

nckubiak@cyf-kr.edu.pl

The deposition kinetics of silver nanoparticles at the Au/SiO₂/PAH and Au/SiO₂/fibrinogen substrates was studied under *in situ* conditions by using the QCM-D, AFM and SEM methods. Measurements were done for various bulk suspension concentrations, flow rates and ionic strengths. A comparison of QCM and SEM results showed that the hydration of the silver monolayers is negligible. This allowed one to derive a universal kinetic equation that describes the mass transfer rate in the cell as a function of the bulk concentration, flow rate and diffusion coefficient. The role of the supporting layer coverage and ionic strength was also systematically studied. The experimental data confirmed a significant increase in the maximum coverage of silver particles with ionic strength that was interpreted as due to the decreasing range of the electrostatic interactions among deposited particles. These experimental results were successfully interpreted in terms of the generalized random sequential adsorption (RSA) model. It was, therefore, concluded that our results derived for the model silver nanoparticle system can be exploited as reference data for the interpretation of protein adsorption kinetics where the dry mass is needed in order to assess the extent of hydration.

ACKNOWLEDGEMENT: This work was supported by the NCN Grant UMO-2012/07/B/ST4/00559

Complex nanoparticles as anticancer drug carriers for prolonged release

B. Császár,^{a,b} É. Kiss,^b L. Nagy Naszályi,^a

^a *Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences of the Hungarian Academy of Sciences, Budapest, Hungary*

^b *Laboratory of Interfaces and Nanostructures, Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary*

csaszar.barbara89@gmail.com

In modern drug research the nanoformulation of drugs is gaining more and more attention since it may ameliorate the absorption of drugs and moderate side-effects. Eflornithine (α -difluoromethylornithine) is a highly water soluble small drug molecule developed in the late 1970s for cancer treatment. It is nontoxic, however, it causes hair-loss in patients. Its main disadvantage lies in its rapid clearance through reins, which renders necessary the i.v. administration of high doses (g/day).

Our aim was to synthesize drug carrier nanoparticles able to prolong the release of eflornithine. We have prepared copolymers of eflornithine with L-(-)-malic acid (in order to provide hydrolysis controlled release of the drug) on the surface of silica@zirconia core@shell particles. The inorganic core had two important roles: providing uniformity in size and allowing the formation of high conversion polymer through the catalytic activity of zirconia.

The morphology, mean size and size distribution of the particles was analyzed by transmission electron microscopy, small-angle X-ray scattering and dynamic light scattering. Fourier-transform infrared spectroscopy allowed for the structural analysis of the polymeric shell. Thermogravimetry coupled to mass spectrometry gave information about the polymerization conversion. Its results confirmed that larger surface area gave rise to higher polymerization conversion. Eflornithine was quantified via colorimetry using picrylsulfonic acid. Drug release kinetics investigations showed that release rate depended on the polymerization conversion: higher conversion could more effectively slow down the leakage of eflornithine.

Acknowledgement

This work was supported by projects OTKA 104928, OTKA 104275, TÁMOP 4.2.4. A/2-11-1-2012-0001 'National Excellence Program', Jedlik projects OM-00162/2007, OM-00161-164/2007 and 2007ALAP1-00070/2008 of the National Office for Research and Technology.

Transport Properties of Perfluorinated MF-4SC Membranes, Modified with Halloysite Nanotubes

A. Filippov, D. Afonin, N. Kononenko
Gubkin Russian State University of Oil and Gas, Moscow, Russia

filippov.a@gubkin.ru

We experimentally found the electro-conductivity and diffusion permeability of perfluorinated cation-exchange membrane MF-4SC (Russian analogue of Nafion-type membrane), which is surface modified with nanotubes of halloysite (Fig.1) during short exposures of a microwave plasma, as a function of an electrolyte concentration. The membrane system is also theoretically investigated using the Nernst-Planck approach. The method of quantitative evaluation of physicochemical parameters of the system (individual and averaged diffusion coefficients and averaged distribution coefficients of ion pairs in the membrane) is further developed. The mentioned parameters of modified membranes on the base of MF-4SC and nanotubes of halloysite are obtained from both experimental data on electro-conductivity and diffusion permeability for different concentration of NaCl and HCl solutions using theoretical calculations by the help of least squares method. The distribution coefficients characterize the level of surface interactions of ions with the ion-exchange material of the membrane matrix. The new model of bi-layer membrane system, which is shown in Fig.2, can be used for refining calculated results with taking into account both diffusive layers. It is shown that grafting the layer of halloysite nanotubes onto the membrane surface noticeably affects exchange capacity as well as structural and transport characteristics of the original perfluorinated membrane. It is revealed that such a membrane does not possess the asymmetry of diffusion permeability as it should be when changing its position inside a measuring cell. We suggest also the new model for calculation of the membrane electro-conductivity. In cooperation with the diffusion model the electro-conductivity model allows more reliable determination of the physicochemical parameters of the modified membrane. Hybrid MF-4SC/halloysite membranes can be productively used for fuel cells and catalysis.

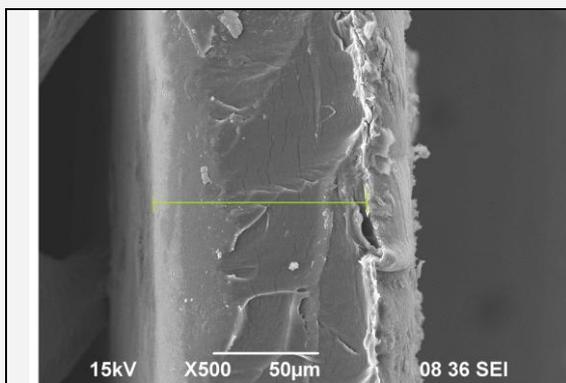


Fig.1. SEM micrograph of the edge of 100µm MF-4SC membrane with applied aluminosilicate (halloysite) nanotubes.

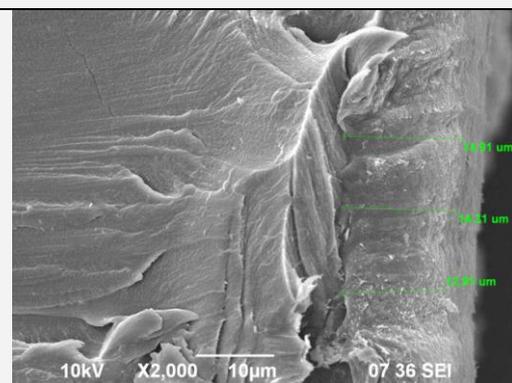


Fig.2. SEM micrograph of the MF-4SC membrane with 15µm layer of aluminosilicate nanotubes.

This work is financially supported by the Russian Science Foundation, project no. 14-19-01045.

Nanoparticle Patterns Characterized by Spectroscopic Imaging Ellipsometry and Atomic Force Microscopy

Peter H. Thiesen,^a Christian Röling,^{a,b} Matthias Duwe,^a ...

^aAccurion GmbH, Göttingen, Germany

^bGeorg-August-Univ., Göttingen, Germany

pt@accurion.com

The tailored organization of nanoparticles is of increasing technical and scientific interest. Silicon-dioxide (SiO₂) nanoparticles may be used for applications which require surface coatings or functional surface patterns to transmit light in the visible range of the spectrum, e.g. superhydrophobic anti-reflection coatings on glass slides¹.

In this work, printed line-shaped patterns of aggregates of SiO₂ nanoparticles on glass substrates were characterized by means of atomic force microscopy (AFM) and spectroscopic imaging ellipsometry. The determination of the line-thickness profiles which are on the sub-micron scale was a matter of particular interest.

We show that imaging ellipsometry is capable of the characterization of SiO₂ nanoparticle patterns with sub-micron layer thicknesses, even on transparent substrates. In a first step, ellipsometric contrast images offer an overview of the homogeneity of the line patterns, and they also yield a first distinction between different types of thickness profiles (Figure 1). In a second step, ellipsometric Δ - Ψ -mapping was carried out to obtain the layer thickness profiles. By applying an ellipsometric model that includes the dense-packing void fraction of the nanoparticles as well as the surface roughness, the results for the layer thickness profiles are in good agreement with AFM measurements.

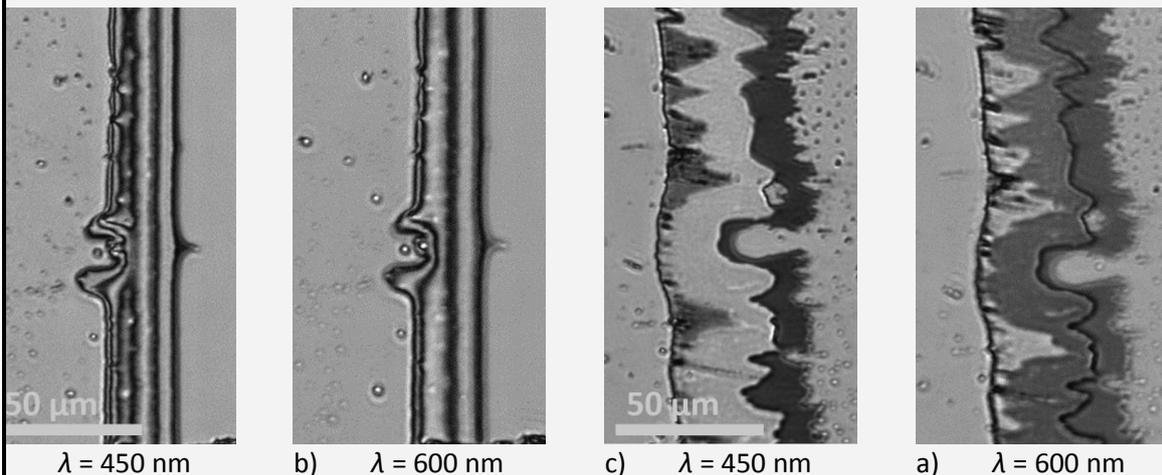


Figure 1: Ellipsometric contrast images of line-shaped aggregates of SiO₂ nanoparticles with continuous (a, b) and stepwise variation (c, d) of the layer-thickness for different wavelengths of the illumination.

References:

1. J. Bravo et. al (2007), *Langmuir*, 23 (13), pp 7293–7298.

Metal Nitride based Nanocomposites as Sustainable Alternative to Current Catalysts

Cristina Giordano*, Guylhaine Clavel, Valerio Molinari

In the search for alternative materials, nanocomposites surely play an important role. They are made by nanofillers loaded on a matrix and are homogeneous from a microscopic point of view. The closer contact between the phases results in properties overlapping, leading to a multifunctional system. Since in principle any phase can be combined, the number of possible combinations and therefore applications is limitless. This multifunctionality is especially important in catalysis, where there are many examples of low performing single catalysts, whose activity was drastically enhanced simply by coupling them¹.

Among selected classes of materials, chosen to find an ideal catalyst, metal nitrides have been receiving increasing attention especially as suitable alternative to more expensive systems. In this choice, however, nickel nitride is hardly considered due to its thermal instability, which makes its synthesis as nanoparticles difficult. Thanks to an atypical sol-gel-based process, we prepared Ni₃N@C nanocomposites made of small (~25 nm), crystalline and well-defined Ni₃N nanoparticles loaded in a carbon matrix².

Remarkably and special advantage of this procedure, the carbon phase stabilizes the nitride without hindering its catalytic properties. Preliminary, yet promising catalytic results were obtained by studying for the first time the activity in hydrogenation reactions directly using H₂. Beside a good activity, even more interesting, a tuned selectivity was observed, compared e.g. with Ni@C. The procedure was extended for the production of other catalytically important nitride nanocomposites.

Once the production of these nanocomposites can be made straightforward, any further modification/combination is in principle possible for the design of tailored systems.

1. Molinari, Esposito, Giordano, Antonietti, *JACS*, 136, 1758, **2014**

2. Clavel, Molinari, Kraupner, Giordano, *Chem. Eur. J.*, 20, 9018, **2014**

cristina.giordano@campus.tu-berlin.de

Fe effect on the optical properties of TiO₂:Fe₂O₃ nanostructured composites supported on SiO₂ microsphere assemblies

C. Márquez-Beltrán^a, J.I. Peña-Flores^a, A.F. Palomec-Garfias^a and E. Sánchez-Mora^a
^a*Instituto de Física de la Benemerita Universidad Autonoma de Puebla*

cmarquez@ifuap.buap.mx

The effect of Fe ion concentration on the morphological, structural, and optical properties of TiO₂ films supported on silica (SiO₂) opals has been studied. TiO₂:Fe₂O₃ films were prepared by the sol-gel method in combination with a vertical dip coating procedure; precursor solutions of Ti and Fe were deposited on a monolayer of SiO₂ opals previously deposited on a glass substrate by the same procedure. After the dip coating process has been carried out, the samples were thermally treated to obtain the TiO₂:Fe₂O₃/SiO₂ composites at the Fe ion concentrations of 1, 3, and 5 wt%. Scanning electron microscopy (SEM) micrographs show the formation of colloidal silica microspheres of about 50 nm diameter autoassembled in a hexagonal close-packed fashion. Although the X-ray diffractograms show no significant effect of Fe ion concentration on the crystal structure of TiO₂, the μ -Raman and reflectance spectra do show that the intensity of a phonon vibration mode and the energy bandgap of TiO₂ decrease as the Fe⁺³ ion concentration increases.

Microencapsulation of Esculin in Alginate-Chitosan Particles

Tsirigotis-Maniecka M.*, Klepacz E.*, Gancarz R.*, Wilk K.A.*

* *Department of Organic and Pharmaceutical Technology, Faculty of Chemistry, Wrocław University of Technology, Wrocław, Poland*

e-mail: marta.tsirigotis@pwr.edu.pl

The microencapsulation technique is an effective and robust method for protecting sensitive substances against a destructive environment and providing controlled release properties. For these reasons it has drawn increasing attention due to its potential applications in the fields of food and drug delivery, cosmetics, biomedicine and textile industry. Our research was conducted in order to investigate the influence of internal and external gelation in emulsification-based techniques upon the alginate-chitosan esculin-loaded microcapsules formation. The selected cargo, esculin: the coumaric glucoside isolated from *Aesculus hippocastanum*, reduces blood vessels fragility, prevents venous stasis and has anti-inflammatory properties. However, it may be partially degradable in aggressive conditions of stomach, thus it is essential to provide its functional release directly in the small intestine. The optimization of the process in relation to ambient temperature provided products with sizes in the range of 35-400 μm , that were mechanically stable during drying. The obtained microparticles were characterized in terms of their morphology and size by polarization microscopy and scanning electron microscopy (SEM). The cargo encapsulation was derived from the spectrophotometric measurements. Their pH-dependent release *in vitro* was performed in relation to stability (pH=2) and feasibility of effective esculin release (pH=7.4). Comparing efficacies of both fabrication processes it can be concluded that the emulsification-based microencapsulation improved the esculin protection under the simulated gastric conditions and promoted its release under intestinal ones. The obtained results enabled to select the most appropriate methodology for the esculin encapsulation in the selected biopolymers. Generally, the microcapsules not only had regular surface morphology and uniform size but also displayed good controlled release of esculin over a long period of time. This research was supported by the subsidy granted by the Polish Ministry of Sciences and Higher Education to the Faculty of Chemistry of Wrocław University of Technology.

Repeated Sol-Gel Synthesis of Alumina Ceramics

A.V. Volkova,^a V.V. Sharypin,^b E.I. Grebeniuk,^a E.V. Golikova,^a L.E. Ermakova^a

^a*Institute of Chemistry Saint-Petersburg state university, Saint-Petersburg, Russia*

^b*Saint-Petersburg National Research University of Information Technologies, Mechanics, and Optics, Saint-Petersburg, Russia*

^c*Research and technological institute of optical materials all-russia scientific center «S.I.Vavilov State Optical Institute», Saint-Petersburg, Russia*

zenit87@bk.ru

Structural and optical alumina-based ceramics is a promising material with a wide variety of applications. Alumina ceramics possesses high hardness, Young modulus, melting temperature, chemical resistant, stable dielectric characteristics and relatively low strength. Low fracture toughness can be enhanced by addition of strengthening additives such as zirconium oxide.

Nowdays there are a lot of techniques for fabrication of oxide ceramics including low-temperature pressureless sol-gel method. We use alumina hydrosols (aeroxide Alu C, 26 nm) for the preparation of molded xerogels at 600 - 900 °C as a green body for ceramic vacuum sintering. However during drying and temperature treatment part of the samples lose their integrity. To minimize raw material losses the well-grinded xerogel powder can be also used as a precursor for so-called "repeated" sol-gel synthesis.

The mechanism of structure formation and the character of particle distribution on gelation stage depend as on dispersion and morphology of precursors and also on their electro-surface characteristics and stability of their sols. Therefore colloid-chemical properties of alumina xerogel particles and their aggregate stability were studied in dependence on salt (NaCl) level and pH and compared with analogues properties of γ -Al₂O₃ aeroxide.

We investigated the influence of synthesis conditions such as pH, acid type and zirconia addition (<1 wt. %) on the characteristics of fabricated xerogels. The molded xerogels were sequentially sintered in air at 1250 °C, 1450 °C and under vacuum at 1800 °C. Structural, physical, mechanical and optical properties of fabricated alumina ceramics were investigated.

This research used resources of the "Innovative technologies of composite nanomaterials", "Interdisciplinary Resource Center for Nanotechnology", "Research Centre for X-ray Diffraction Studies" of SPbSU. This work was supported by SPbSU, research project No. 0.37.179.2014, Russian Presidential Program for Support of Leading Scientific Schools, project No. NSh-2744.2014.3 and by Government of Russian Federation, Grant 074-U01.

Release study of selected terpenes from nanostructured lipid carriers

Elwira Lasoń *, Elżbieta Sikora, Jan Ogonowski

Institute of Organic Chemistry and Technology, Cracow University of Technology, Poland

* - elason@chemia.pk.edu.pl

Monoterpenes, apart from their fragrance properties and biological activity, are known as penetration enhancers. They rapidly and reversibly promote percutaneous penetration of drugs, additionally they penetrate through the skin as well [1]. On the other hand di- and triterpenes are known from their significant biological activity and can act as drugs, therefore their own penetration and release from carriers should be better examined. Lipid nanoparticles have demonstrated by now a great capability to protect labile compounds mainly for pharmaceutical and cosmetic applications and they could be applied to deliver active ingredients through oral, parenteral and topical routes [2,3]. Representatives of mono- (geranic acid), di- (forskolin) and triterpenes (ursolic acid) alone, were used for release study from nanostructured lipid carriers (NLC). The influence of the terpenes chemical structure on their release profile were investigated. Terpene-loaded NLC were prepared by the ultrasonification method using modified beeswax as a solid lipid and caprylic/capric triglyceride as a liquid lipid. The systems were stabilized by alkylpolyglucoside. Physicochemical properties of the obtained formulations, such as particle size, size distribution, polydispersity index and zeta potential (ZP) were studied by using Zetasizer Nano ZS Malvern Instrument. In vitro release studies of the geranic acid, forskolin and ursolic acid were performed at the 32°C, using cellulose membrane and the mixture of PBS/ethanol as a receptor solution. The obtained data confirmed a high physical stability of the terpene-loaded formulations and showed that the prepared systems are suitable carriers for controlled release of different kind of terpenes.

Literature

1. Cal K., Janicki S., Sznitowska M., In vitro studies on penetration of terpenes from matrix-type transdermal systems through human skin, *Int J Pharm.*, 224, (2001), 81–88
2. Müller R.H., Radtke M., Wissing S.A., Solid lipid nanoparticles (SLN) and nanostructured lipid carriers (NLC) in cosmetic and dermatological preparations, *Adv. Drug Deliv. Rev.*, 54 (1), 2002, 131–155
3. Pardeike J., Hommoss A., Müller R.H., Lipid nanoparticles (SLN, NLC) in cosmetic and pharmaceutical dermal products, *Int. J. Pharm.*, 366, 2009, 170–184

EFFECT OF REACTION CONDITIONS ON SYNTHESIS OF TI BASED METAL ORGANIC FRAMEWORKS IN TWO DIFFERENT REACTORS

Gonca Çalışkan¹, H. Banu Yener¹, Berrin İkizler¹, Şerife Şeref Helvacı^{1,a}, Fehime Çakıcıoğlu Özkan²

1. Ege University, Department of Chemical Engineering, 35040, Izmir, Turkey

2. Izmir Institute of Technology, Department of Chemical Engineering, 35430, Izmir, Turkey

a. Corresponding author (sshelvaci@gmail.com.tr)

ABSTRACT: Metal Organic Frameworks (MOFs) of which investigations recently in great demand are a new class of hybrid and porous materials constructed from metal clusters or ions with organic ligand linkers. The most important features that distinguish it from other hybrid structure are large surface area, large pore volume, and low density. So they have emerged as interesting materials for various applications in energy storage, CO₂ adsorption, hydrocarbon adsorption/separation, catalysis, sensor, magnetism, drug delivery, luminescence. Within this scope, Ti-MOFs which has such a wide application area were synthesized by solvothermal method using titanium tetraisopropoxide (TTIP) as Ti ion source and terephthalic acid (TPA) as organic ligand and the effects of the types of the reactor (stirred and autoclave reactor), reaction temperature (95 °C and 120 °C), reaction time (72h, 144h) and washing effect were investigated. According to FTIR, XRD, TGA, SEM, BET analysis results, optimum reaction conditions to obtain high surface area were determined as 120 °C in autoclave reactor for 72 h and 1/2 n_{Ti}/n_{TPA} molar ratio. Homogeneous disk and spherical shape Ti-MOF particles including micropores were synthesized at optimum reaction conditions with well developed crystal structure and high BET specific surface area as 1280 m²/g.

Keywords: Ti-MOF, Terephthalic acid, Titanium tetraisopropoxide, Solvothermal

Presenting author's email address: goncocaliskan89@gmail.com

Effect of nano-emulsions composition on the release of topical agents used in dermatoses treatment

Małgorzata Jaworska^{1*}, Elżbieta Sikora¹, Jan Ogonowski¹, Michał Zielina²

¹ - Faculty of Chemical Engineering and Technology, Institute of Organic Chemistry and Technology, Cracow University of Technology,

Address: Warszawska St. 24, 31-155 Cracow, Poland

² - Faculty of Environmental Engineering, Institute of Water Supply and Environmental Protection, Cracow University of Technology

Address: Warszawska St. 24, 31-155 Cracow, Poland

*mjaworska@chemia.pk.edu.pl

Dermatosis is defined as a disorder involving lesions or eruptions of the skin that are acute (lasting days to weeks) or chronic (lasting months to years). They are caused by local or systemic immunologic factors (e.g., allergic reaction). Acute inflammatory dermatosis conditions include erythema multiforme (EM), pruritus (urticaria), and eczema [1].

Topical drugs (drugs applied directly to the skin) are a mainstay of treating skin disorders. Corticosteroids are the main topical drugs used to relieve an inflammation (swelling, itching, and redness) of the skin. The inflammation of the skin happens as a result of allergy or irritation of the skin, and is caused by the release of various substances that are important in the immune system [2].

The second most common used group of topical agents are retinoids. They are the foundation for the treatment of acne because they normalize the keratinization process. Moreover they increase the turnover of follicular epithelial cells, corneocytes are shed at an accelerated rate and comedones are extruded [3].

Nano-emulsions are a new form of cosmetic and pharmaceutical products. They are liquid, kinetic stable, colloidal dispersions with the droplet size in the range of 20-200 nm. As a cosmetic or pharmaceutical base, they show some advantages comparing to classic emulsions, e.g. higher surface area that make them as an effective transport system, kinetic stability against sedimentation, flocculation and coalescence, easy preparation, long term stability, high solubilization and capacity of incorporate active substances. They are one of the most promising formulations used to enhance pharmaceutical bioavailability of active substances such as following drugs: Sandimmune® and Sandimmun Neoral® (cyclosporin A), Norvir® (ritonavir), and Fortovase® (saquinavir), Sporanox® (itraconazole), tamoxifen, paclitaxel and dacarbazine [4].

The aim of this work was to determine the release of selected topical agents such as fluocinolone acetonide (corticosteroid) and isotretinoin (retinoid) depending on the applied formulations. The nano-emulsions based on fractionated coconut oil, wheat germ oil and isopropyl myristate stabilized by Polisorbate 80 were compared. The nanoemulsions were prepared by stepwise addition of water to the mixture of polisorbate/oil/topical agent, at room temperature. The mean droplet size was determined by a dynamic light scattering measurement using Malvern Zetasizer Nano ZS. Drug release study of the actives was carried out using the Spectra/Por Standard Regenerated Cellulose (RC) membrane, at the temperature $T=32^{\circ}\text{C}$. The concentration of active agents in the receptor solution was analyzed by UV-Vis spectroscopy method. The results have shown that nanoemulsions can be used as carriers for controlled release of topical agents used in dermatoses treatment.

[1] Weinberg M.A., Diagnosis and Treatment of Acute Inflammatory Dermatoses, US Pharm. 2009, 34(4):HS-1-HS-6.

[2] Kanee B., Clinical studies with topical fluocinolone acetonide in the treatment of various dermatoses, Can Med Assoc J. 1963, 88, 999-1003.

[3] Cyrulnik AA, Viola KV, Gewirtzman AJ, Cohen SR. High-dose isotretinoin in acne vulgaris: improved treatment outcomes and quality of life. Int J Dermatol. 2012, 51(9), 1123-30.

[4] Jaworska M., Sikora E., Ogonowski J., Nanoemulsions. Characteristics and methods for preparation, Przem Chem. 2014, 93 (7), 1087 – 1092.

Growth and disintegration of silver nanowires in tubular J-aggregates

Egon Steeg

The reduction of AgNO_3 in the presence of tubular J-aggregates is used to prepare silver nanowires with 7 nm in diameter and lengths exceeding micrometers [1]. Here, we report on the influence of chloride ions on growth and dissolving of the wires. In presence of oxygen and a ligand the chloride ions are able to etch silver nanostructures by oxidizing neutral silver atoms back to ions [2]. This oxidative etching is more effective along defect zones than on defect free single crystals. Silver nanowires grown in the template structures are dissolved by addition of NaCl by this process and the silver is converted into AgCl while the tubular template is conserved. The dissolution of the Ag nanowires is explained by their structure which shows multiple twin boundaries. The transport of the oxidized Ag atoms is explained by transport across the tubular wall.

[1] D.M. Eisele et al., J. Am. Chem. Soc. 132 (2010) 2104.

[2] Y. Zheng et al., Chem. Mater. 2014, 26, 22-33

Characterization of Nanoemulsion-based Nanocarriers for Organoselenium Compound Delivery

M. Pietka-Ottlik,^a A. Lewinska,^b A. Jaromin,^c K. Wilk,^a

^a*Department of Organic and Pharmaceutical Technology, Faculty of Chemistry, Wrocław University of Technology, Wrocław, Poland*

^b*Faculty of Chemistry, University of Wrocław, Wrocław, Poland*

^c*Department of Lipids and Liposomes, Faculty of Biotechnology, University of Wrocław, Wrocław, Poland*

magdalena.pietka@pwr.edu.pl

During the last few decades it was found that synthetically available organoselenium compounds are active immunostimulants, inhibitors of enzymes, antioxidants, anti-inflammatory, antitumor, antiviral and antimicrobial agents¹⁻⁵. Although these compounds have a great potential as new perspective pharmaceuticals their practical use is still limited due to low solubility in water. Thus, the purpose of our study was to develop an effective nanocarrying system for selected organoselenium compounds.

The present work was carried out to explore the potential of a series of ionic dicephalic-type surfactants *N,N*-bis[3,3'-(dimethylamine)propyl]alkylamide dihydrochlorides C_n(DAPACl)₂ (n=11,13,15) for stabilization of oil-in-water (o/w) nanoemulsions. Cargo-loaded nanocarriers contained ebselen (2-phenyl benziselenazol-3(2*H*)-one) or its analogues. From several pseudo-ternary phase diagrams, arranged with various oils eg. isopropyl myristate, isooctane, oleic acid, vegetable oils and Capmuls, the most promising nanoemulsion systems were selected. The structures contained various ratios of surfactant and oil phase that affected the characteristic of droplets. Structural parameters of the assemblies were characterized by dynamic light scattering (DLS) – size, polydispersity and zeta-potential, transmission electron microscopy (TEM) – morphology, and turbidimetric technique – kinetics stability. Additionally, the EPR spin probe technique was used to achieve information about local mobility, microenvironment (polarity, viscosity, hydration and degree of order) and interactions.

Results of our studies provide guidelines for design of new nanoemulsion-based systems for bioactive organoselenium compounds delivery.

References:

1. Mugesh G. et al., Chem. Rev., 101, 2125 (2001)
2. Nogueira CW. et al., Arch Toxicol., 85(11), 1313 (2011)
3. Azad GK, Tomar RS., Mol Biol Rep., 41(8) 4865 (2014)
4. Wojtowicz H., et al., Farmaco, 59(11), 863 (2004)
5. Pietka-Ottlik M., et al., Chem Pharm Bull, 56.1423 (2008).

This work was financially supported by the National Science Centre (NCN) under grant no. UMO-2013/09/D/ST5/03814.

HIGH SPECIFIC AREA POROUS MATERIALS OBTAINED BY NANOPARTICLE-LADEN LIQUID FOAMS

D. Zabiegaj, M. T. Buscaglia, E. Santini, M. Ferrari, L. Liggieri, F. Ravera
CNR-Institute for Energetics and Interphases, via De Marini 6, 16149 Genoa (I);

MAIN TOPIC: Micro- and Nanostructured Materials

Using previously developed method [1,2] some titania and carbon porous materials have been obtained, presenting open cell structure and high specific surface area. According to this methodology, particle laden wet foams are solidified by in situ polymerization which occurs between organic Poly(vinyl alcohol) and cross-linker DHF (gel casting), previously dissolved in the liquid phase. So obtained green bodies are then treated, following a high temperature process.

This work pointed out that the structure of the final porous materials strongly depends on the composition of the adsorption layers stabilizing the precursor foams. That is why a systematic characterization of the surface properties of particle dispersions in association of short chain ionic surfactants, and crossed with the characterization of the bulk dispersion by Dynamic Light Scattering (DLS) and ζ -potential measurements have been carried out, allowing the appropriate formulation of the initial dispersion. The obtained results allowed selecting the best conditions in which the transfer of particles to the liquid-air interfaces is favoured, independently of the particle nature, size or shape, like in case of presented here carbon or titanium particulates, providing stable foams utilized as a 3D skeleton for the final particle based porous material. The final characterisation of obtained materials is then applied, both, from the point of view of the morphology, via SEM analysis, and as concerns the gas adsorption ability or their specific surface area.

[1] D. Zabiegaj, E. Santini, E. Guzmán, M. Ferrari, L. Liggieri, F. Ravera, *J. Nanoscience and Nanotechnology*, DOI:10.1166/jnn.2015.9730

[2] D. Zabiegaj, E. Santini, E. Guzmán, M. Ferrari, L. Liggieri, V. Buscaglia, M. T. Buscaglia, G. Battilana, F. Ravera, *Colloids Surf. A* 438, 132-140, **2013**

Selective Enhancement of Fluorescence Using Photonic Crystal Films

Seo-Hyun Jung, Woo Ram Song, Wonjoo Lee, Song Ju Park, Ho-Cheol Kang, and Jong Mok Park*

Korea Research Institute of Chemical Technology, 45 Jongaro, Jung-gu, Ulsan 681-802, Korea
*jmpark@kriict.re.kr

ABSTRACT

Photonic crystals, composite materials that contain spatial modulations in their refractive index, have been widely investigated owing to their unique optical properties. Potential applications of photonic crystals have been introduced in many fields, such as reflective coatings on lenses, color pigments in paints and inks, waveguides for directing the propagation of light along a specific path, various optical sensors, solar cells, and many other optical components. We report a method to enhance fluorescence using bilayers of photonic crystal films. In our method, the photonic band-gap of an underlying photonic crystal film could be easily modulated by changing silica particle size and the distance between ordered spherical silica particles and matrix. We prepared bilayer photonic crystal films; one film recycles the excitation energy of fluorescent, and the other film selectively enhances selected wavelength of emission. Then, when a fluorescent polymer solution was spin-coated on the photonic crystal film, we observed overall enhancement of fluorescence as well as the distinct enhancement at selected wavelength owing to the photonic band-gap of the underlying photonic crystal films.

Key words : Photonic crystals, silica, fluorescence, selective enhancement

Physicochemical properties of biologically modified carbon sorbent

A.E. Wiącek*, M. Ciołek

Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

*a.wiacek@poczta.umcs.lublin.pl

Modified carbons are regarded as adsorbents for various contaminants from air and wastewater. The aim of work was to estimate sorptive capacity of base carbon and biologically modified carbon in the removal of dyes which are contaminants from different kinds of wastewaters. The solutions of chitosan or starch were chosen for biological modification. Such water-soluble polymers are known as effective aids for flocculation of colloidal particles and are applied for water clarification, sludge dewatering and pulp sedimentation. However, polysaccharides have high flocculation ability for industrial suspensions, there is no detailed information concerning their dosage for carbon flocculation. For that reason, quantitative studies of flocculation abilities of starch or chitosan were performed on carbon suspension. Biopolymer derivatives proved to be effective biodegradable flocculants. The kinetic curves of various carbon sedimentation have been detailed as dependence of changes of opacity border in time. Applying chitosan requires doses 1 to 2 times higher as compared to those of starch flocculants to reach comparable sedimentation ability of carbon. During the adsorption process concentration of the examined dye was 1.25×10^{-2} M in all cases. Sorption abilities of carbons were expressed by the mass balance relationship. In the case of virgin carbon it was 2.3×10^{-5} mol/g, and after chitosan or starch solution modification, 3.8 and 3.4×10^{-5} mol/g, respectively. The adsorption theoretical model such as Freundlich or Langmuir one, was selected. In case of methyl blue the highest and comparable removal efficiency was for the base and chitosan modified carbon, but lower about 7.7% for the starch modified carbon. The experimental data show that the modified carbon can be used for decontamination of wastewater or flocculation agent depending on kind and concentration of polysaccharide.

Support from Maria Curie Initial Training Network “Complex Wetting Phenomena” (Project number 607861) is highly appreciated.

Scientific and environmental expertise assess the effect of triclosan on the environment of Kazakhstan

N.Bekturganova¹, Sh.Sh.Amarkhail², S.Aidarova³, A.Sharipova⁴,
E.Lygina⁵, S.Lyubchik⁶, M.Estrela⁷

¹⁻²Applied chemistry department, Kazakh national technical university named K.Satpayev, Almaty, Kazakhstan

³⁻⁴International Postgraduate institute "Excellence polytech", Kazakh national technical university named after K.Satpayev, Almaty, Kazakhstan

⁵⁻⁶Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal

⁷ISQ - R&D Department, Instituto de Soldadura e Qualidade, Portugal

Keywords triclosan, environment, ecology, present and future.

Main topic: triclosan.

Nowadays the substances, previously invented by chemists, useful for people and the environment are "unprofitable". One of these is triclosan. Triclosan is chlorinated diphenyl ether with a hydroxyl group in the o-position relative to the ether linkage. It is practically insoluble in water, but soluble in most polar organic solvents and oils.

The use of triclosan by humanity is very extensive. Such wide application of the triclosan is due to its antibacterial activity on broad spectrum of gram-negative and gram-positive bacteria, including some antibiotic-resistant strains. Therefore, since the 70s of the last century it has begun to be actively introduced into production. Triclosan is widely used in household hygiene (antibacterial soaps, mouth rinses, lotions, deodorants, cosmetics). Triclosan is often used in medicine and radiation therapy.

But, as the analysis of the state of affairs today show, along with the benefit for people triclosan brings its danger. For example, microbiologists say that excessive use of triclosan leads to the development of the organism resistance to antibiotics; triclosan dust irritates the skin and eyes; it amplifies some allergic reactions. In addition, there are the views of unwholesome influence of triclosan on the environment. Because of the high potential of bioaccumulation in aquatic organisms triclosan is toxic to plants growing in sandy soil, and it demonstrates the high toxicity against a number of the inhabitants of freshwaters - plants, fish and invertebrates, and its toxicity is increased with water acidification. Freshwater algae are particularly sensitive to triclosan.

According to this, many manufacturers of household and cosmetic products are beginning to refuse the inclusion of triclosan in the composition of their products. But a problem cannot be solved only by refusal. Also there is a doubt in the question of the antibacterial action activity of triclosan effectively fight bacteria, which is previously widely used in advertising.

However, there are some works to refute the "accusations" against triclosan. They are about the alleged unreliability (non-repeatable) results obtained by experiments.

This suggests that the question of the future use of triclosan is very relevant. The potential environmental consequences should not be underestimated and ignored. Constant monitoring of triclosan in the environment, as well as the continuation of the toxicological and ecotoxicological studies is needed.

There is a question about the case in our country. Unfortunately, the literature review of the Kazakhstan researchers work has showed that this problem topic is scarcely explored. Therefore, the aim of our research was to study the effect of triclosan on people and the environment. To achieve this goal it is necessary to determine the presence of triclosan in the samples of drinking water, wastewater and thawed. If present in the waters, cleaning by adsorption on adsorbents of domestic production should be planned.

Presenting author's email: bektur_n@mail.ru

Spontaneous vesicles in the Suwannee River humic substances/DTAC system: Implications for the supramolecular architecture of humic substances

A.A. CHAABAN^{a,b}, B. LARTIGES^a, V. KAZPARD^b, C. PLISSON-CHASTANG^c,
P. VICENDO^d, C. CAILLET^e

*a. UNIVERSITY of TOULOUSE 3 - PAUL SABATIER, UMR5563 Géosciences Environnement
Toulouse (GET), Toulouse, France*

*b. LEBANESE UNIVERSITY, Plateforme de Recherche et d'Analyses en Sciences des
l'Environnement (PRASE-EDST), Beirut, Lebanon*

*c. UNIVERSITY of TOULOUSE 3 Institut des sciences biologiques (INSB), UMR5099
Laboratoire de biologie moléculaire des eucaryotes (LBME), Toulouse, France*

*d. UNIVERSITY of TOULOUSE 3 Institut de chimie (INC), UMR5623 Interactions
Moléculaires et Réactivité Chimique et Photochimique (IMRCP), Toulouse, France*

*e. UNIVERSITY of LORRAINE - CNRS, UMR7360 Laboratoire Interdisciplinaire des
Environnements Continentaux (LIEC), Nancy, France*

E-mail: abdulmirshaban@hotmail.com

Humic substances (HS), operationally classified into fulvic acid, humic acid, and humin according to their solubility, are ubiquitous organic compounds in soils and aquatic systems. Long regarded as macromolecules or slightly branched polymers that can coil or adopt an extended conformation according to solutions properties, HS are now envisioned as supramolecular associations of small heterogeneous molecules that can be disrupted in the presence of organic acids. To decide which of the two structural concepts, polymeric or supramolecular, is appropriate; we probe the organization of humic nanocolloids by adding various concentrations of Dodecyl-trimethylammonium chloride (DTAC), a cationic surfactant molecule, to Suwannee river fulvic and humic acids. Adding an oppositely charged amphiphilic molecule to humic colloids is expected to induce a drastic restructuration of the humic architecture driven by both electrostatic and hydrophobic interactions. The type of association reached between HS and DTAC is probed using turbidity measurements, Dynamic Light Scattering (DLS), Electrophoretic mobility, Cryogenic Transmission Electron Microscopy and fluorescence spectroscopy.

Depending on DTAC concentration, various molecular structures including humic-rich vesicles, globules, disks, DTAC-rich vesicles (unilamellar and multilamellar), mixed micelles, are successively evidenced. The phase diagram behaviour is consistent with those typically encountered in catanionic systems. Protein-like fluorophores, not initially detected in the reference HS, are evidenced upon the molecular reorganization. Such soft-matter approach strongly supports a supramolecular architecture of HS and provides new tools to assess the molecular characteristics of HS constituents.

Key words: Humic substances, Cryogenic Transmission Electron Microscopy, Cationic Surfactant, Fluorescence spectroscopy, Packing parameter, Polymer Macromolecule, Supramolecule.

PHOTOCATALYTIC PURIFICATION OF PRODUCED WATER

S.B.Aidarova¹, A.A. Sharipova¹, N.Bekturganova¹, M. Estrela², O. Lygina³, S. Lyubchik³

¹ Kazakh national technical university named after K.I.Satpayev, Almaty, Kazakhstan

² Instituto de Soldadura e Qualidade (ISQ); Department of Environment, Lisboa, Portugal

³ Universidade Nova de Lisboa, Lisboa, Portugal

The environmental situation which caused by the activity of the industry especially of oil and gas requires the use of efficient methods of water purification from organic contaminants. One of the most popular methods is photocatalysis with TiO₂. The photocatalytic behaviour of TiO₂ has been, and continues to be, the subject of much research. A great deal of this has been directed at its use in applications involving the photoreactions of organic materials, in particular the photodestruction of organic pollutants, 'self-cleaning windows', and photocatalysis of organic compounds in the solid, liquid, and gas phases. The aim is to investigate the use of novel TiO₂ sol-gel coatings to destroy a model organic waste stream and produced water.

Based on obtained results current sol-gel methods from literature were investigated and determined that the most suitable sol-gel preparation method was the Mills method. The photocatalytic properties of the coatings with UV and visible light were investigated. The optimal coating thickness was determined and it was twice coated. The coatings were modified with lanthanide ions and the concentration effect of the lanthanide ions was investigated and the optimal concentration was found.

Based on obtained results, the best coating is Nd(NO₃)₃*6H₂O with a concentration 0.25wt%. It reduced MB concentration from 100% to 6% under UV light and from 100% to 63% under visible light, i.e. 94% of MB concentration under UV light and 37% under visible light were destroyed. The physical properties of this coating show high results. Therefore this coating is suitable for further investigation in order to apply it to purify produced water in the oil and gas industry.

Poster: **Adsorption deinking of waste paper using polymers granules**

S. Schwarz , G. Petzold,
Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Hohe Straße 6, Germany

*simsch@ipfdd.de

Recycling of papers by flotation deinking is a very important process, especially in Germany or Western Europe. As found previously, instead of air flotation, ink can be effectively removed by adsorption on polymer surfaces (granules) such as polyamide or polypropylene [1]. In the following this process is called “adsorption deinking”. Compared with the conventional process it works at significantly higher solid content (about 20%) and therefore the consumption of water and energy can be drastically reduced.

The aim of the present work was hence to study the “chemistry” of “adsorption deinking” in dependence on different types of paper such as newspaper or magazine paper. The experiments were made according to the INGEDE- method 11, using additives such as oleic acid (0.8%), sodium hydroxide (0.6%), and sodium silicate (1.8%) at pH of 8. This process can be characterized not only by the degree of ink adsorption (colour of polymer granules), but also by the charge (polyelectrolyte titration; PCD Müttek) and the dynamic surface tension [2] of the deinking suspension in presence of different papers.

The low surface tension of the “surfactant-mixture” increases by adding printed paper, demonstrating that the surfactant will be adsorbed on the ink and/or the fibre. The extent of this change depends on the properties of papers or inks. Most efficient systems in adsorption deinking had a higher surface tension and a lower charge in suspension, compared with other samples.

- [1] G. Petzold, S. Schwarz, *Coll. Surf. A* **2015** in press,
<http://dx.doi.org/10.1016/j.colsrfa.2015.01.084>
- [2] G. Petzold, S. Schwarz, *Polyelectrolyte Comp. in Flocc. Appl. In Polyelectrolyte Comp. II. Adv. in Polymer Sci.* **2013** 256; 25-66

Oral presentation: Chitosan - Adsorption of heavy metal ions

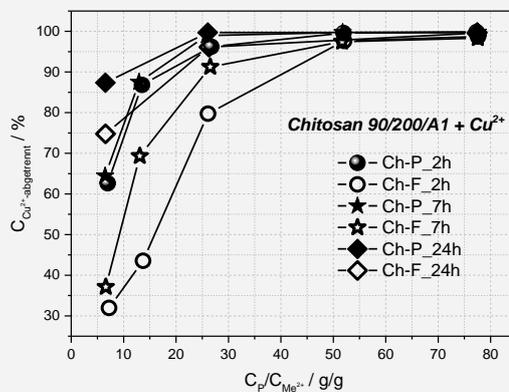
Simona Schwarz, Mandy Mende

Leibniz-Institut für Polymerforschung Dresden e.V., Department of Polymers and Dispersions,
Germany

Email: simsch@ipfdd.de

As a result of industrial activities and technological changes, a high and continuously decreasing amount of heavy metals and heavy metal containing effluents are released into the environment by different industrial nations. These metals can not be degraded. Furthermore, because of their toxicity, they are highly detrimental to the environment and human health. Heavy metals accumulate in the food chain and become permanent pollutants in the environment. In the human body they accumulate in different organs where they cause serious damage.

The removal of heavy metals with chitosan flakes from a dilute aqueous solution was investigated. Metal removal was also studied using extinction measurement, NTU and size measurements. The adsorption capacity of the chitosan flakes for the investigated metal ions was determined at different concentration and pH values. Mostly the removal of the metal ions is nearly 100%.



Adsorption process of Cu ions on chitosan powder (P) or flakes (F) in dependence on time

Poster Novel Amphiphilic Starch Derivatives: Flocculation Efficiency and Investigations towards Sticky Reduction

Simona Schwarz¹, Sabine Genest^{1,2}, Gudrun Petzold¹, Svetlana Y. Bratskaya³

¹ *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany*

² *Organische Chemie der Polymere, Technische Universität Dresden, 01062 Dresden, Germany*

³ *Institute of Chemistry, Far East Branch of Russian Academy of Sciences, 159, Prosp. 100-letiya Vladivostoka, Vladivostok 690022, Russia*

Flocculation properties of amphiphilic cationic potato starch derivatives of varying degrees of substitution (DS) of hydrophobic benzyl- and cationic 2-hydroxypropyl-trimethylammonium moieties have been investigated in dispersions of kaolin and silica to identify interplay between charge density and hydrophobicity. In addition, these amphiphilic starch derivatives have been used to remove substances which impact negatively the paper production process when using recycled paper, so called stickies. A model suspension has been studied using a multitude of different measurement techniques with the aim to predict a “sticky potential”.

It was shown that moderate hydrophobic substitution leads to the decrease of efficient flocculant dose and increase of flocculation window width. Amphiphilic starch derivatives with high DS of hydrophobic moieties showing strong hydrophobic association are effective only at significantly higher doses but in a broader concentration range compared to cationic starch of the same DS. Joint analysis of adsorption isotherms and flocculation test data has revealed that the surface coverage required to induce phase separation ranges between 10 and 25 % and is minimal for amphiphilic starch derivatives. [1] When systematically studying the interactions between the novel amphiphilic starch derivatives and the model suspension, it turned out that dynamic surface tension is a very suitable property to characterize the surface active compounds in the model suspension giving additional information about the sticky potential of waste water, e.g. white water, being a new and sensitive method to describe the parameter “hydrophobicity”. Moderate cationic and hydrophobic starch derivatives are assumed to be the most effective ones for sticky removal. [2]

References

[1] Bratskaya, Schwarz, S. et.al. *Macromolecular Materials and Engineering* 299 (2014) 722-728

[2] Genest, S. ; Schwarz, et.al. *Starch/Stärke* 65 (2013) 999-1010

'Artificial leaf' device for hydrogen production from microalgae immobilised on fabric/biocomposite

A.A.K. Das,^a M.M.N. Esfahani,^b N. Pamme,^a V.N. Paunov^a

^aDepartment Of Chemistry, University of Hull, Hull, United Kingdom

^bDepartment of Engineering, University of Hull, Hull, United Kingdom

a.das@hull.ac.uk

The green algae *Chlamydomonas reinhardtii* cc-124 can produce hydrogen by direct photolysis under anaerobic conditions in sulphur free environment without releasing harmful by-products. Hydrogen generation via photobiological routes using photobioreactors has been reported to achieve favourable efficiencies (10-20%) compared to photochemical or semiconductor routes.

We report the generation of hydrogen from microalgae cells, *C. reinhardtii*, immobilised within a polyester fabric in a microfluidic device akin to an artificial leaf. We significantly increased the solar energy harvesting capacity of the microalgae by immobilising the cells within a polyester fabric material and alginate hydrogel matrix. The artificial leaf device for H₂ generation contains the microalgae/fabric composite sandwiched between two vascular networks of microfluidic channels with one at the bottom delivering nutrients and water to the cells and the other on the top to harvest the produced hydrogen gas. The efficiency of hydrogen generation by the microalgae immobilised in the artificial leaf device is much higher compared to the suspension culture in a photobioreactor (Figure 1). In essence, we form a cellular biocomposite which mimics the function and stability of natural leaves for the efficient photo-generation of hydrogen.

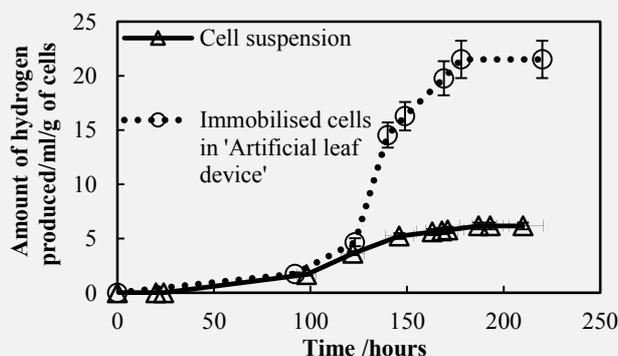


Figure 1. The volume of hydrogen gas produced as a function of incubation time of the suspended and immobilised *C. reinhardtii* cells in a 1 litre photobioreactor and artificial leaf device, respectively, per gram of cell.

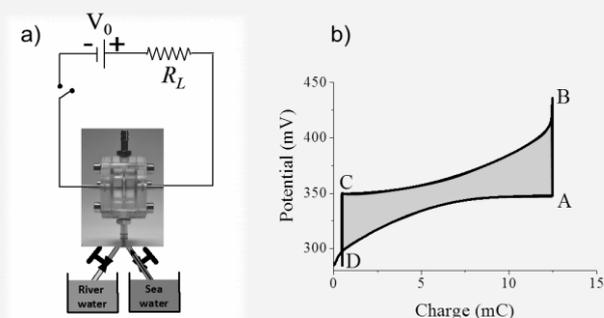
We also succeeded in immobilizing two symbiotic species of microorganism using a combination of cationic and anionic polyelectrolytes in an artificial biofilm where both of them retained their viability. The multiple layers of artificial biofilms can be used simplify the nutrient delivery system through the formation of a symbiotic food chain. Our method for fabrication of immobilized algal cells has the potential for scaling up and possible applications for hydrogen generation.

Effect of Electrode Interface Properties on Energy Production based on Double Layer Expansion

M.L. Jiménez, M.M. Fernández, S. Ahualli, G.R. Iglesias, A.V. Delgado
University of Granada, Granada, Spain

jimenez@ugr.es

Mixing fresh and salty water is a source of energy present in the mouths of the rivers. One method for extracting this energy is based on the dependence of the electric double layer capacitance on the salinity of the solution. In this so-called CDLE method (Fig. 1), one pair of electrodes are charged in presence of salty solution at a certain potential (Fig. 1b, point A), then salty and fresh solutions are exchanged in open circuit, resulting in an increase of the potential difference between electrodes (point B). Hence, by connecting again the external voltage source, and due to this increase of the potential difference, there will be an spontaneous back current until the voltage at the electrodes and external source equal again (point C). The cycle is closed by exchanged again fresh to salty water (point D) [1].



There are some experimental and simulation works that support the viability of this method [2,3], although the efficiency is still low. The aim is now to improve the power that can be obtained, and for that purpose we offer a few actions on *i)* the cycle, *ii)* the material for the electrodes, including the size of the pores, the hydrophobicity of the surface, and adsorption of polyelectrolytes; and *iii)* the solution, particularly, effect of multivalent ions and temperature.

[1] D. Brogioli, *Phys. Rev. Lett.* **103** (2009) 058501.

[2] M. Bijmans, O. Burheim, M. Bryjak, A. Delgado, P. Hack, F. Mantegazza, S. Tenisson and H. Hamelers, *Energy Procedia* **20** (2012) 108.

[3] M.M. Fernández, S. Ahualli, G.R. Iglesias, F. González-Caballero, A.V. Delgado, M.L. Jiménez, *J. Colloid Interface Sci.* doi-10-1016-jjcis201408009.

Aknowledgements

Financial support: COST CM1101; MINECO, Spain (FIS2013-47666-C3-1-R), Junta de Andalucía, Spain (PE2012-FQM-0694).

The use of nanoparticles in redox flow cells

H. Parant^a, A. Colin^b

^a*Centre de Recherche Paul Pascal, Bordeaux, France*

^b*Centre de Recherche Paul Pascal, Bordeaux, France*

parant@crpp-bordeaux.cnrs.fr

Since renewable energies emerged, the storage energy has become a significant issue in order to control the supply and demand of on-grid energy. Well-known conventional batteries (lithium batteries, alkaline batteries...) use at least one solid compound (Li, Ni, Cd...) and are very efficient. However, redox flow cells are non-negligible alternatives. The basic principle is the same as conventional batteries except the fact that all the reagents are in liquid form. The two reagents (anolyte and catholyte) enter in contact with the current collectors thanks to hydrodynamic pumping. After cycling, the products are stored in large tanks. For industrial use, the vanadium couples V^{2+}/V^{3+} and V^{5+}/V^{4+} are the most studied. Although the delivered power is not as high as for lithium batteries, power and energy in redox flow cells can be decoupled which implies a possible improvement of both aspects separately. Indeed, energy is linked to the size of the storage tanks whereas power is related to the efficiency of electronic transfer between the electrolyte and the current collector. To improve energy storage, a particular attention was recently given to nanoparticles in dispersion which are much more efficient than small molecules in solution. In particular, lithium manganese oxide is a good candidate for an industrial use in redox flow cells since it could be dispersed in water and does not need sulfuric acid medium to react unlike vanadium species. However, the major challenge is the conductivity of such dispersions: the addition of a conductive material as carbon is necessary but increases the difficulties in the formulation dispersion (viscosity, stability...). After describing the formulation strategies of $LiMn_2O_4$ /carbon dispersions, a first part will be dedicated to the reactivity of nanoparticles on carbon solid electrodes. Then, an original design of a redox flow cell using a microfluidic approach will be described and tested.

**Saponins: A renewable, biodegradable and active surfactant.
From the synthesis of monodisperse lattices to antibacterial properties.**

C. Schmitt^{a,c}, J. Gigault^{b,c}, V. A. Hackley^c,

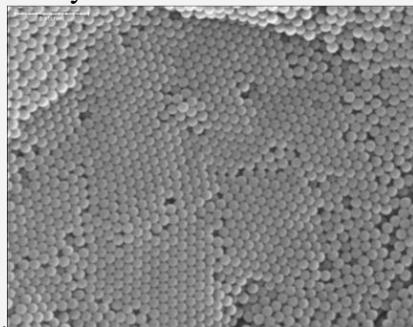
B. Grassl^a, G. Lespes^a, A.-L. Bulteau^a and S. Reynaud^a

^aIPREM, UMR 5254, CNRS/UPPA, 2 av. Angot, 64053 Pau cedex 9, France

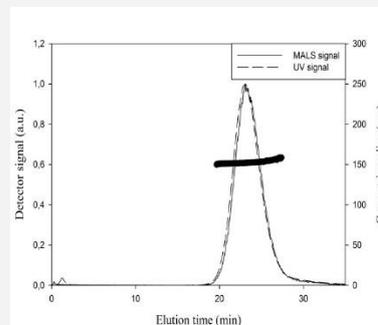
^bEPOC - OASU UMR 5805 Equipe LPTC, CNRS/Université de Bordeaux, 351 Cours de la Libération, 33405 TALENCE cedex, France

^cNational Institute of Standards and Technology, Materials Measurement Science Division, 100 Bureau Drive, MS 8520, Gaithersburg, MD 20899-8520, United States of America.
stephanie.reynaud@univ-pau.fr

There is a growing interest in the natural and green surfactants due to its excellent functional properties and being biologically and environmentally safe as well as ecologically adaptable. Our work first demonstrates the use of saponins as biodegradable and renewable surfactants for emulsion polymerization. This chemical has been extracted from soapnuts by microwave assisted extraction and characterized in terms of surfactant properties prior to emulsion polymerization. The results in terms of particle size distribution and morphology control have been compared to those obtained with classical nonionic (NP40) or anionic (SDS) industrial surfactants. Microwave extracted saponins were able to lead to latexes as stable as standard PS latex as showed by the CMC and CCC measurements. The saponins stabilized PS particles have been characterized in terms of particle size and distribution by Dynamic Light Scattering and Asymmetrical Flow Field Flow Fractionation. Monomodal and monodispersed particles ranging from 250 to 480nm in terms of diameter with a particle size distribution below 1.03 have been synthesized.



(a)



(b)

Polystyrene particles obtained with 4wt-% of saponins vs. monomer. ESEM image $\times 10,000$ (a) and A4F analysis (b).

These results showed that saponins represent a new biodegradable and renewable surfactant with a very low CMC, insignificant salt-sensitivity and low pH-sensitivity. Lastly, recent works showed anti-microbial activity of pure extract of saponins. In view of these applications, it was interesting to study the functional properties of our saponin-stabilized lattices. Dried films made from our latexes containing crude bio-surfactant as saponins maintains similar functional properties as a chemically extracted and purified saponins: antibacterial and antifungal activities have been successfully demonstrated. The study is highlighting the economical use of crude saponins as a green and active surfactant.

Leachate treatment by inorganic membranes

Boubekeur Asli, **Aissa Belouatek**, Abdelkader Chougui, Khaled Zaiter
Laboratoire (E.S.N.T.A) ; faculté des sciences exactes et de l'informatique,
Université Mostaganem Algérie 27000.

Abstract

This work focuses on the development of ceramic membranes and their application in the treatment of liquid effluents polluted. Including leachate, qualitative analyzes were performed on different leachate from the landfill of Tiaret (west of Algeria), the use of modified ceramic membranes gave a total retention (100%) of heavy metals, as regards to the nitrites and nitrates retention rate was higher than 96%.The reduction rate of the chemical oxygen demand (COD) has reached more than 90 % for a good duration of treatment, using five different types of membranes in the treatment of three leachates, These membranes , monolayers and double layers of local slip of kaolin modified with various additions of zirconium oxide and alumina , symbolized by M1 , M2 , M3, MD1 and MD2

Key words: membrane filtration, leachate, flow, effluent

Influence of Composite Core/Shell Nanostructures to NO Pollutant Oxidation

S. Karapati,^{a,b*} T. Giannakopoulou,^a N. Todorova,^a N. Boukos,^a D. Dimotikali,^b C. Trapalis,^a

^a*Institute of Nanoscience & Nanotechnology, NCSR Demokritos, 153 10, Athens, Greece*

^b*Department of Chemical Engineering, NTUA, 157 80, Athens, Greece*

s.karapati@inn.demokritos.gr

Core/shell materials has attracted the attention of scientific community the last decades as for their catalytic applications. Shell protects core from inactivation and aggregation and its porous structure facilitates the access of air pollutants which could be oxidized to environmentally friendly products under UV-irradiation. The main goal of this study is the synthesis of core (TiO₂) / shell (SiO₂) nanoparticles, modified with alkaline compounds in order to enhance NO pollutant oxidation and limit the concentration of toxic intermediate NO₂ product.

The size distribution and surface charge of nanoparticles in water was examined by Dynamic Light Scattering (DLS) and Zeta Potential. The surfactants grafted to TiO₂ was investigated through Thermal Analysis (TG/DTA) and Infrared Spectroscopy (FT-IR). Finally, NO oxidation was examined in accordance with the standard ISO / DIS 22197-1:2007 method.

The modified nanoparticles showed weight losses and exothermic peaks up to 500°C. They also depicted reduced aggregation in water than unmodified TiO₂. Increase of NO oxidation was recorded, attributed to reduced aggregation of titania (core) and easy accessibility of pollutant to core through porous SiO₂. TiO₂ / SiO₂ nanoparticles showed increased NO₂ production, a fact attributed to the acid nature of SiO₂ shell.

The addition of alkaline compounds in composites resulted in NO_x removal increase and limitation of NO₂, the concentration of which remained low.

Keywords : photocatalysis, core (TiO₂), shell (SiO₂), alkaline earth metals, NO₂

Luminescent “light funnel” based on PbS colloidal nanoparticles

*I.M. Kislyakov^{1,2}, S.K. Evstropiev^{1,2}, I.A. Bagrov¹, I.M. Belousova^{1,2},
Yu. A. Gatchin², K.V. Dukelskiy^{2,3}, V.M. Kiselev¹,*

¹ - JVC “Vavilov State Optical Institute”, Saint-Petersburg, Kadetskaya linaya, 12, Russia.

² - National Research University of Information Technologies, Mechanics and Optics, Saint-Petersburg, Kronversky pr., 49, Russia.

³ - The Bonch-Bruевич Saint-Petersburg State University of Telecommunications, Saint-Petersburg, Moika 61, Russia.

Different materials containing PbS quantum dots (QDs) are perspective for numerous applications in laser applications, solar energetic, photonics, and medicine. Colloidal chemical methods are fast and simple way of QDs preparation.

In this work we present the results of the preparation of the suspension and coatings containing PbS QDs stabilized by high-molecular ($M_s=1300000$) polyvinylpyrrolidone (PVP). PbS suspensions were prepared from mixed water - propanol-2 solution of Na_2S and $\text{Pb}(\text{NO}_3)_2$ at the presence of PVP.

Experiments show that PbS suspensions and coatings demonstrate strong luminescence in NIR spectral range (1100-1200 nm) at the excitation of visual light with different wavelengths. Luminescent properties of our suspensions non-linearly depend on the power of exciting irradiation and, also, they are changing during storage at room temperature.

The composite PbS/PVP coatings deposited on glass surface demonstrate strong luminescent in NIR spectral range also.

Also, in this work the changes of luminescent properties of PbS suspensions, stabilized by high-molecular polyvinylpyrrolidone, after irradiation by visual light, have been investigated. It has been demonstrated that luminescent properties of suspensions non-linearly depend from the power of exciting irradiation. Light irradiation leads to increase of light absorption of PbS suspensions and changes the intensity of their luminescence. Photo-stimulated changes of luminescent properties can be explained by the acceleration of the evolution of metastable aggregates of close-packed PbS nanoparticles.

Fig.1 demonstrates SEM photo of PbS/PVP composite coating prepared from our suspension. It can be seen that numerous aggregates having the shape of “worm” are randomly disposed in polymer matrix.

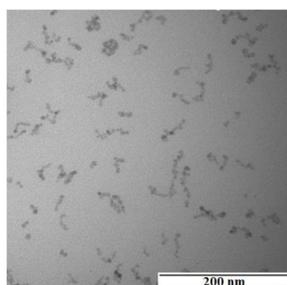


Fig.1 SEM photo of PbS/PVP composite coating

Mechanism of Spontaneous Motions of the Oil Droplet on an Aqueous Phase

M. Fujinami

*Dept. of Applied Chemistry & Biotechnology, Chiba University,
1-33 Yayoi, Inage, Chiba 263-8522, Japan*

fujinami@faculty.chiba-u.jp

The quasi-elastic laser scattering (QELS) method enables us to measure the surface and interface tension non-invasively by monitoring the frequency of capillary waves with a laser[1]. It is, therefore, very suitable for clarification of the non-equilibrium phenomena at the surface and interface. Much attention has been paid to a lot of phenomena on the spontaneous motion of the oil droplet on an aqueous phase. I deliver on a talk on some applications by QELS method to clarify the mechanism of the spontaneous motion of the oil droplet.

A spontaneous vectorial motion of a 1-hexanol droplet on a 0.58 vol% aqueous phase was investigated. The surface tension gradients in the front and rear sides of a 1-hexanol droplet were compared and the velocity of the alcohol droplet strongly correlated to the difference of the inverse of the recovery distances of the surface tensions between the front and rear sides. This result indicated that the spontaneous alcohol droplet motion was governed by the imbalance in the Marangoni convection flow induced by the asymmetric surface tension distribution.

Another is the amoeba-like motion of an oil droplet with a fatty acid on an aqueous phase with a cationic surfactant. After the surface tension of the aqueous phase became constant, the blebs were induced in the oil droplet repeatedly. It was found that some domains were formed in the oil droplet and the acid and surfactant complexes apparently adsorbed or desorbed partially along the edge of the oil droplet during the bleb formation by visualizing them with the fluorescence particles and the carbon power.

[1] T. Nomoto, T. Toyota, M. Fujinami, *Anal. Sci.* **2014**, 30, 707.

Macroscopic Hierarchical Structures Organized by Liquid Crystalline Inorganic Nanosheets under Electric Field

Teruyuki Nakato*, Yoshihiro Nono, Emiko Mouri

Department of Applied Chemistry, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata, Kitakyushu, Japan

nakato@che.kyutech.ac.jp

Inorganic nanosheets prepared by exfoliation of layered crystals have around 1 nm thickness and several micrometers lateral size form colloidal liquid crystals (LCs).¹⁾ In the colloidal LCs, we may organize macroscopic structures with electric fields because of collective nature of the LC state and the large mesogen size of the nanosheets.^{2,3)} We report herein hierarchical organization of macroscopic structure under electric field in the colloidal LCs of niobium oxide nanosheets.⁴⁾ We employed a two-stage process composed of the growth of LC domains, which is called tactoids hereafter, and subsequent application of an AC electric field for the organization. In this process, the tactoid size defined by the period for the tactoid growth as well as the relative direction of the gravity and electric field applied to the grown tactoids were the controlling factors of the final texture. The tactoid size determined the characteristic lengths of the final structures because they worked as the secondary building units which were aligned along the electric field. As the result, macroscopic structures with net-like and stripe textures having the characteristic lengths of sub-mm to mm were realized in the nanosheet LCs as shown in Figure 1. Parallel and orthogonal applications of the gravity and electric field yielded the net-like (Figure 1a) and stripe (Figure 1b) textures, respectively.



Figure 1. Macroscopic colloidal structures of the niobate nanosheet LC obtained under an AC electric field applied (a) parallel and (b) perpendicular to gravity.

- 1) T. Nakato, N. Miyamoto, *Materials*, **2009**, 2, 1734.
- 2) T. Nakato, K. Nakamura, Y. Shimada, Y. Shido, T. Houryu, Y. Iimura, H. Miyata, *J. Phys. Chem. C*, **2011**, 115, 8934.
- 3) T. Nakato, Y. Nono, E. Mouri, M. Nakata, *Phys. Chem. Chem. Phys.*, **2014**, 16, 955.
- 4) N. Miyamoto, T. Nakato, *Adv. Mater.*, **2002**, 14, 1267.

The antimicrobial activity of ZnO particles and its mechanisms

Yves Chevalier,^a Julia Pasquet,^b Emmanuelle Couval,^b Dominique Bouvier,^b Marie-Alexandrine Bolzinger^a

^a *University of Lyon 1, LAGEP, Villeurbanne, France*

^b *Strand Cosmetics Europe, Lentilly, France*

chevalier@lagep.univ-lyon1.fr

Zinc oxide (ZnO) is used for its antimicrobial properties in pharmaceutical products and as a preservative of topical formulations. The antimicrobial properties of ZnO particles have been studied in order to disclose their relationships with their physicochemical properties and to assess the mechanisms of its antimicrobial activity.

The antimicrobial activity of four different ZnO grades against four bacteria, molds and yeasts was assessed using disc diffusion tests and a broth dilution method. The crystallite size and the porosity of polycrystalline aggregates appeared the most relevant parameters that control the antimicrobial efficacy [1].

ZnO acts by three strain-dependent mechanisms that the relative contributions were assessed: release of Zn²⁺ ions, photogeneration of Reactive Oxygen Species (ROS), and microbial cell damaging by direct contact. Release of Zn²⁺ in water was slow and showed a complex dissolution / precipitation behavior. The solubility of ZnO in broth medium was quite high (1000 ppm) because of the complexation of Zn²⁺ ions by proteins [2]. Therefore, all ingredients of formulations influence the ZnO activity [3,4]. Binding of ZnO particles was detected by electron microscopy and zeta potential measurements of ZnO-bacteria mixtures. The generation of ROS under light and in the dark was monitored by titration of H₂O₂.

[1] Antimicrobial activity of zinc oxide particles on five micro-organisms related to their physicochemical properties. Pasquet J et al. *Int. J. Pharm.* **2014**, *460*, 92-100.

[2] The contribution of zinc ions to the antimicrobial activity of zinc oxide. Pasquet J et al. *Colloids Surfaces A* **2014**, *457*, 263-274.

[3] Zinc oxide as a new antimicrobial preservative of topical products: interactions with common formulation ingredients. Pasquet J et al. *Int. J. Pharm.* 2015, *479*, 88-95.

[4] Zinc oxide: a new preservative for cosmetic and dermopharmaceutical products. Pasquet J et al. *Int. J. Cosmet. Sci.* submitted.

Intracellular medium of living cells - a viscoelastic liquid or a gel?

J.-F. Berret

*Matière et Systèmes Complexes, UMR 7057 CNRS Université Denis Diderot Paris-VII, Bâtiment
Condorcet, 10 rue Alice Domon et Léonie Duquet, 75205 Paris, France*

jean-francois.berret@univ-paris-diderot.fr

When submitted to rotational magnetic field, micron size wires with specific para- or ferromagnetic properties behave as embedded rheometers, and represents interesting probes for micro-rheology. Here, we use rotational magnetic spectroscopy to measure the shear viscosity of the cytoplasm of living cells, and address the question of whether the cytoplasm is a viscoelastic liquid or a gel. The main result of the study is the observation of a rotational instability between a synchronous and an asynchronous regime of rotation [1,2], found for both murine fibroblast and human cancer cell lines (Figure 1). For wires of magnetic susceptibility $\chi = 3.6$, the transition occurs in the range $0.01 - 1 \text{ rad s}^{-1}$. The determination of the shear viscosity ($\eta_0 = 10 - 100 \text{ Pa s}$) and shear elastic modulus ($G = 5 - 20 \text{ Pa}$) confirms the viscoelastic character of the cytoplasm. In contrast to earlier studies however, it is concluded that the interior of living cells is best described in terms of viscoelastic liquid, and not in terms of elastic gel.

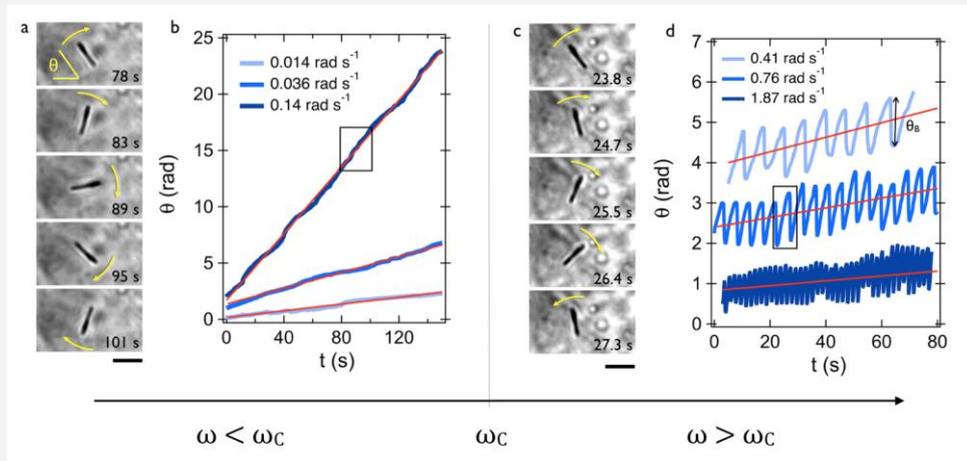


Figure 1: **a)** Optical microscopy images of a $2.8 \mu\text{m}$ internalized wire subjected to a rotating field of 14 mT and the frequency of 0.14 rad s^{-1} . **b)** Time dependences of the angle $\theta(t)$ at varying frequencies $\omega = 0.014, 0.036$ and 0.14 rad s^{-1} . **c)** and **d)** Same representation as in **a)** and **b)** but for angular frequencies ($0.41, 0.76$ and 1.87 rad s^{-1}) above the critical frequency $\omega_c = 0.15 \text{ rad s}^{-1}$.

[1] Frka-Petesic, B.; Erglis, K.; Berret, J.-F.; Cebers, A.; Dupuis, V.; Fresnais, J.; Sandre, O.; Perzynski, R., *J. Magn. Magn. Mater.* **2011**, *323*, 1309-1313.

[2] Chevry, L.; Sampathkumar, N. K.; Cebers, A.; Berret, J. F., *Phys. Rev. E* **2013**, *88*.

Salt effects on surfactant free microemulsions

Sebastian Schöttl,^a Werner Kunz,^a Thomas Zemb,^b Dominik Horinek^a

^aUniversity Regensburg, 93053 Regensburg, Germany

^bICSM Marcoule, 30207 Bagnols sur Cèze Cedex, France

Dominik.Horinek@ur.de

Aggregate formation in ternary systems in the absence of a classical surfactant component has been studied in the last years experimentally and by computer simulations. Here, we study the salt effects on aggregation in water/ethanol/octanol mixtures by means of atomistic molecular dynamics simulations. We find that different salts influence the aggregation in different ways. Some salts lead to a distinct increase of aggregate formation, some not, see Fig. 1. The different influence of the different salts is discussed in relation to the subject of ion specific Hofmeister effects. In this field tremendous advance has been made during the last decade in linking ion effect on the stability of colloidal systems to the interfacial properties of individual ions.

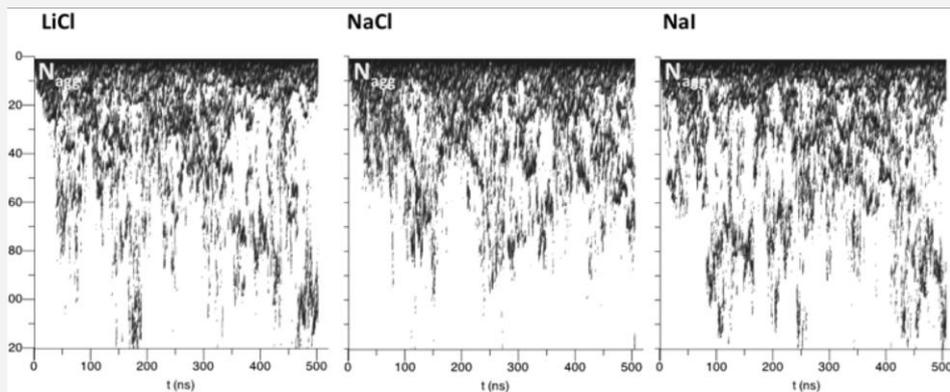


Figure 1: Aggregate size distribution as a function of simulation time.

Biaxial nematic phase in mineral plate-rod suspensions doped by anisometric particles: statistical-thermodynamic study of stability

E.P.Sokolova, A.Yu.Vlasov,

Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia

drew-v@yandex.ru

Binary dispersions containing prolate and oblate hard particles may form the biaxial nematic phase (Nb). Herein we focus on the effect of the shape and size of a doping component (long rods (L) or thin plates (T)) upon stability of the Nb phase with respect to de-mixing into uniaxial nematics, viz., a rod-rich (N+) and a plate-dominated (N-) ones, in a binary mixture of uniaxial rods (R) and plates (P) with relatively small aspect ratios. We employ the model of a fluid formed by rectangular parallelepipeds, with their symmetry axes aligned along a space-fixed Cartesian frame, collective particle interactions being treated in the 3rd virial approximation.

The Nb phase in a binary R–P sub-system set up of particles with equal volumes and aspect ratios ($\gamma_R = 5$, $\gamma_P = 1/5$) is metastable with respect to N+ ÷ N- de-mixing. Aspect ratios of the admixture rods (L) spanned the interval $6 \leq \gamma_L \leq 10$. The second-order N+-Nb and N--Nb phase boundaries were located numerically from the data on biaxiality phase parameters in the vicinity of bifurcation points. The curvature of the biaxial branches of the Gibbs energy was analyzed by explicit calculation employing Jensen's inequality. Admixing of even small amounts of long rods or thin plates ($\gamma_T = 1/10$) showed up to enhance thermodynamic stability of the Nb phase within a spacious domain of the composition triangle. A case of a calamitic dopant shows that the stability region of the Nb phase expands with an increase in L-component particle volume given constant γ_L .

This work was supported by Russian Foundation for Basic Research (Grants # 13-03-01111 and 15-03-09316).

Understanding Polymer Encapsulation through Modeling and Simulation

Freda C. H. Lim,^a and Michael B. Sullivan,^b

*Institute of High Performance Computing, Agency for Science, Technology and Research,
Singapore*

limch@ihpc.a-star.edu.sg

The sustained and controlled or stimulated release of chemical actives at targeted sites has gained popularity in various consumer and personal care-related applications in recent years. Applications such as the surfactant-triggered-release capsule of softener in detergents or conditioner in shampoos and the timed-release capsules of cosmetics are already available in the consumer market. These encapsulation materials can be made up of amphiphilic molecules such as lipids and block-copolymers with different hydrophilic-lipophilic ratios. By changing the functional groups attached to these molecules, we can engineer the desired delivery properties for the encapsulating agent. However, in the design of new materials for encapsulation of chemical actives, there is often an element of trial-and-error in experiments. An understanding of the molecular details of interactions is often lacking and materials scientists rely on their chemical intuition and experience for these. As a result, the learning cycle-time can be long and tedious while the transferability of the experience may be limited.

With the ever increasing computational power and the advent of new algorithms, molecular modelling is becoming increasingly useful as a tool to aid in the design of new encapsulation materials either by adding to the fundamental understanding of the interaction mechanisms at atomistic scales or by speeding up the learning cycle that leads to better chemical intuition.

In this talk, we will share our use of molecular-dynamics simulation to study the atomistic behaviour of PEG-PS block-copolymers in solutions of different concentrations and in the presence of model chemical actives with different hydrophobicity. The objective of this work is to understand how polymer structure and composition affects its properties and to use this knowledge to support the process of new materials design.

The impact of nonelectrostatic interactions of electrolytes at redox electrodes

Drew F. Parsons

School of Engineering and IT, Murdoch University, Perth WA, Australia

Email: D.Parsons@murdoch.edu.au

Specific ion (Hofmeister) effects are observed throughout colloid science and related disciplines. These are shifts in observed measurements which depend on the specific identity of an electrolyte solution, observed in a wide range of measurements including colloidal aggregation, zeta potential, pH, surface tension, bubble coalescence, protein cloud points, etc. Specific ion effects are not anticipated by standard electrostatic theory where ions are represented only by charge. But they can be explained as a consequence of nonelectrostatic properties of ions, through both nonelectrostatic physisorption [1] and chemisorption [2,3] of ions at surfaces.

Nonelectrostatic properties of an electrolyte affect the energy storage characteristics of supercapacitors (which have no charge transfer between electrolyte and electrode) [4]. Predictions from the new theory are consistent with measured capacitances [5].

The theory is now extended to describe the effect of nonelectrostatic properties of electrolytes on redox systems (batteries, electrowinning) where electron transfer takes place between electrolyte and electrode.

The theory is a variation of the constant potential system. The chemisorption energy for the classic constant potential condition in colloid theory involves physisorption of a single potential determining ion [2]. In a redox system the chemisorption (charge transfer) energy is determined by physisorption of both donor and acceptor species in the electrolyte rather than a single potential determining ion.

The nonelectrostatic physisorption energy of donor and acceptor ions introduces a previously unexplored source of ion specificity which shifts the total free energy of the electrolyte-electrode system, affecting electrode wettability and forces between electrodes and other surfaces.

References

- [1] D.F. Parsons, B.W. Ninham, Nonelectrostatic Ionic Forces between Dissimilar Surfaces: A Mechanism for Colloid Separation, *J.Phys.Chem.C* 116 (2012), 7782-7792
- [2] V. Deniz, D.F. Parsons, Effect of Nonelectrostatic Ion Interactions on Surface Forces Involving Ion Adsorption Equilibria, *J.Phys.Chem.C* 116 117 (2013), 16416-16428
- [3] D.F. Parsons, A. Salis, The impact of the competitive adsorption of ions at surface sites on surface free energies and surface forces, *J.Chem.Phys.* 142 (2015), 134707
- [4] D.F. Parsons, Predicting ion specific capacitances of supercapacitors due to quantum ionic interactions, *J.Coll.Int.Sci.* 427 (2014) 67-72
- [5] D.F. Parsons, Supercapacitors have an asymmetric electrode potential and charge due to nonelectrostatic electrolyte interactions, *Coll.Surf.A* 460 (2014), 51-59

Abstract

We use a combination of simulations and a simple theoretical approach to investigate interactions between neutral conducting surfaces, immersed in an electrolyte solution. The study is conducted at the primitive model level, necessitating the use of multiple image reflections.

Our work also includes comparisons with predictions by the well-known Ninham-Yaminsky (NY) theory for these systems. As far as we know, this is the first time that this theory has been evaluated against simulations. The NY theory is accurate for 1:1 salt solutions against non-adsorbing surfaces, but predicts qualitatively incorrect net interactions for solutions containing asymmetric salts. Another drawback with the NY theory is that it is unable to treat ion-specific adsorption.

In addition to the simulations, we have developed a simple classical density functional theory, called the "image Poisson-Boltzmann" (iPB), which accounts for the dielectric discontinuities. This theory is remarkably accurate, even for an asymmetric 2:1 (or 1:2) salt, giving essentially quantitative agreement with the simulations, even when the NY theory is qualitatively incorrect. For instance, the total surface interactions in 2:1 (or 1:2) salt solutions are repulsive at long range. This is nicely captured by iPB, whereas NY theory predicts a monotonic attraction.

An important additional advantage of the iPB approach is that ion-specific adsorption can be included in the theory, without loss of accuracy. The ability to account for ion-specificity is of crucial importance for studies on metal particle dispersions, such as gold sols. Finally, given the density functional formulation of the iPB it would be relatively straightforward to move beyond the mean-field level, and to include other mechanisms, such as excluded volume effects, and connectivity (for more complex ions).

Towards predicting the stability of protein-stabilized emulsions

Roy J.B.M. Delahaije^a, Harry Gruppen^a, Marco L.F. Giuseppin^b and Peter A. Wierenga^a

^aLaboratory of Food Chemistry, Wageningen University, Bornse Weilanden 9, 6708 WG,

Wageningen, The Netherlands

^bAVEBE, Prins Hendrikplein 20, 9641 GK, Veendam, The Netherlands

roy.delahaije@wur.nl

The protein concentration is known to determine the stability against coalescence during formation of emulsions (figure 1A). Recently, it was observed that protein concentration also influences the stability of formed emulsions against flocculation as a result of changes in ionic strength (figure 1B). In both cases, the stability was postulated to be the result of a complete coverage of the interface. By combining the current views on emulsion stability against coalescence and flocculation with new experimental data, an empiric model was established to predict emulsion stability based on protein molecular properties such as hydrophobicity. It was shown that besides protein concentration, the adsorbed layer (i.e. adsorbed amount and interfacial area) dominates emulsion stability. Surprisingly, the emulsion stability was also affected by the adsorption rate. From these observations, it was concluded that a completely covered interface indeed ensures the stability of an emulsion. The contribution of adsorption rate and adsorbed amount on the stability of emulsions was combined in a surface coverage model. For this model, the adsorbed amount was predicted from the protein radius, surface charge and ionic strength. Moreover, the adsorption rate, which depends on the protein charge and hydrophobicity, was approximated by the relative hydrophobicity. The model already showed good quantitative correspondence with experimental data, and was furthermore shown to be applicable to describe data from literature.

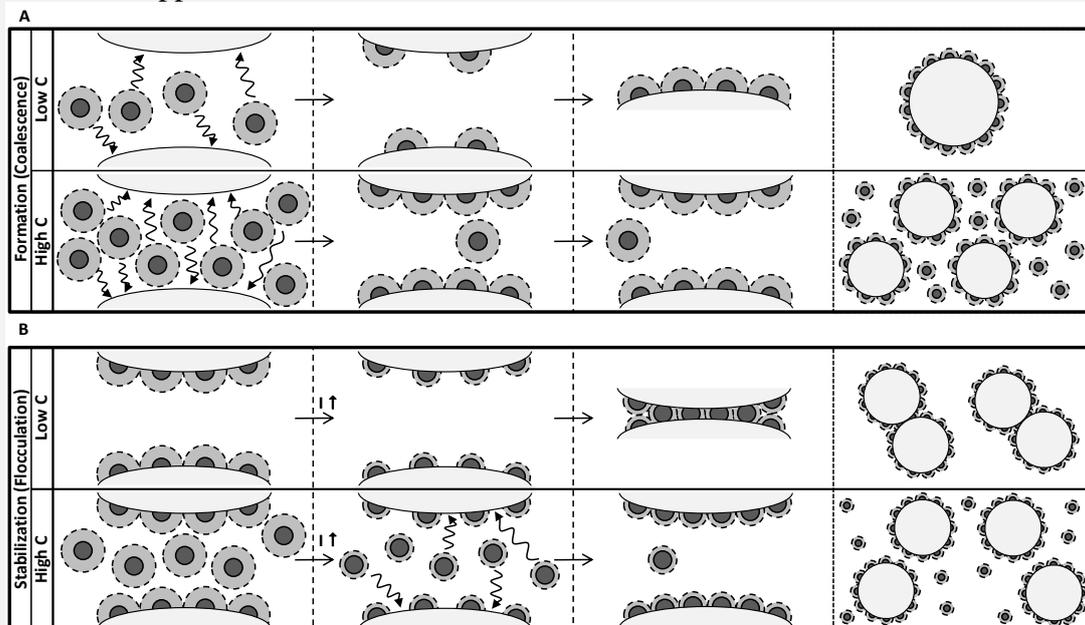


Figure 1. Effect of low and high protein concentration on the emulsion stability against coalescence during formation (A) and against flocculation after formation (B). The effective radius of an adsorbed protein is a combination of protein radius (dark grey) and the Debye screening length (light grey).

Computer Simulation of the AOT Reverse Micelle in Supercritical Carbon Dioxide

G. V. Mudzhikova, E. N. Brodskaya

Institute of Chemistry, St. Petersburg State University, Petersburg, Russia

galinam.chem@gmail.com

Supercritical carbon dioxide (SCCD) is an available and environmentally safe solvent that works well with an efficient technology of regeneration. This is the reason for the wide interest in its application for supercritical fluid extraction. Micellar extraction is one of the most promising fields related to this problem.

Reverse micelles of Aerosol OT (AOT, sodium bis(2-ethylhexyl) sulfosuccinate) in the medium of supercritical carbon dioxide have been simulated by the molecular dynamics method. For the first time, the micelle in a ternary system of water–AOT– SCCD is simulated by describing the surfactant and the supercritical liquid on the base of a coarse-grained approach.

It is shown that structural and energetic characteristics of the micelle are, with a good accuracy, described within the framework of simplified models. Allowance for the quadrupole component of the interaction energy decreases the hydrophobic effect and facilitates the formation an aqueous cavity in the micelle center, with the density inside the cavity being close to that of bulk water. Therewith, all surfactant ions are located near the surface to form an ionic layer. Due to the mutual dissolution of water and SCCD, the thickness of the surface layer increases and the eccentricity of the aggregate decreases to compare with a micelle formed in a hydrocarbon. The micelle retains its layered molecular structure and energetic stability.

The penetration of water into the region of the supercritical liquid enhances its contact with AOT ions, thereby increasing the coordination numbers and the heights of the peaks in the pair distribution curves. At the same time, the calculation of the potential interaction energy in the system has shown a trend toward a reduction in the internal energy of the system in the medium of supercritical carbon dioxide.

This work is supported by the Russian Scientific Foundation, the project no. RNF-14-13-00112

Kinetics of the bubble collisions and rupture at resting and vibrating liquid/gas and liquid/solid interfaces – experiment and modelling

J. Zawala, A. Niecikowska, K. Małysa

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul.

Niezapominajek 8, 30-239 Krakow, Poland

Knowledge of the mechanism of bubble bounce is crucial for deeper insight into kinetics and mechanism of the bubbles coalescence and the three-phase contact formation. Outcomes of the bubble collisions and the probability of rebound are factors of significant importance in many industrial processes involving multiphase flows. For example in flotation separation, where bubble-particle capture is at the heart of the process the bubble-grain aggregate can be formed only during mutual contacts (millisecond timescale). Thus, prolongation of the contact time by reducing the probability of bouncing should increase the attachment efficiency. On the other hand the highest degree of dispersion of the air phase is desired in this process, so the bubble coalescence phenomenon is unfavourable. Therefore, control of the degree of dispersion of bubbles is of crucial importance from the practical point of view and can be achieved by controlling the most important factors determining the bubble coalescence, that is, the kinetics of drainage and rupture of the liquid films formed and separating the colliding bubbles and/or the bubbles and solid surfaces.

The paper presents results obtained in experiments and numerical modeling of the kinetics of the bubble collisions and rupture (coalescence or three phase contact – TPC – formation) at undisturbed and vibrating, with control acceleration, liquid/air and liquid/solid interfaces. The phenomena occurring during collisions and bouncing of air bubbles of radius 0.50-0.88 mm (impact velocity within the range of 26-37 cm/s) at various interfaces were monitored using high-speed video recordings. The movies recorded were analysed frame-by-frame to determine variations of the bubble velocity and shape deformations during the collisions. Moreover, the bubble coalescence and the TPC formation times, i.e. the time intervals from the moment of the first collision till the bubble rupture, were determined (t_c and t_{TPC} , respectively). The values of the t_c and t_{TPC} determined for resting interfaces were a reference in respect to the second kind of the experimental series where the interfaces were vibrating. It was found that the kinetics of the bubble collision and rupture significantly depended on the experiment conditions. At undisturbed interfaces the bubble ruptured and the coalescence or TPC formation was observed to depend on the bubble size, but generally it happened within a millisecond timescale (from ... to 100 ms). For vibrated surfaces the bubble collisions and bouncing could be prolonged almost indefinitely, for properly adjusted the vibration frequency and amplitude. Moreover, at the vibrating solid surfaces the outcome of the bubble collisions and bouncing was independent of the surface hydrophilic/hydrophobic properties. In addition, the deformation degree of the bubble was practically constant, i.e., it stopped to change with the collision number both for liquid/gas and liquid/solid interfaces. The analysis of the bubble deformation degree showed that this effect is related to a constant bubble deformation, which resulted in a constant radius of the liquid film, large enough to prevent the draining liquid film to reach its rupture thickness. Results of numerical simulations performed confirmed this hypothesis. The CFD simulations results showed also that the thickness reached by the separating liquid film at the moment of collision is higher for higher bubble impact velocity and larger deformation ratio.

Structure and interaction mechanism of a polyelectrolyte complex: A dissipative particle dynamics study

E. Meneses-Juárez,^a M González-Melchor,^a Umapada Pal^a, Francisco Rivas-Silva and César Márquez-Beltrán^a

^aInstituto de Física “Luis Rivera Terrazas”, Benemérita Universidad Autónoma de Puebla, Apartado Postal J-48, Puebla, 72570, México.

emeneses@ifuap.buap.mx

The mechanism of complex formation of two oppositely charged linear polyelectrolytes dispersed in a solvent is investigated by using dissipative particle dynamics (DPD) simulation. In the polyelectrolyte solution, the size of the cationic polyelectrolyte remains constant while the size of the anionic chain increases. We analyze the influence of the anionic polyelectrolyte size and salt effect (ionic strength) on the conformational changes of the chains during complex formation. The behavior of the radial distribution function, the end-to-end distance and the radius of gyration of each polyelectrolyte is examined. These results showed that the effectiveness of the complex formation is strongly influenced by the process of counterion release from the polyelectrolyte chains. The radius of gyration of the complex is estimated using the Fox-Flory equation for a wormlike polymer in a theta solvent. Addition of salt in the medium accelerates the complex formation process, affecting its radius of gyration. Depending on the ratio of chain lengths a compact complex or a loosely bound elongated structure can be formed.

Ion Specific Effects on the Self-assembly of Cationic Surfactants : Experimental and Computational Approaches

A. Malinenko,^a M. Porrini,^a C. Liu,^b X. Chao,^b S. Nlate,^a D. Bassani,^c R. Sauers,^b
D. Case,^b M. Laguerre,^a L. Romsted^b and R. Oda^a

^a *Chimie et Biologie des Membranes et des Nano-objets (CBMN),
CNRS UMR 5248 (France)*

^b *Dept. of Chemistry & Chemical Biology, Rutgers University (USA)*

^c *Institut des Sciences Moléculaires (ISM), CNRS UMR 5255
(France)*

a.malinenko@iecb.u-bordeaux.fr

In 1888 Franz Hofmeister discovered that salts influence the conformational stability and solubility of proteins and therefore several counterions can be ordered in a series which bears his name. Association colloids such as micelles, microemulsions and vesicles, composed of ionic amphiphiles, correlate too with Hofmeister series. Nowadays, a thorough understanding of the aspects of the Hofmeister series still remains a challenge in colloid and interface science.

In the present study, making use of physical chemistry experimental techniques, like conductivity, fluorescence quenching and chemical trapping, flanked by atomistic molecular dynamics simulations, we gained some crucial results concerning interfacial and structural properties of the cationic amphiphiles aggregates under investigation. Specifically, we looked into the specific effects on the self-assembly of 10-2-10 gemini surfactants. As for monoatomic anions, the effects that halides exert on the micelle structure correlate well with their different size. Whereas, in the case of polyatomic anions, the results show a higher degree of complexity.

The molecular dynamics simulations, for the first time, are able to corroborate and validate the measurements obtained with chemical trapping experiments. We demonstrated that arenediazonium probe can properly accommodate in the micelle (Figure 1) by sampling the interfacial area and the computed interface molarities of three Hofmeister anions agree remarkably well with the experimental values.

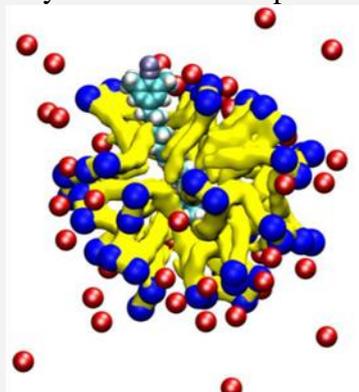


Figure 1: 10-2-10 micelle composed of 27 gemini amphiphiles (yellow surface and blue beads for aliphatic tails and polar heads respectively), together with arenediazonium probe (white, cyan and blue balls for hydrogen, carbon and nitrogen atoms respectively) and with Cl⁻ counterions (red balls)

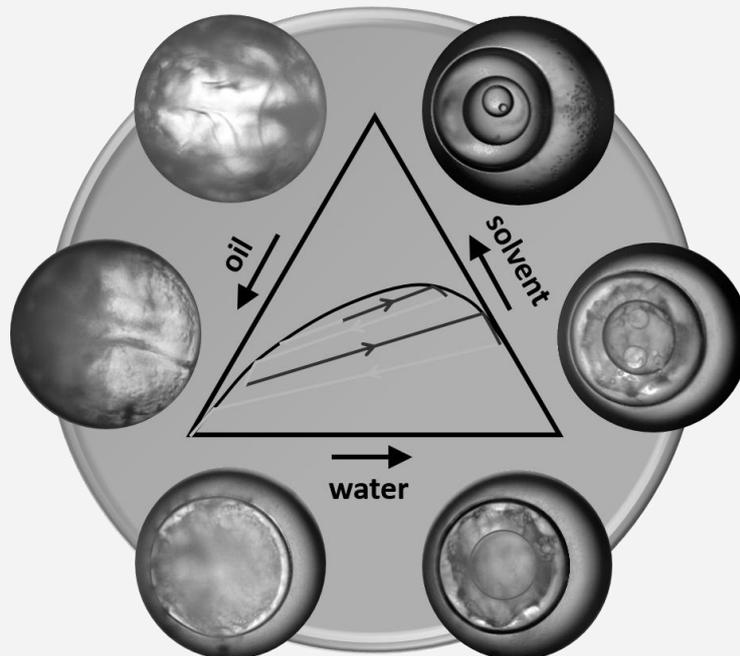
Tailoring of Bijel fibers and membranes by mass transfer-induced liquid-liquid phase separation of ternary mixtures

Martin F. Haase,^a Jasna Brujic^b

^a*Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, USA*

^b*Center of Soft Matter Research, Department of Physics, New York University, New York, USA*
haasemf@googlemail.com

Multiple emulsions with an "onion" topology are useful vehicles for drug delivery, biochemical assays, and templating materials. They can be assembled by ternary liquid phase separation by microfluidics, but the control over their design is limited because the mechanism for their creation is unknown. Herein we show that phase separation occurs through self-similar cycles of mass transfer, spinodal decomposition or nucleation, and coalescence into multiple layers. Mapping out the phase diagram shows a linear relationship between the diameters of concentric layers, the slope of which depends on the initial ternary composition and the molecular weight of the surfactant. These general rules quantitatively predict the number of droplet layers (multiplicity), which we used to devise self-assembly routes for polymer capsules and liposomes. Moreover, we extended the technique to the assembly of lipid-stabilized droplets with ordered internal structures.



Microfluidic-assisted Generation of Monodisperse Highly Ordered Bio-based Polymer Foams

S. Andrieux^a, W. Drenckhan^b, C. Stubenrauch^a

^aUniversität Stuttgart, Institut für Physikalische Chemie, Stuttgart, Germany

^bLaboratoire de Physique des Solides, Université Paris-Sud, Orsay, France

sebastien.andrieux@ipc.uni-stuttgart.de

Monodisperse highly ordered polymer foams can be prepared using liquid templates generated *via* Lab-On-a-Chip techniques. A possible route is generating liquid foam templates^{1,2} and solidifying them *via* gelation or polymerisation depending on the nature of the precursor in the liquid phase. Another route is generating High Internal Phase Emulsions (HIPE)³ followed by the solidification of the continuous phase. The liquid templates can self-arrange under gravity and confinement leading to highly ordered structures with a periodicity that may be retained during solidification. In preliminary previous work the biopolymer chitosan was used to form monodisperse hydrogel foams *via* millifluidics that were then dried into solid foams². We optimised this system by working solely with bio-based compounds such as a sugar surfactant and genipin (a molecule extracted from gardenia) as cross-linker. The formulation of the base system required a thorough study of the gelation of chitosan to allow the template to self-order and remain stable. Moreover both the foam templating and emulsion templating (using an oil as the dispersed phase) route were investigated using a flow-focusing microfluidic device.

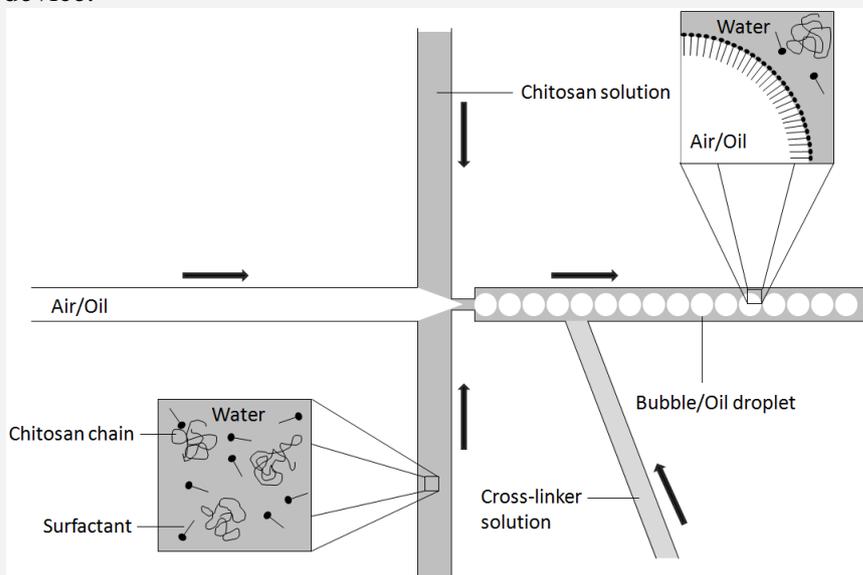


Figure 1: Microfluidic-assisted generation of monodisperse chitosan emulsions (oil as dispersed phase) or wet foams (air as dispersed phase) with a flow-focusing geometry.

[1] A. van der Net et al., *Colloids and Surfaces A* **346**, pp. 5–10, 2009.

[2] A. Testouri et al., *Macromolecules* **43**(14), pp. 6166–6173, 2010.

[3] M. Costantini et al., *J. Mater. Chem. B* **2**(16), pp. 2290–2300, 2014.

On how to control the pore size of monodisperse, highly ordered polystyrene foams

J. Elsing,^a W. Drenckhan,^b C. Stubenrauch,^a

^a*Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

^b*Laboratoire de Physique des Solides, Université Paris-Sud – CNRS UMR 8502, Bâtiment 510, 91405 Orsay, France*

jonas.elsing@ipc.uni-stuttgart.de

We present a novel foam templating route for the synthesis of ordered, monodisperse polystyrene foams. Note that pure styrene cannot be foamed even in the presence of surfactants! This problem can be circumvented by foaming a styrene-in-water emulsion which has a high styrene content of 64.5 vol% [1]. While the emulsion is prepared via “normal” ultrasonification, foaming is carried out with a pressure driven microfluidic flow-focussing device which allows generating a monodisperse foam. Since the foamed styrene-in-water emulsion remains stable during polymerization the liquid foam structure is retained and thus serves as a template for the resulting solid polystyrene foam. With this technique we are able to produce monodisperse polystyrene foams with pore sizes in the range from 95 μm to 320 μm . The pore size of the solid foam is given by the bubble size of the liquid foam, which, in turn, can be adjusted by varying the gas pressure and the emulsion pressure, respectively. However, the gas volume fraction and the bubble size cannot be controlled independently with one chip – for this purpose different chip geometries must be combined. Furthermore, the range of available bubble sizes is limited for one chip. Thus, to have access to a broader range of bubble sizes we utilize different channel sizes (100 μm , 190 μm and 300 μm diameter at the orifice). We will present our latest results and discuss the relation between pore size, polymer density and pore connectivity.

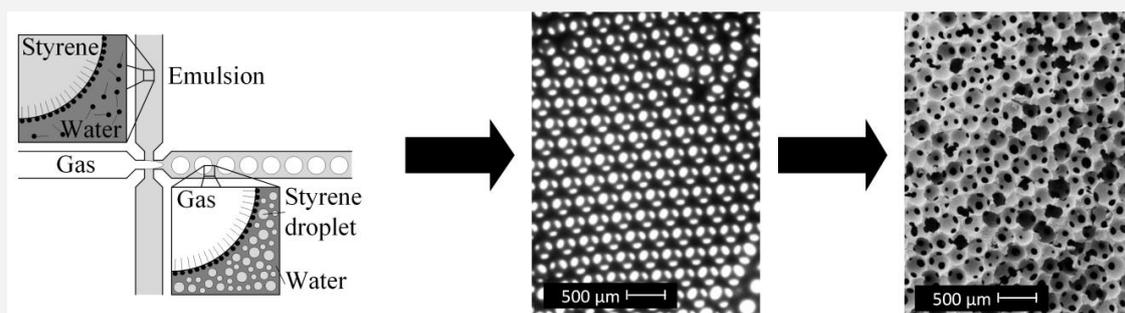


Figure 1: Concept of foaming an emulsion by means of a flow-focussing microfluidic device (left). Obtained ordered, monodisperse liquid foam (middle), and resulting polymer foam (right) [2].

[1] Schüler, F., Schamel, D., Salonen, A., Drenckhan, W., Gilchrist, M.D., Stubenrauch, C., *Angew. Chem. Int. Ed.*, 51, 2213-2217, 2012.

[2] Quell, A., Elsing, J., Drenckhan, W., Stubenrauch, C., *Adv. Eng. Mat.*, 2015, accepted.

Contribution of Droplet- or Jet-Based Microfluidics under High Pressure in Polymer Chemistry

E. Mignard

CNRS, LOF, UMR 5258, F-33600 Pessac, France

emmanuel.mignard@u-bordeaux.fr

There are now many ways to obtain microfluidic devices with more or less complex design. Even if one wants to work with high pressures at small scales, there are still some technological solutions, though more limited, to achieve this goal. One can fabricate Silicon-Pyrex based microfluidic devices or use commercial tubing and connectors like stainless steel or fused silica capillary tubing. And thanks to the works done in several disciplines for many years, chemists can now use microfluidics to enhance the control of concentrations of chemicals, as well as their mixing, their residence time and the thermal transfer. Thus, chemists can investigate chemical reactions more accurately, obtain more data or synthesize original small particles.

By using high-pressure resistant devices, one can use supercritical carbon dioxide (scCO₂). It has emerged as a viable “green” alternative to organic solvents for polymer synthesis and processing as carbon dioxide is stable, abundant, non-flammable and nontoxic. As for any other supercritical fluids, scCO₂ exhibits a liquid-like density, a viscosity close to those of gas, and the diffusivity of light molecules in scCO₂ is significantly increased relative to that measured in the liquid. All these fluid properties and others are finely tuned according to the working temperature and/or pressure. This is specific to supercritical fluids. Eventually, the selective solvation power of scCO₂ can also be used to solubilize a wide variety of chemical compounds, or to extract some from a complex mixture.

In this communication, I will present the advantages in using 1) aqueous droplets or 2) jet of organic solvent, both in scCO₂ by using a high-pressure resistant coaxial capillary microreactor. Aqueous droplets filled with hydrophilic monomer allow the heterogeneous synthesis of polymer, while jet of organic solvent allows the forming of quite monodisperse polymer particles with sizes ranging from micro to nano.

Electrowetting-induced surface ageing at drop scale

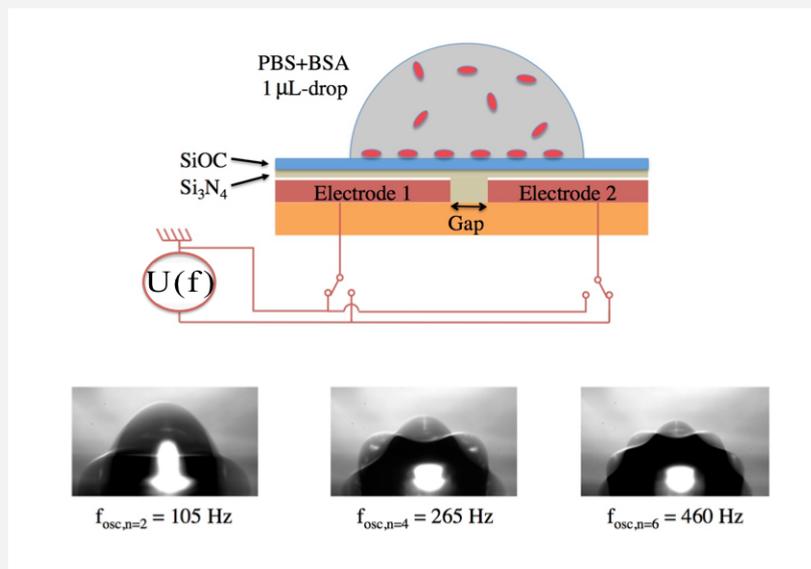
J. Theisen,^a L. Davoust^b

^aGrenoble-INP / CNRS, SIMAP, 1130 rue de la piscine, 38402, Saint Martin d'Hères, France

^bUniv. Grenoble-Alpes, SIMAP, 1130 rue de la piscine, 38402, Saint Martin d'Hères, France

JOHANNES.THEISEN@cea.fr

This paper addresses surface ageing in digital microfluidics. A model system based on bovine serum albumin (BSA)-laden sessile drop is selected. BSA is used because it is currently involved in heterogeneous reactions on (BSA-coated) oxide surfaces [1]. AC coplanar ElectroWetting-On-Dielectrics (EWOD), also increasingly used in digital microsystems for medical assays, is implemented for driving capillary oscillations of the latter drop. The frequency of EWOD actuation is considered as a control parameter. A key feature is that BSA molecules exhibit a frequency-dependent affinity for the solid substrate underneath the drop. As demonstrated from Michelson interferometry at drop apex, the drop surface also experiences a significant change of its liquid-gas surface pressure but due to the very fast kinetics of BSA adsorption there, it is not found dependent on EWOD frequency. These results are confirmed by time-dependence of the solid-liquid surface pressure measured from dynamic contact angle (DCA) imaging. A numerical model for the drop convective flows driven by EWOD-induced oscillations is developed to deal with the weak coupling with BSA transport, and therefore, to help the investigation of streaming-enhanced ageing of the substrate. A large stirring efficiency is made evident near the moving contact line due to a steady eddy arising in the Stuart layer at the highest oscillating mode ($n = 6$). EWOD actuation at moderate frequency (500 Hz) is then found to be a convenient way to continuously adsorb and pack BSA molecules along the solid-liquid surface. Conversely, if the aim is to prevent molecular adsorption, EWOD at high frequency (> 1 KHz), commonly used in digital systems, must be preferred instead.



[1] Bashir, R.; Gomez, R.; Sarikaya, A.; Ladisch, M. R.; Sturgis, J.; Robinson, J. P. (2001) Adsorption of avidin on microfabricated surfaces for protein biochip applications. *Biotechnol. Bioeng.*, 73, 324–328

Two-Compartments Macroporous Polymer Capsules

E. Loiseau,^a F. Niedermair,^b G. Albrecht,^b A. R. Studart^a

^a*Department of Materials, Complex Materials, ETH-Zurich, Zurich, Switzerland*

^b*BASF Construction Solutions GmbH, Trostberg, Germany*

eve.loiseau@mat.ethz.ch

Porous microcapsules are of great interest in diverse applications, ranging from encapsulation for controlled release, to filtration and purification systems in analytical science or to catalyst support.

Here, we demonstrate a novel method to obtain two-compartments microcapsules: the first compartment in the capsule's core, the second inside the porous structure of the capsule's shell.

The microcapsules are produced by microfluidics, using water-oil-water (W/O/W) double emulsion templates. The capsule's shell is formed by UV-polymerization of an oil phase consisting of a mixture of acrylate monomers with a liquid porogen. During polymerization this mixture phase segregates, creating a network of polymer beads permeated by the porogen and polymeric skin that seals the surfaces of the shell. The embedded porogen forms a second compartment permitting the encapsulation of an additional compound. With this method, di-epoxy and di-amine were simultaneously but separately encapsulated inside one single capsule, providing a rich platform for the future design of microcapsule systems for adhesives or self-healing materials.

Furthermore, the shell compartment offers new possibilities of trigger mechanism. Capsules produced with porogens with low boiling point exhibit an explosive behavior when submitted to a thermal shock. We combined these capsules with magnetic particles and used magnetic hyperthermia to achieve the release of the capsules' content within seconds and without over-heating the surrounding matrix.

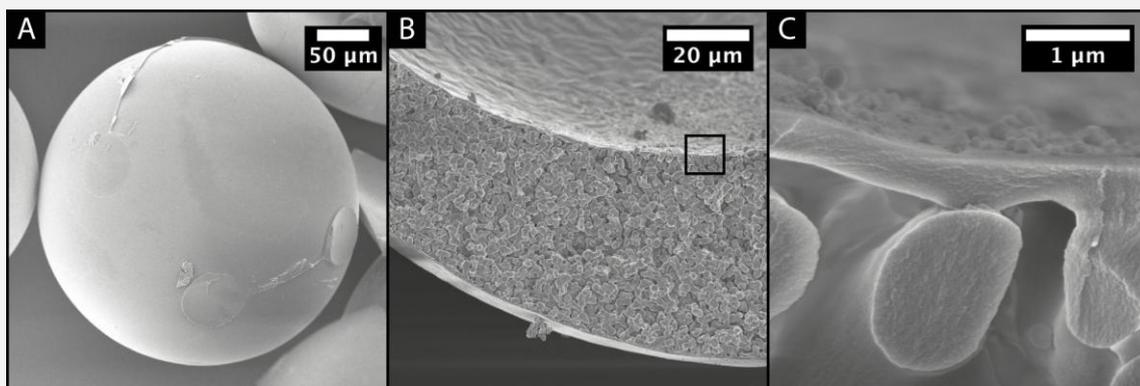


Figure: Two-compartments capsule produced with 15 wt % pentane (A). Cross-section of the shell (B) consisting of a network of polymer beads wetted by the porogen and sealed by a polymer skin (C).

Modified flow focusing for synthesis of PLGA nanoparticles for controlled release of therapeutic compounds

Jiang Xu,^{a,b} Frank Gu,^b Annie Colin,^a

^a Centre de Recherche Paul Pascal, Université de Bordeaux, Bordeaux, France

^b Department of Chemical Engineering, University of Waterloo, Waterloo, Canada

jiang.xu@u-bordeaux.fr

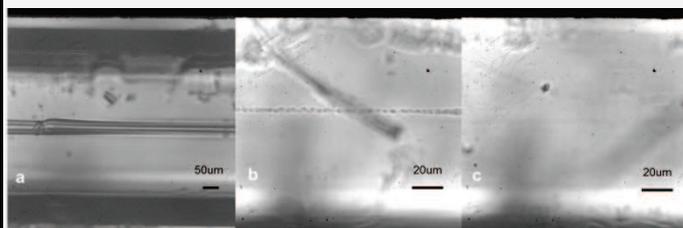
Background and Introduction

Important parameters of polymeric nanoparticles (NPs) synthesized by traditional microfluidics like drug loading efficiency, size and distribution, release profile, etc., must be optimized before the controlled release becomes a reality. Here we proposed a modified microfluidic flow focusing method using a partially water-miscible precursor solution for synthesis of polymeric nanoparticle drug carriers. This microfluidic platform satisfied the requirements of defined NP size, high drug encapsulation efficiency, low polydispersity and rapid screening and optimization at the same time.

Experiments

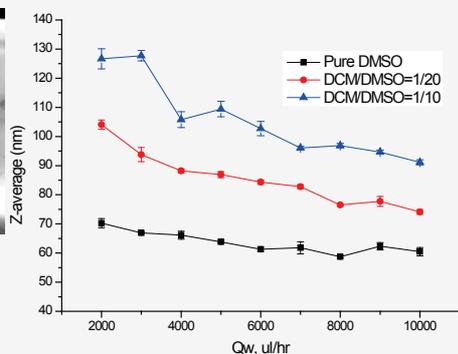
The microfluidic device was constructed from that a tapered round glass capillary was inserted into a square glass capillary. In the co-flow and coaxial geometry, the two fluid phases flow in the same direction (Figure 1); the dispersed phase (PLGA dissolved in mixed solvents of DCM and DMSO) flows inside the round capillary and the continuous phase (0.5% SDS aqueous solution) flows between the round and square capillaries.

Results and Discussions



Left: Figure 1. Evolution process of the organic fluid. (a) Stable jet; (b) Jet transferred to microdroplets; (c) Microdroplets transferred to NPs.

Right: Figure 2. Impact of volume fraction of DCM in dispersed phase on PLGA NPs size



An evolution process of “Jet to Microdroplets to Nanoparticles” of the dispersed phase was first observed (Figure 1) by our group because of using the partially water-miscible solvent, which combined features from both of traditional emulsion-based[1] and rapid-mixing-based[2] microfluidic methods and thus maintained high drug encapsulation efficiency and a small particle size.

By tuning the flow ratio of O/W, polymer concentration and volume fraction of immiscible component (V_{DCM}) in the dispersed phase, we could produce uniform NPs (PDI<0.1) and tune the particle size (60~150nm) easily and precisely (Figure 2). In addition, size of PLGA NPs from higher polymer concentration and V_{DCM} groups were found more sensitive to flow ratio changes, which could offer us a broader selection range of NPs size.

Reference.

[1] Xu et al., *Small*, 2009

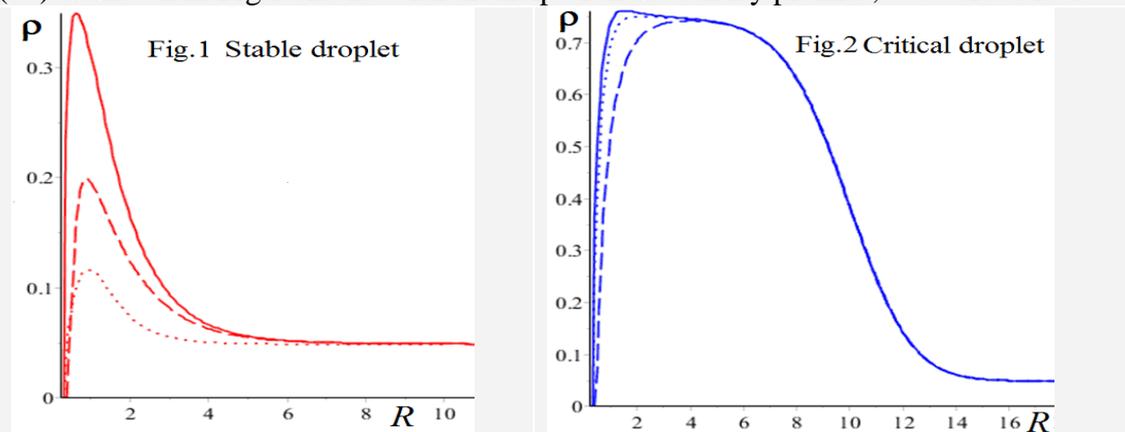
[2] R. Karnik, F. Gu et al., *Nano Letters*, 2008.

How to separate contributions from surface tension, disjoining pressure, and electric field in inhomogeneous nanodroplet

Alexander K. Shchekin, Tatyana S. Lebedeva and Dmitry V. Tatyanyenko
St Petersburg State University, St Petersburg, Russian Federation
akshch@list.ru

The density functional theory applied to small nano- and microdroplets gives us a tool to find clear answers to many problems which had been raised a long time ago but still stay actual for colloid and interface science. One of such problems is a problem of detailed thermodynamic description of stable and critical droplets corresponding to the minimum and maximum of the work of droplet formation at heterogeneous nucleation on ions and charged nanoparticles. This description requires a knowledge of a fine structure in density and polar properties of inhomogeneous liquid droplet or film in presence of strong central electric field, molecular field of the substrate and structural ordering of the solid substrate surface. Previously we have considered [1] the thermodynamics of ion- and charge-induced nucleation within the Gibbs method of dividing surfaces with account of contribution of the disjoining pressure of the thin liquid film in the central electric field of the charged particle. However we took the dielectric permittivity for a substance in the liquid film as constant and used ad hoc approximations for the structural contribution to the disjoining pressure.

As a simple but illustrative variant of the density functional theory, we used in this report the local gradient density functional approach with varying dielectric permittivity as a function of local density. This approach taken in the spirit of paper [2] is applicable both for the Lennard-Jones and polar systems, and in particular for nucleation in water vapor. It allowed us to find the density profiles for water stable and critical droplets in the cases of heterogeneous nucleation on uncharged particle with molecular field (...), charged particle without molecular field (---) and charged particle with molecular field (—) as shown in Fig.1 and 2. With the help of these density profiles, we were able to



separate the contributions from surface tension, disjoining pressure, and electric field and compare them with ad hoc models.

This work was supported by St. Petersburg State University (grant 11.37.183.2014).

References

- [1.]A.K. Shchekin, T.S. Podguzova, Atmospheric Research, 101 (2011), 493-502.
- [2.]H. Kitamura, A. Onuki, J. Chem. Phys., 123 (2005), 124513.

PEDOT:PSS THIN FILMS MODIFIED BY POST-TREATMENT USING A MICROFLUIDIC STAMP

L.J. Romasanta, G. Lebrun, B. Pavageau, J.B. Salmon, J. Leng
Laboratoire de Futur LOF 178, avenue du Dr Schweitzer F-33608 Pessac, France

laura.romasanta@solvay.com

Polyethylenedioxythiophene (PEDOT) is a semi-conducting polymer generally coupled with polystyrenesulfonate (PSS) to improve its processability, resulting in water-based dispersions with low conductivity values, typically from 10^{-5} to 10 Scm^{-1} for commercial solutions. The conductivity of these PEDOT:PSS solutions have been reported to significantly increase with the use of secondary co-solvents by post-treatments.

In this work we report the post-treatment effect of different dopants (ethylene glycol EG, dimethylsulfoxide DMSO and 1-ethyl-3-methylimidazolium tetracyanoborate EMIM TCB) on a PEDOT:PSS thin film spin coated on a glass substrate. The post-treatment was performed using a PDMS stamp with embossed microchannels which allowed to soak locally the PEDOT:PSS thin film with the aforementioned dopants.

The post-treatment modified the conformation of PEDOT:PSS film inside the channels as evidenced by Raman spectroscopy. The band between 1400 and 1500 cm^{-1} ($C_{\alpha}=C_{\beta}$ symmetric stretching of thiophene ring), showed a red shift after the different post-treatments, evidencing a structural reorganization from the benzoid to the quinoid structure. Moreover, the post-treatments with DMSO and EG altered PEDOT:PSS morphology such that short and circular grains were generated. Finally, these local post-treatments provided also the electrical conductivity necessary to exploit the Joule heating effect, which was quantified by thermal imaging experiments at different voltages (Figure 1).

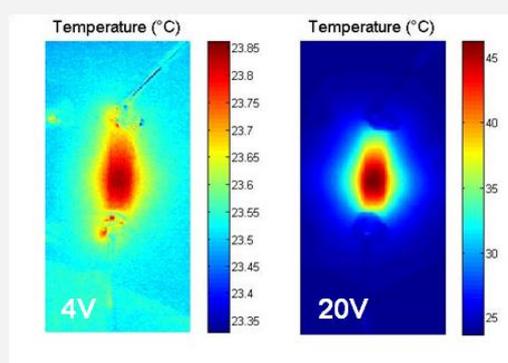


Figure1. Joule heating effect at different voltages for PEDOT:PSS film locally post-treated with DMSO

Saturation and Supersaturation Measurement of Hydrophobic Solute with Micropipette Manipulation Technique

K. Kinoshita,^a E. Parra,^a A. Utoft,^a D. Needham,^{a,b}

^a Center of Single Particle Science and Engineering, FKF, University of Southern Denmark, Odense, Denmark

^b Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, USA

koji@sdu.dk

We have been developing the micropipette manipulation technique for fundamental study in colloid and surface chemistry, including interfacial tensions, dynamic adsorption of surfactants at interfaces, microdroplet and bubble dissolution, and the precipitation and microclassification of solutes [1-3]. Here, we report new applications of this technique to saturation, supersaturation, and precipitation of hydrophobic solutes from organic solution as single microdroplets.

Using a two-pipette technique we inject single microdroplet of chloroform solution into water (**Figure 1**). This method allows to form and trap the single microdroplet in the middle of the chamber while continuously visualizing it, achieving perfect control over droplet size and concentration. Chloroform was chosen as the solvent due to its water immiscibility and finite solubility (8.15 mg/ml), leading to its gradual dissolution and simultaneous concentration of the solutes inside the droplet. For a series of hydrophobic solutes ($\log P=5\sim 24$), they all surpass their solubility limits (C_s) and precipitate out from

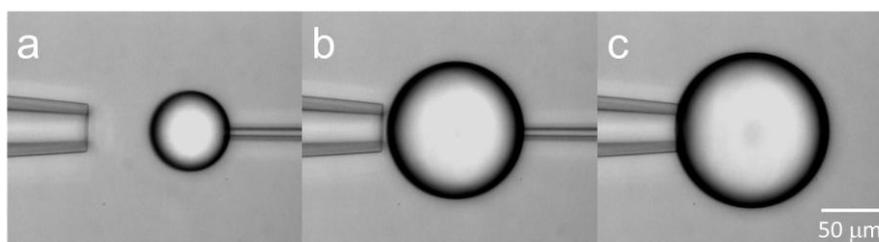


Figure 1. Two-pipette system, with a delivery (right) and a holding pipette (left), used here to visualize the dissolution of a single chloroform microdroplet.

solution at certain supersaturation concentrations (C_{ss}), which were accurately measured at room temperature. Solubility limits C_s were also assessed, by re-swelling the final particles into a chloroform-saturated water environment. Then, the degree of supersaturation $\sigma = (C_{ss}-C_s)/C_s$ was calculated for each material, [cholesteryl-stearate ($\sigma = 1.2$), cholesterol (3.3), fluoranthene (3.8) and triolein (8.5)]. We correlated the σ values with interfacial tensions, cohesive energy densities and melting points. See also hydrophilic solute saturation and supersaturation in the companion poster [4].

[1] Lee et al., *Langmuir*, 2001, **17**, 5537

[2] Su et al., *Langmuir*, 2013, **29**, 13339

[3] Aniket et al., *J. Pharm. Sci.*, 2014, **104**, 640

[4] Utoft and Needham, ECIS, Bordeaux, 2015

Dissolution Rates, Supersaturation, Nucleation and Solubility of NaCl in Single Water Micro Droplets into Organic Liquids

A. Utoft^a, D. Needham^{a,b}

^aCenter of Single Particle Science and Engineering, FKF, University of Southern Denmark, Odense, Denmark

^bDepartment of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, USA

aum@sdu.dk

When a solute is present in an aqueous droplet, both the water activity and the dissolution rate are lowered when compared to pure water droplets dissolving in octanol. The main parameter to control this effect is the activity of water (a_w). Following the work by Duncan and Needham to model the dissolution profiles of both gas-in-liquid [1] and liquid-in-liquid [2], we extended the Epstein-Plesset (EP) model to include the saturation fraction of water at the droplet interface (f_1) as a function of a_w to predict the dissolution of NaCl solution droplets in the concentration range from 0.1 – 12 M.

Experiments were performed on a micropipette setup and recorded until nucleation occurred (**Figure 1A**). By knowing initial NaCl concentration and droplet size, the concentration of NaCl in the water at the point of nucleation (supersaturation) was calculated. Assuming constant mass of NaCl (NaCl has a limited solubility and partition into octanol, $\log P = -3.0$), we measured the solubility in water by positioning a third micropipette containing water close to the NaCl crystal, and used the driving force of chemical potential to re-solubilize the NaCl crystal.

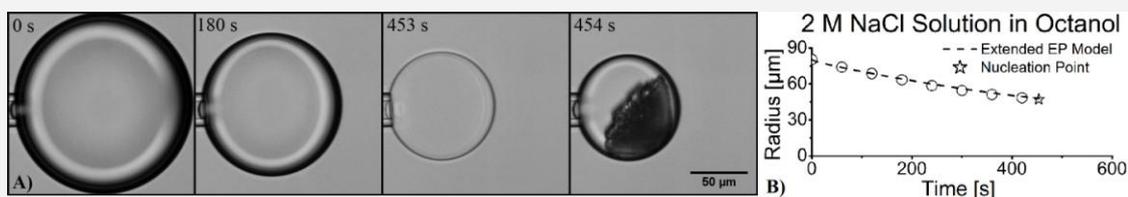


Figure 1 A) NaCl solution (2.0 M) dissolving in octanol. **B)** Dissolution profile, R vs t.

The dissolution profile (**Figure 1B**) was modeled by the extended EP model. The point of nucleation for 22 droplets were used to calculate supersaturation concentrations of 10.2 ± 0.3 M. The point of total re-solubilization measured solubility as 5.5 M, in good agreement with gravimetrically measured solubility of 5.4 M. Both concentrations were used to calculate the degree of supersaturation as either the factor $S=C_{ss}/C_s$ or $\sigma=(C_{ss}-C_s)/C_s$, this in turn were used to predict the critical nucleate size.

1. Duncan and Needham, *Langmuir*, 2004. **20**, 2567.
2. Duncan and Needham, *Langmuir*, 2006. **22**, 4190.

Fabrication of compartmentalized hydrogel microparticles in the size range of blood cells

Anna Pittermannová^a, Aleš Zdražil^a, Martin Ullrich^a, František Štěpánek^a,
Jérôme Bibette^b

^a*Department of Chemical Engineering, University of Chemistry and Technology, Prague,
Technická 3, 166 28 Prague 6, Czech Republic*

^b*Laboratoire Colloïdes et Matériaux Divisés, Ecole Supérieure de Physique et de Chimie
Industrielles, 10 rue Vauquelin, 750 05 Paris, France*

anna.pittermannova@vscht.cz

Recent research in the field of drug delivery systems has resulted in the first prototypes of chemical robots - hydrogel composite microparticles, which are able to store, release and chemically process active components encapsulated in the particles as a result of external radiofrequency signals [1]. Early prototypes fabricated by drop-on-demand inkjet printing [2,3] have characteristic dimensions $\sim 50 \mu\text{m}$. However, for applications in drug delivery, it is necessary to further reduce the characteristic dimension of the hydrogel particles to that of the red blood cells, i.e. by a factor of 10 in diameter (a factor of 1000 in volume), which is a challenging task.

In the present work, compartmentalized microparticles were synthesized from a calcium alginate gel matrix and contain several functional components, namely iron oxide nanoparticles for radiofrequency heating and MRI visualisation, liposomes for the storage and release of active molecules of their precursors, and optionally also immobilised enzymes that facilitate the conversion of pro-drugs to active substances. Liposomes are spherical structures formed by a phospholipid bilayer, which are able to release the active matter in response to temperature. The permeability of liposomes can be significantly increased once they are heated above its phase transition temperature. The needed temperature change is achieved by iron nanoparticles upon exposure to external radio-frequency magnetic field.

Monodisperse microparticles with the required size were prepared by using microfluidic techniques. Microparticles were synthesized right on the chip using a flow focusing device where the continuous phase is oil with Ca^{2+} ions and the disperse phase is aqueous solution of sodium alginate. The flow focusing regime produces w/o emulsion and the gelation of particles is started due to diffusion of Ca^{2+} ions from the continuous phase to the emulsion droplets. The iron nanoparticles and liposomes were encapsulated. The stability of liposome in the alginate microparticles was investigated and the first remotely triggered released experiments were conducted.

References:

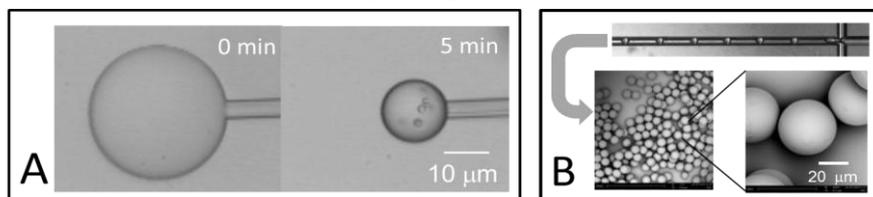
- [1] Ullrich M., Hanuš J., Štěpánek F., "Remote control of enzymatic reaction in compartmentalized microparticles: a system for the delivery of unstable actives", *Chem. Eng. Sci.* 125, 191-199 (2015)
- [2] Hanuš J., Ullrich M., Dohnal J., Singh M., Štěpánek F., "Remotely controlled diffusion from magnetic liposome microgels", *Langmuir* 29, 4381-4387 (2013)
- [3] Haufová P., Dohnal J., Hanuš J., Štěpánek F., "Towards the inkjet fabrication of artificial cells", *Coll. Surf. A* 410, 52-58 (2012)

PLGA Microsphere Formation from Single Microdroplets to Microfluidic Scale-Up

K. Kinoshita^a, R. de Bruijn^b, E. Parra,^a A. Utoft^a, E. Laureano^c, D. Needham,^{a,c}
^a Center of Single Particle Science and Engineering, FKF, University of Southern Denmark,
Odense, Denmark
^b EmulTech B.V., Eindhoven, The Netherlands
^c Department of Mechanical Engineering and Materials Science, Duke University, Durham,
North Carolina, USA
koji@sdu.dk

Poly (lactic-co-glycolic acid) (PLGA) is well established as a biodegradable polymer carrier for drug encapsulation and drug-depot delivery. However, the lack of fundamental morphological studies of *in situ* polymer microsphere formation makes it difficult to understand its emulsification and solidification in various environments. Building on previous studies [1-3], the micropipette technique can be used to evaluate solvent dissolution, precipitation, phase behaviour, and surface properties of different compounds as single microdroplets. Here, we report the direct observation, in real time, of the formation of single PLGA microspheres by precipitation from different solvents, such as ethyl acetate (EA) and dichloromethane (DCM) by using micropipette manipulation technique. These data then guide conditions for microchannel scale-up that can now produce 10g of polymer microsphere's per hr.

Shown in **Figure 1**, PLGA/EA microdroplets (diameter: 40 μm) are created by micropipette injection (inner diameter: 5 μm) into an aqueous solution of polyvinyl alcohol (PVA) (**Figure 1A, 0 min**). Over time (**5 min.**), the microdroplet loses EA into the aqueous phase and its volume decreases (PLGA concentration increased). At the same time, however, some water dissolves into the organic droplet forming water inclusions once PLGA reached a certain concentration, 1.1 g/cm^3 . Finally, all solvent leaves and PLGA precipitates out as a solid microbead. On the other hand, PLGA/DCM microdroplets did not show any inclusions since water solubility in DCM is more than 10 times lower than that in EA. By using EmulTech's microfluidic method, PLGA/DCM microdroplets create smooth microspheres (**Figure 1B**). We will present more details at the meeting regarding the effects of polymer concentration, solvent solubility and stabilizers for PLGA sphere formation, and scale up. This is the basis now for including APIs that can also be hygroscopic, and would influence drug release.



[1] Rickard et al., J. Pharm. Biophys. J., 2010, **98**, 1075. [2] Lee et al., Langmuir, 2001, **17**, 5537
[3] Su et al., Langmuir, 2013, **29**, 13339

Towards a colloidal model system of fluorescent monodisperse emulsion droplets

MF Meissner,^a A Seddon,^{a,b} J Eggers^c CP Royall^{a,d}
^a*H.H Wills Physics Laboratory, University of Bristol, Bristol, UK*
^b*Bristol centre for functional nanomaterials, University of Bristol, UK*
^c*School of Mathematics, University of Bristol, Bristol, UK*
^d*School of Chemistry, University of Bristol, Bristol, UK*

m.meissner@bristol.ac.uk

Current work on monodisperse oil in water emulsions largely concerns droplets so large that brownian motion is negligible [1,2]. We aim to generate micron scale monodisperse oil in water emulsions for the development of a colloidal model system of fluorescent emulsion droplets for coordinate tracking under confocal microscopy. To this end, Polydimethylsiloxane microfluidic devices were explored as a method to generate monodisperse oil emulsions. Polymer coated PDMS devices were used to generate monodisperse dodecane in aqueous sodium dodecyl sulfate (SDS) droplets with a mean radius of 35 μ m [3]. We have developed 3 μ m aperture flow focussing devices based on [4] to generate highly uniform Fluorinert FC-40 droplets in aqueous SDS with mean radii as low as 1.5 μ m and polydispersity below 5%. By varying the flow rate ratio and the device geometry a wide range of different droplet sizes and dispersities was attained.

[1] Clusel, Maxime, et al. "A 'granocentric' model for random packing of jammed emulsions." *Nature* 460.7255 (2009): 611-615.

[2] Desmond, Kenneth W., et al. "Experimental study of forces between quasi-two-dimensional emulsion droplets near jamming." *Soft Matter* 9.12 (2013): 3424-3436.

[3] Royall, C. P. et al. "In search of colloidal hard spheres," *Soft Matter*, 9, (2013): 17-27 *cover image*.

[4] Anna, Shelley L., Nathalie Bontoux, and Howard A. Stone. "Formation of dispersions using "flow focusing" in microchannels." *Applied physics letters* 82.3 (2003): 364-366.

Self-Healing Gold Nanoparticle Assemblies and Applications

E.A. Smirnov,^a M.D. Scanlon,^b P. Peljo,^a H.H. Girault^a

^a Laboratory of Physical and Analytical Electrochemistry (LEPA), Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland

^b Department of Chemistry and the Tyndall National Institute, University College Cork, Cork, Ireland

evgeny.smirnov@epfl.ch

Films and coatings of nanoparticles (NPs) are key components in many emerging technologies due to their distinctive opto-electrical, biological and magnetic properties. In this case, soft interfaces, such as liquid-liquid interfaces (LLIs), can serve as a perfect platform to self-assemble 2D as well as 3D films of NPs. Since the discovery of the metal liquid-like films (MELLFs) by Yogev and Efrima in their pioneering work in 1988¹, many attempts have been made to improve the synthetic procedure and investigate the properties of such films.²⁻⁴

Here, we introduce a novel and facile approach to encapsulate macroscopic droplets with AuNPs in a way that does not require functionalization of AuNPs or covalent linkers. Simply contact between an aqueous citrate stabilized colloidal AuNP solution and an oil phase incorporating tetrathiafulvalene (TTF), with subsequent vigorous shaking of the system, leads to the formation of a continuous shining gold film in a stepwise manner (Fig.1A).⁵ The obtained AuNPs assemblies are dynamic in nature allowing them to self-heal after re-dispersing process.

Among potential applications there are: facilitated electron transfer across LLIs and electrocatalysis (Fig.1B), optical filters and mirrors with tuneable properties (Fig.1C), as well biphasic SERS and micro-droplets encapsulation to create containers.

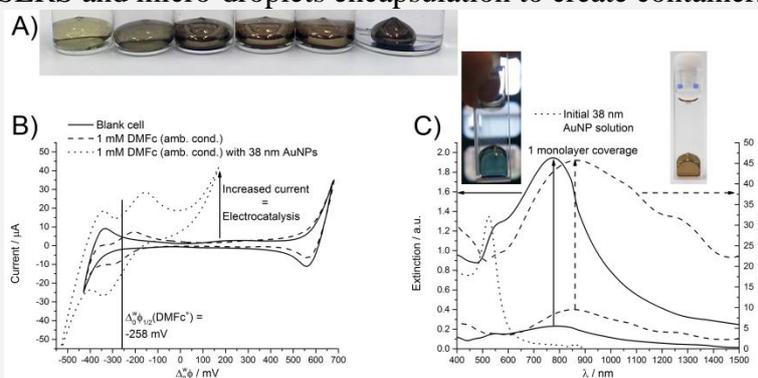


Figure 1. A) Stepwise increasing of AuNP coverage of the LLI between water and 1,2-dichloroethane (1, 2, 4, 6, 8 and 35 ml of 38 nm AuNP solution), B) Electrocatalysis of O₂ reduction by decamethylferrocene (DMFc) on AuNPs at water-trifluorotoluene interface, C) Tuneable optical properties to create filters and mirrors at water-1,2-dichloroethane interface: UV-Vis spectra and corresponding photos.

References:

1. D.Yogev *et al*, DOI:10.1021/j100331a042
2. D.Yogev *et al*, DOI:10.1021/j100347a056
3. B.Kowalczyk *et al*, DOI:10.1039/c0nr00381f
4. D.Wang *et al*, DOI:10.1039/b511911a
5. E.Smirnov *et al*, DOI: 10.1021/nn503644v

Interfacial modification of TiO₂ Particles: The key towards a new design in developing applications in gas separation membranes

E. Cao,^{a,b} E. Prouzet,^a V. Héroguez^b

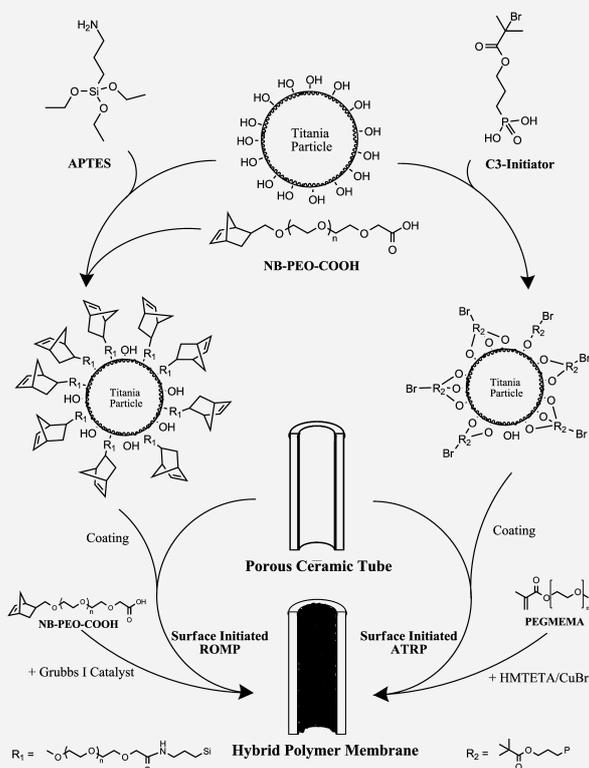
^aUniversity of Waterloo – Department of Chemical Engineering, Waterloo, CANADA

^bUniversité de Bordeaux – Laboratoire de Chimie des Polymères Organiques (LCPO), CNRS UMR 5629, Pessac, FRANCE

edgar.cao@enscbp.fr

Hybrid materials, and more specifically organic/inorganic nanocomposite materials, have been an area of materials research that has generated great interest from a plethora of fields. The material design lies on improving the interface between different components, such as mechanical resistance for inorganic materials, and specific properties found in the organic component. However, modifications of porous supports are difficult, as the radius of curvature restricts the ability of anchoring groups to bind to the surface¹.

In our work, we present a scalable solution using interfacial modified titania particles with either a silane based route or a commercially available organophosphonic acid linker² to develop a new class of membranes that are situated on porous ceramic supports. Using this method of membrane design, we are able to create uniform membranes on porous curved or flat surfaces with ease, thereby enabling greater control on the final membrane structure. We will explain how each of the various routes work, their design parameters and their subsequent performance when producing the membrane.



1. Bernardoni, F., Kouba, M. & Fadeev, A. Y. Effect of Curvature on the Packing and Ordering of Organosilane Monolayers Supported on Solids. *Chem. Mater.* **20**, 382–387 (2008).

2. Cao, E., Prouzet, E. & Héroguez, V. Organic-inorganic hybrid materials designed by controlled radical polymerization and mediated using commercial dual functional organophosphorous coupling agents. *New Journal of Chemistry* **38**, 6081–6087 (2014).

Non-additive simple potentials for pre-programmed self-assembly

C. I. Mendoza, D. Salgado-Blanco,
Instituto de Investigaciones en Materiales, UNAM, Mexico, D.F., Mexico

cmendoza@iim.unam.mx

A major goal in nanoscience and nanotechnology is the self-assembly of any desired complex structure with a system of particles interacting through simple potentials. To achieve this objective, intense experimental and theoretical efforts are currently concentrated in the development of the so-called “patchy” particles. Here we follow a completely different approach and introduce a very accessible model to produce a large variety of pre-programmed two-dimensional complex structures. Our model consists of a binary mixture of particles that interact through isotropic interactions that is able to self-assemble into targeted lattices by the appropriate choice of a small number of geometrical parameters and interaction strengths. We study the system using Monte Carlo computer simulations and, despite its simplicity, we are able to self assemble potentially useful structures such as chains, stripes, Kagomé, twisted Kagomé, honeycomb, square, Archimedean and quasicrystalline tilings. Our model is designed such that it may be implemented using discotic particles or, alternatively, using exclusively spherical particles interacting isotropically. Thus, it represents a promising strategy for bottom-up nano-fabrication.

Reference:

Daniel Salgado-Blanco and Carlos I. Mendoza, “Non-additive simple potentials for pre-programmed self-assembly”, *Soft Matter* **11**, 889 (2015).

Nanometer-size polyoxometalates anions adsorb strongly on neutral soft surfaces

Pierre Bauduin¹, Bappaditya Naskar¹, Veronique Nardello-Rataj², Olivier Diat¹

¹Institut de Chimie Séparative de Marcoule (ICSM)

UMR 5257 (CEA/CNRS/UM/ENSCM)- bat. 426, BP 17171, 30207, Bagnols sur Céze, France,

²Université Lille Nord de France, Université Lille 1, EA 4478, Chimie Moléculaire et Formulation, F-59655 Villeneuve d'Ascq, France

pierre.bauduin@cea.fr

Polyoxometalates (POMs) are nanometric metal-oxide anions with unique chemical and physical properties.[1] During the last ten years, significant efforts have been made to graft alkyl chains on POMs to acquire surface activity and self-assembly properties, which is essential for catalysis applications and for producing organic-inorganic hybrid materials with desired nanostructures.[2-3] We show here that POMs based surfactants are produced spontaneously through non-covalent interactions in water by simply mixing non-ionic surfactants with a POM. The most common POMs of Keggin's type, tungstosilicate ($\text{SiW}_{12}\text{O}_{40}^{4-}$) and tungstophosphate ($\text{PW}_{12}\text{O}_{40}^{3-}$), have indeed an unexpected strong tendency to adsorb on polar and electrically neutral interfaces i.e. here on water-micelle and water-air interfaces. The highlight of this general property of POMs deepens our understanding of the many biological effects of POMs, such as their antiviral and antitumor activities.

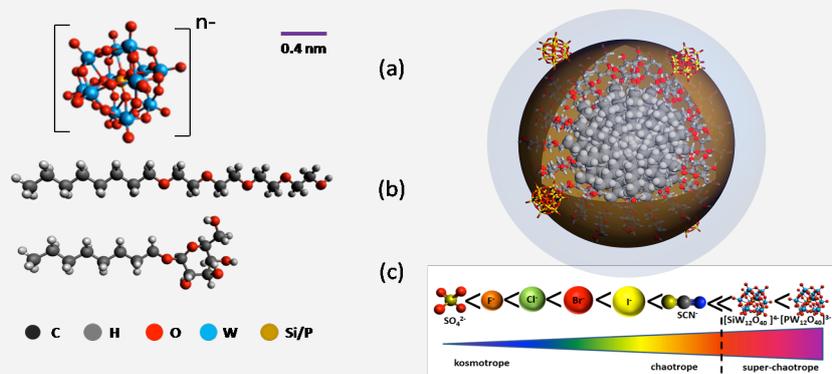


Figure 1 – Chemical structures of (a) POM: $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ (SiW^{4-}) or $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (PW^{3-}); $n = 4$ (Si) and 3 (P), (b) tetraethyleneglycol mono-octyl ether (C8E4), and (c) n-octyl-β-D-monoglucoside (C8G1). Sketch of a C8G1 micelle covered by a POM anion. Hofmeister's series from kosmotropic (salting-out) to chaotropic (salting-in) anions, POM were found to act as super-chaotropic anions.

References:

1. Long, D. -L.; Burkholder, E.; Cronin, L. Polyoxometalate clusters, nanostructures and materials: From self-assembly to designer materials and devices. *Chem. Soc. Rev.* **2007**, 36, 105-121.
2. Jallet, V.; Guillemot, G.; Lai, J.; Bauduin, P.; Nardello-Rataj V.; Proust, A. Covalent amphiphilic polyoxometalates for the design of biphasic microemulsion systems. *Chem. Comm.* **2014**, 50, 6610-6612.
3. Landsmann, S.; Wessig, M.; Schmid, M.; Cölfen, H.; Polarz, S. Smart Inorganic Surfactants: More than Surface Tension. *Angew. Chem. Int. Ed.* 2012, 51, 5995 –5999.

Robust synthesis and self-assembly of raspberries-like nanoresonators using microevaporators

Sergio Gomez-Graña,^{a,b} Stéphane Mornet,^a Etienne Duguet,^a Jean-Baptiste Salmon,^b Jacques Leng,^b Mona Tréguer-Delapierre^a

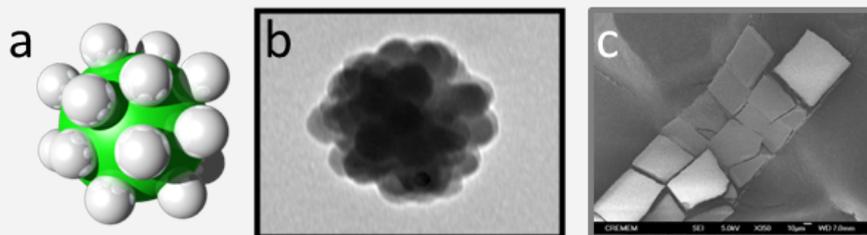
^aICMCB-CNRS Univ. Bordeaux, 87 Ave du Dr A. Schweitzer, 33608 Pessac Cedex (France)
^bLaboratoire du Futur, UMR 5258, F-33600 Pessac, France, and RHODIA

sergio.gomez.grana@gmail.com

Development of new nano-objects to achieve new properties or functions is one of the major challenges in nanosciences and nanotechnology. In this context, hybrids nanosystems, combining different materials of different nature in the same nanoparticle, offer a wide range of new and unexplored possibilities. Proper design of a hybrid nanoparticle permit a control over the interactions of material components, bringing the possibility to combine different confinement-induced properties, create new ones or introduce new functionalization or addressing possibilities.

Herein, we present a successful synthesis and the subsequently self-assembly of raspberry-like metallic nanoclusters. The use of conventional dielectric cores or patchy ones^[1], developed via polymer chemistry, allows to control precisely the number and the location of metallic particles^[2] located at their surface. Precise study of their optical properties, at a single nanoparticle level, was investigated via spatial-modulation spectroscopy (SMS) technique. It reveals novel plasmonic effects with important impact in the fields of nanooptics, nanophotonics and metamaterials^[3] operating in the visible frequencies.

The combination of nanochemical engineering with microfluidic self-assembly technique, enables us to obtain homogeneous optical materials with a high degree of bulkiness. The microfluidic evaporators method enables a rapid and easy characterization using spectroscopic ellipsometry and allows one to make optical devices, such as lenses, filters, modulators using suitable thin soft molds and filling them with nanoparticles.^[3]



References

- [1] A. Désert, C. Hubert, Z. Fu, L. Moulet, J. Majimel, P. Barboteau, A. Thill, M. Lansalot, E. Bourgeat-Lami, E. Duguet and S. Ravaine, *Angew. Chem. Int. Ed.*, **52** (2013), 11068.
- [2] P. Massé, S. Mornet, E. Duguet, M. Tréguer-Delapierre, S. Ravaine, A. Iazzolino, JB Salmon, J. Leng, *Langmuir*, **29** (2013), 1790.
- [3] J. Angly, A. Iazzolino, JB Salmon, J. Leng, S. Chandran, V. Ponsinet, A. Desert, A. Le Beulze, S. Mornet, M. Tréguer-Delapierre, M. Correa-Duarte, *ACS Nano*, **7** (2013), 6465.

Mechanism of Au(III) Reduction by Chitosan and Its Derivatives: from Plasmon to Luminescent Gold Nanoparticles

Alexander Pestov^a, Alexander Nazirov^b, Evgeny Modin^c, Svetlana Bratskaya^b

^a - *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of RAS,*

20, S. Kovalevskoy str., Yekaterinburg 620990, Russia

^b - *Institute of Chemistry, Far East Branch of RAS,*

159, prosp.100-letiya Vladivostoka, Vladivostok 690022, Russia

^c - *Far Eastern Federal University, 8, Sukhanova St., Vladivostok 690950, Russia*

sbratska@ich.dvo.ru

Biogenic synthesis of metal nanoparticles attracts an increasing interest due to its compliance with the principles of “green” chemistry, non-toxicity, and biocompatibility of fabricated materials. The polycation nature of chitosan is particularly favorable for gold nanoparticles synthesis, since, on the one hand, chitosan effectively binds $[\text{AuCl}_4]^-$ ions, and on the other hand, stabilizes formed nanoparticles due to the high affinity of N-containing functional groups to the surface of metallic gold.

Despite numerous reports on chitosan and its derivatives application for Au nanoparticles synthesis, neither the mechanism of Au(III) ions reduction by chitosan nor the chemical structure of the reaction by-products has been investigated in details. The influence of functional fragments in chitosan macromolecule on the morphology of the gold nanoparticles and mechanism of Au(III) reduction also remains unknown.

In this report we present comprehensive study of Au(III) reduction mechanism by chitosan and the series of its N-derivatives containing N-heterocyclic substituents. The data obtained using UV-vis spectrophotometry, viscosimetry, colloid titration, and ^1H and ^{13}C NMR spectroscopy enabled us to propose mechanism of Au(III) reduction by chitosan and its derivatives. Regardless of the type of functionality in substituted chitosan formation of gold nanoparticles starts with complexation of Au(III) and hydrolysis of adjacent glycoside bond. The products of hydrolysis act as main reducing species. Reduction rate and size of the gold nanoparticles strongly depend on polymer-Au(III) complex stability and metal/ligand ratio.

We have shown that introduction of imidazole fragments to chitosan allows fabrication of gold nanoparticles with average size of 2 nm, which exhibit strong luminescence but no plasmon resonance properties.

Financial support from Russian Science Foundation (project № 14-13-00136) is gratefully acknowledged.

Bimodal Magnetic Distribution of Monodisperse Nanoparticles

J. van Rijssel, B.W.M. Kuipers, B.H. Erne
*Van 't Hoff Laboratory for Physical and Colloid Chemistry,
Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands*

b.h.erne@uu.nl

Magnetic properties of superparamagnetic nanoparticles depend strongly on size. The dipole moment scales with particle volume, and doubling the size may even change the magnetization dynamics by more than 10 orders of magnitude.[1] The distribution of magnetic dipole moments in a superparamagnetic sample may in principle be obtained from analyzing its magnetization as a function of the strength of the external magnetic field. Rather than assuming a monomodal log-normal distribution of the dipole moments, as is usually done, we developed a mathematical approach inspired from the way that hydrodynamic size distributions are calculated in dynamic light scattering.[2] Re-examining the properties of magnetic iron oxide nanoparticles that we synthesized earlier by different colloidal chemical methods,[3] we found that depending on the recipe, the magnetic size distribution agrees well or not at all with the physical size distribution from electron microscopy. Some particles with merely 3 percent polydispersity of the physical size were found to have 35 percent polydispersity of the effective magnetic size, and furthermore, the magnetic dipole moment distribution was found to be bimodal rather than monomodal.[4] These discrepancies stem from imperfect crystallization of the particles, that divides them into zones with different magnetic properties.

[1] R.E. Rosensweig, *J. Magn. Magn. Mater.* **252**, 370 (2002).

[2] J. van Rijssel et al., *J. Magn. Magn. Mater.* **353**, 110 (2014).

[3] B. Luigjes et al., *J. Phys. Chem. C* **115**, 14598 (2011).

[4] J. van Rijssel et al., *J. Magn. Magn. Mater.* **380**, 325 (2015).

Near-UV–Induced Shaping of Silver Nanoprisms Self-Assembled on Photocatalytic Titanium Dioxide Film

G. Panzarasa,^a G. Soliveri,^b S. Ardizzone,^b G. Marra^c

^a*Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale “Amedeo Avogadro”, Alessandria, Italy*

^b*Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy*

^c*Eni Research Centre for Renewable Energies and Environment, Novara, Italy*

guido.panzarasa@unipmn.it

Citrate-stabilized silver nanoprisms (mean side length 40 nm, mean thickness 5 nm) [1] have been self-assembled on the surface of highly photoactive titanium dioxide films, deposited on silicon or transparent substrates by an electrochemically-assisted technique [2]. Self-assembly was aided by functionalizing the titania surface with 3-aminopropyltriethoxysilane (APTES) to exploit the electrostatic interaction between positively charged amine groups and negatively charged silver nanoprisms. Silver nanoprisms were distributed evenly on the surface and their shape was not affected by the deposition process as confirmed by electron microscopy.

However, by irradiation with 365 nm-UV light for less than 1 h, dramatic changes in both the shape and surface distribution of attached silver nanoprisms were caused (Figure 1). While the bigger prisms changed into discoidal particles, the smaller dissolved. Such new particles displayed different plasmonic properties compared to pristine nanoprisms.

Titanium dioxide is known to produce highly reactive oxygen species, such as hydrogen peroxide and hydroxyl radical, under UV irradiation. Silver nanoprisms display relevant optical properties in the form of surface plasmon resonance, also they are sensitive to reactive oxygen species [1]. Both photocatalytic and plasmonic aspects must be considered to delineate the photoshaping mechanism.

By performing the irradiation through a photomask, defined patterns with micrometer resolution could be easily obtained even on transparent substrates, opening new scenarios, for example, development of surface enhanced Raman scattering (SERS) sensors.

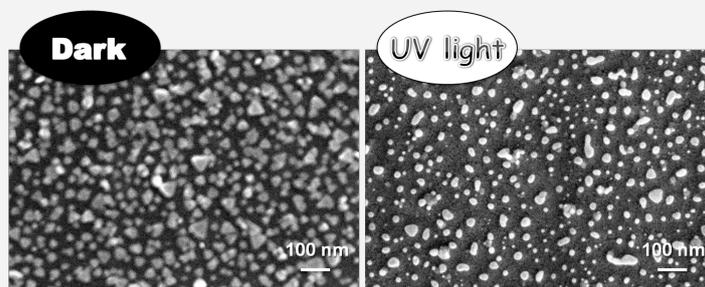


Figure 1. Self-assembled silver nanoprisms on APTES-functionalized titanium dioxide in the dark (left) and after UV irradiation (right).

[1] Yang, Y. et al. *ACS Nano* **2014**, *8*, 4902–4907.

[2] Maino, G. et al. *J. Nanopart. Res.* **2013**, *11*, 1-10.

Guido Panzarasa wishes to apply for the “Enzo Ferroni” award.

Effective Diffusivity of Colloidal Particle Multilayers

Paweł Weroński, Piotr Batys, Magdalena Nosek, Michał Skoczek
J. Haber Institute of Catalysis and Surface Chemistry, PAS, Krakow, Poland

ncwerons@cyf-kr.edu.pl

We have presented results of our theoretical and experimental studies of diffusion through layer by layer assembled multilayers of monodisperse colloidal particles. We have used a Monte Carlo model^{1,2} to create a number of virtual multilayers of hard spheres at a solid-liquid interface, at various surface coverages and numbers of single layers. For each of the multilayers, we have determined its mean thickness, porosity, tortuosity, and effective diffusion coefficient.³ From our simulation results, we have determined the effective diffusion coefficient as a function of the mean surface coverage and layer number of multilayer. We have also tested our theoretical results experimentally. We have produced five multilayers of polystyrene latex particles of the diameter 800 nm on the surface of gold disk electrodes. For each of the multilayers, we have conducted measurements of the limiting diffusion current at the rotating electrodes, dependent on the layer's effective diffusivity.⁴ We have also used an ultra micro balance to determine the mass and mean single-layer surface coverage of each multilayer. We have compared the experimental and theoretical multilayers in terms of the equivalent thickness of stagnant solution layer.⁵ We have found a good agreement between the numerical simulations and experiments at the surface coverage below 0.45. Our experimental results have also suggested that at higher surface coverages the colloidal particle multilayers have collapsed and formed heterogeneous structures.

References

- ¹ P. Batys, P. Weroński, *J. Chem. Phys.* 137 (2012) 214706
- ² P. Batys, M. Nosek, P. Weroński, *Appl. Surf. Sci.* 332 (2015) 318
- ³ P. Batys, P. Weroński, *Modelling Simul. Mater. Sci. Eng.* 22 (2014) 065017
- ⁴ P. Batys, M. Nosek, M. Skoczek, P. Weroński, *Electrochimica Acta* 164 (2015) 71
- ⁵ P. Weroński, M. Nosek, P. Batys, *J. Chem. Phys.* 139 (2013) 124705

Synthesis and Characterization of Au-Fe₃O₄ Dumbbell Nanoparticles

E. Alp, N. Aydogan,
Hacettepe University, Chemical Engineering Department, Ankara, Turkey

erdemalp@hacettepe.edu.tr

Dumbbell-shaped asymmetric nanoparticles have been studied as multifunctional nanostructures in recent years. Their optical and magnetic properties provide usage in many diverse platforms [1]. Iron oxide nanoparticles are used in the areas of data storage, hyperthermia therapy, magnetic resonance imaging (MRI) as contrast agent, etc. Au nanoparticles are available for various applications due to their optical and catalytic properties. Biocompatible Au-Fe₃O₄ dumbbell nanoparticles are advantageous to be used in biomedical application. Easy modification of iron oxide and gold sides of Au-Fe₃O₄ dumbbell nanoparticles allows them to obtain bifunctional nanostructure. In this work, asymmetric nanostructures were obtained by epitaxial growth of iron oxide nanoparticles on Au seeds. TEM results show that approximately 5 nm sized monodisperse oleylamine capped Au nanoparticles were successfully synthesized in chloroform and modified with oleylamine in which interparticular distances of oleylamine capped gold nanoparticles were equal to each other. Iron oxide nanoparticles were grown at 300°C with conventional heating process in the presence of oleic acid and oleylamine. Several parameters can effect the growth of nanoparticles such as the concentration of oleylamine capped Au nanoparticles and amount of iron precursor. By following a systematic approach, the reaction yield was increased with the optimization of various parameters such as concentration, temperature and type of iron precursors. Thus, approximately 5-15 nm sized Au-Fe₃O₄ dumbbell nanoparticles were synthesized efficiently via conventional heating process.

[1] Sun et al., Nano Letters, 2005.

A comparative Study: Synthesis of SPIONs in air and N₂ atmosphere

E. Alp, N. Aydogan,
Hacettepe University, Chemical Engineering Department, Ankara, Turkey

erdemalp@hacettepe.edu.tr

Magnetic nanoparticles can be used in several applications ranging from biomedicine to data storage. Hydrophilic iron oxide nanoparticles are more important from a practical point of view, especially in biomedical applications. Only sub-20 nm iron oxide nanoparticles could exhibit superparamagnetic properties. There are several approaches present for synthesis of nanoparticles below that critical size [1]. In this work, superparamagnetic iron oxide nanoparticles (SPIONs) were synthesized via co-precipitation method both under air and N₂ atmosphere. The effects of the pH and ionic strength on morphology, geometry and size of SPIONs were investigated systematically. Characterization of SPIONs was carried out with Atomic Force Microscopy, Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometer, X-ray diffraction and Static Light Scattering measurements. In Fig. 1, TEM images of sub-20 nm sized SPIONs that have been synthesized successfully under both air and N₂ atmosphere are given. By adjusting the pH and the ionic strength, growth mechanisms of particles were changed in different precipitation environments. In N₂ medium, co-precipitation of iron salts resulted spherical iron oxide nanoparticles while the shape control was harder for the synthesis, which was performed under air atmosphere. Thus, SPIONs were synthesized with various geometries such as rod, cubic or spherical.

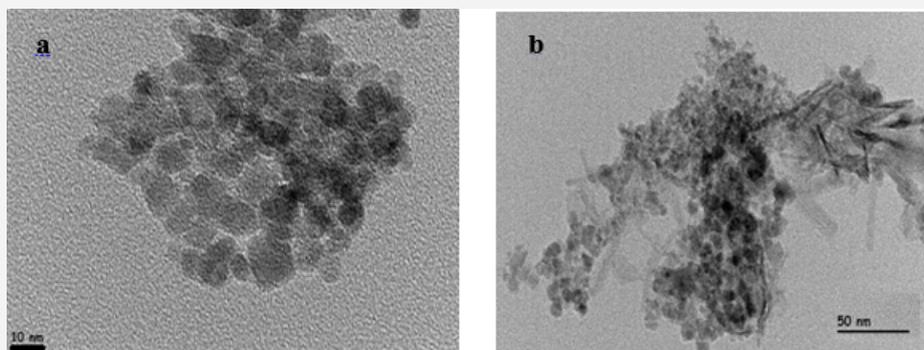


Figure 1. TEM images of iron oxide nanoparticles synthesized at pH=13 under different atmospheres a) N₂ (Scale bar: 10 nm) b) air (Scale bar: 50 nm)

[1] Jeong et al., *Int. J. Mol. Sci.*, 2013.

Charging Mechanisms of the Composite Surfaces: Potentiometric Titration Studies

D. Čakara

*Centre for Micro and Nano Sciences and Technologies and Department of Biotechnology,
University of Rijeka, Rijeka, HR-51000 Croatia*

dcakara@uniri.hr

The methodology for studying the pH-dependent charging of the composite polyelectrolyte/nanoparticle surfaces by means of high-precision potentiometric titrations with ionic strength control is presented. The experimental charging isotherms were determined for several systems with different surface morphologies in which the forces that govern the charging behaviour are either purely electrostatic, or interplaying electrostatic and hydrophobic. These include the strongly cationic poly(diallyldimethylammonium chloride) adsorbed to weakly acidic silica or carboxylate latex surfaces [1,2], weakly basic spherical brushes of poly(N,N dimethylaminoethylmethacrylate) at poly(styrene) surface [3], and chitosan adsorbed on cellulose fibers [4]. The experimentally determined isotherms can be fitted in terms of models which take into account the dissociation reactions and the electrostatic interactions at the Poisson-Boltzmann level.

[1] Čakara, D.; Kobayashi, M.; Skarba, M.; Borkovec, M. *Colloid. Surface. A* 2009, 339, 20–25.

[2] Čakara, D.; Chassagne, C.; Gehin-Delval, C.; Borkovec, M. *Colloid. Surface. A* 2007, 294, 174-180.

[3] Roudot, A.; Pantoustier, N.; Larquet, E.; Čakara, D.; Perrin, P. *Abstr. Pap. Am. Chem. S.* 2006, 231, 290.

[4] Čakara D., Fras L., Bračić M., Stana-Kleinschek K., *Carbohydr. Polym.*, 2009, 78, 36.

Mesoporous Particle Formation on the Superamphiphobic Surface

Sanghyuk Wooh¹, Hannah Huesmann², Muhammad Nawaz Tahir², Maxime Paven¹,
Doris Voller¹, Wolfgang Tremel², Periklis Papadopoulos¹, Hans-Jürgen Butt¹
¹Max-Planck-Institut für Polymerforschung, Mainz, Germany
²Mainz University, Mainz, Germany

wooh@mpip-mainz.mpg.de

A superamphiphobic surface - both superhydrophobic and superoleophobic - has low interfacial energy, trapping air in microscopic protrusions. [1] Due to the low adhesion of the liquid to the surface, the shape of the droplet is determined by minimizing the interfacial energy between liquid and air. Recently, using this unique surface property, a new concept of polymer microparticle synthesis from polymer powder or directly from monomers on a superamphiphobic surface was demonstrated. [2] In this study, we introduce a drying fabrication method of mesoporous particles from nanoparticle (NP) dispersion on the superamphiphobic surface. The liquid repelling property of superamphiphobic surface allows forming spherical microparticles from NP dispersion droplet after water evaporation. Through this new environmental friendly fabrication method, mesoporous particles with various sizes, materials, and structures were produced by simple parameter alternation. Furthermore in order to develop for multiple particle formation process, the multi-nanodroplet-dispenser (Nanoplottter) was employed, and successfully produced large amounts of smaller than 10 μm -size mesoporous particles continuously.

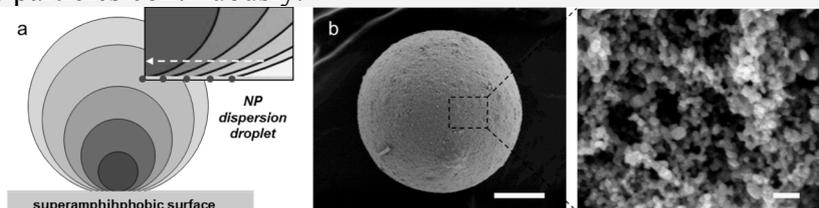


Figure 1: a. Drying fabrication method of mesoporous particle. b. Scanning electron microscope image of mesoporous particle from NP dispersion.

References:

- [1] X. Deng, L. Mammen, H.-J. Butt, D. Vollmer, *Science* 2012, 335, 67.
- [2] X. Deng, M. Paven, P. Papadopoulos, M. Ye, S. Wu, T. Schuster, M. Klapper, D. Vollmer, H.-J. Butt, *Angew. Chem. Int. Ed.* 2013, 52, 11286.

Engineering new patchy particles for directed assembly

C. Hubert^{a,c}, C. Chomette^b, P.E. Rouet^a, M. Sun^b, A. Perro^c, E. Duguet^b, M Tréguer-Delapierre^b, S. Ravaine^a

^aCRPP-CNRS Univ. Bordeaux, 115 Ave du Dr A. Schweitzer, 33608 Pessac Cedex (France)

^bICMCB-CNRS Univ. Bordeaux, 87 Ave du Dr A. Schweitzer, 33608 Pessac Cedex (France)

^cISM Univ. Bordeaux, 351 cours de la libération, 33405 Talence Cedex (France)

hubert@crpp-bordeaux.cnrs.fr

In this communication, we report on a new route to synthesize patchy nanoparticles with a controlled number of patches or dimples as well as on their potential use as building blocks for the elaboration of new supracolloids with unusual morphology and optical properties.

The so-patchy particles were derived from colloidal molecules [1] made of a central silica core surrounded by a precise number n of polystyrene satellite nodules [2,3]. we succeeded in promoting the growth of the silica core of these colloidal molecules. While growing, the silica surface conforms to the shape of the PS nodules. After functionalization of the inter-nodule surface area and dissolution of the polystyrene nodules, homogeneous batches of silica particles with n well-located patches at their surface can be produced in large quantities [4]. The patchy character of the silica particles was evidenced by TEM characterization (see Figure) as well as regioselective functionalization.

These patchy particles offer the unique capability of creating new nano-objects suitable for many applications such as metamaterials, photonics, etc. For example, they can be used to elaborate nanocages of noble metal with a controlled number of holes as well as complex supracolloids by assembly with other nanoparticles.

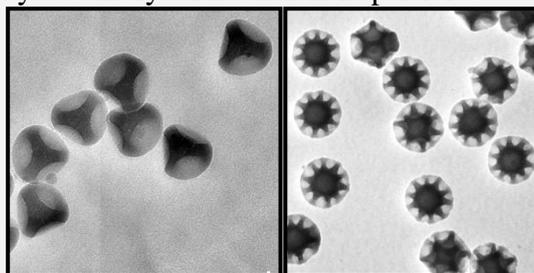


Fig. TEM image of silica particles with four (left) and twelve (right) patches defined here as dimples [4].

[1] E. Duguet, A. Désert, A. Perro and S. Ravaine, Chem. Soc. Rev. 2011, 40, 941

[2] A. Perro, E. Duguet, O. Lambert, J. C. Taveau, E. Bourgeat-Lami and S. Ravaine, Angew. Chem., Int. Ed. 2009, 48, 361.

[3] A. Désert, I. Chaduc, S. Fouilloux, J.C. Taveau, O. Lambert, M. Lansalot, E. Bourgeat-Lami, A. Thill, O. Spalla, S. Ravaine and E. Duguet, Polym. Chem. 2012, 3, 1130

[4] A. Désert, C. Hubert, Z. Fu, L. Moulet, J. Majimel, P. Barboteau, A. Thill, M. Lansalot, E. Bourgeat-Lami, E. Duguet and S. Ravaine, Angew. Chem. Int. Ed. 2013, 52, 11068..

Self-Standing Dual Responsive Microgel Crystals

S. S. Prasath^{a*}, J. Brijitta^a, B.V.R Tata^b and K. Chennakesavulu^c

^aCentre for Nanoscience and Nanotechnology, Sathyabama University,
Chennai– 600 119, Tamil Nadu, India

^bCondensed Matter Physics Division, Material Science Group, Indira Gandhi Centre for
Atomic Research, Kalpakkam-603102, Tamil Nadu, India

^cDepartment of Chemistry, Sathyabama University, Chennai– 600 119,
Tamil Nadu, India

*E-mail: teenprasath89@gmail.com

Monodisperse allylamine functionalized Poly(N-isopropylacrylamide-co-Acrylic acid) (PNIPAM-co-Acrylic acid) microgel particles have been synthesized by free radical precipitation polymerization. It is observed that immediately after synthesis the microgel particles self-assemble into crystalline order without undergoing heating/cooling conditions. These crystals are also found to self-stand in water (medium of synthesis) without settling down (Fig. 1). This is the first report of self-standing self-assembled microgel crystals based on PNIPAM. The change in size of the microgel particles in a dilute suspension as a function of temperature and pH is measured using dynamic light scattering technique and the charge density on the particles has been determined using conductivity measurements. The average size of the particles at pH 4.25 is found to be $554 \text{ nm} \pm 19 \text{ nm}$ with effective surface charge density, $\sigma = 1.12 \mu\text{C}/\text{cm}^2$. The self-standing nature of the microgel crystals is due to the high surface charge density imparted by the amine groups of allylamine. The presence of allylamine group in the backbone of PNIPAM-co-acrylic acid is confirmed by performing FTIR and NMR measurements. The structure of the microgels crystals has been determined by recording a series of optical sections at various depths in the microgel crystal using a confocal laser scanning microscope. The 3D pair correlation function $g(r)$ is determined from the particle (x,y,z) co-ordinates for a set of optical slices in a given volume of the crystal. 3D $g(r)$ of the allylamine functionalized PNIPAM-co-acrylic acid is found to be face centered cubic (fcc). The results of the study will be presented.



Fig. 1: Photograph of the self-standing self-assembled allylamine functionalized PNIPAM-co-acrylic acid Microgel crystals.

Unravelling the multi-scale structure of precipitated silica aggregates by dedicated pathways

*B. Courtois, K. Roger, B. Biscans, M. Meireles
Laboratoire de Génie Chimique, Université de Toulouse, Toulouse, FR

* brice.courtois@ensiacet.fr

Reinforcing precipitated silica systems have complex hierarchical structure that results from optimized synthesis parameters. Yet we lack rational design tools to link these parameters (reactant concentration, pH, hydrodynamic...) to the final material properties (specific area, porosity...). We aim at understanding the mechanisms leading to micro and nano-structures and therefore at providing tools to tune these structures. Here we investigate a common synthesis for amorphous silica involving a two-steps acidification of a sodium silicate solution, in a semi-batch reactor.

First, an acidification leads to a multitude of precipitation, aggregation and resolubilization events. The growth of particles, prior to gel formation, can be varied by tuning the physico-chemical properties. A theoretical prediction within the Smoluchowski frame was successfully compared to a set of data describing the kinetics of particles growth. We can thus control the outcome of this first step, which is essential for the subsequent step.

Then, the gel is maintained at pH 9 under continuous addition of reactants and later further acidified to pH 4.5 leading to the final material. Physico-chemistry is responsible for interactions between particles, chemistry controls molecular bonding, and hydrodynamic ensures the homogeneity of the parameters (pH, temperature...). However, since the parameters are coupled with each other, mechanisms determination is challenging. Our strategy is to uncouple the different effects through a comparison of the reference synthesis with simpler pathways (Figure 1). We investigate the multi-scale structure using a combination of physical method as Cryogenic Transmission Electron Microscopy, Static Light Scattering and Small Angle X-ray Scattering.

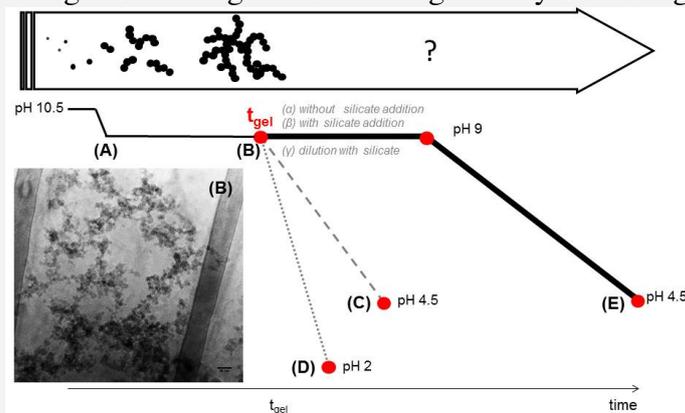


Figure 1: Formation of nanostructured silica gels using the two-step precipitation process performed in this study and described by European Patent EP 0 493 263 A1. Other pathways (indicate in grey) will be investigated to elucidate the role of part of the industrial pathway (indicate in black). Cryogenic Transmission Electron Microscopy picture showing gel state.

Lipid decorated Iron-oxide nanoparticles for simultaneous cancer therapy and diagnosis.

L. Paduano,^(a,b) A. Luchini^(a,b), G. Vitiello^(b,c), G. D'Errico^(a,b), L. Menichetti,^(d)

^a Dipartimento di Scienze Chimiche, Università degli Studi di Napoli "Federico II", Complesso Universitario di Monte S. Angelo, via Cintia, 80126 Naples, Italy.

^b CSGI – Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase.

^c Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli "Federico II", Piazzale Tecchio 80, 80125 Naples, Italy.

^d Institute of Clinical Physiology, CNR, Pisa, Italy

Luigi.paduano@unina.itl

Iron-oxide (Fe_3O_4) nanoparticles have been functionalized for theranostic application in improved cancer detection *via* Magnetic Resonance Imaging (MRI) and treatment. A versatile functionalization protocol based on hydrophobic interactions among amphiphilic target molecules was optimized. In the present case, the inorganic nanoparticle surface was coated with a layer constituted of a mixture of a biocompatible phospholipid (16LPC) and an amphiphilic ruthenium (ToThyCholRu) complex. This latter is a novel antiproliferative molecule we have recently developed and tested with very encouraging results. In the proposed case, the ToThyCholRu agent is reversibly bound on the nanoparticles surface, and thus can be easily released in order to explicate its anticancer activity. Here, we describe the characterization of functionalized Fe_3O_4 nanoparticles through several scattering techniques such as light scattering and small-angle neutron scattering, and their interaction with bio-mimic cell membranes by neutron reflectivity. *In vitro* bioactivity of the nanoparticles effect, both in the presence and absence of ToThyCholRu, on several cells lines will be also present. Finally, MRI images for the presented system will be discussed in light of their potential use.

References

Mangiapia, G.; Vitiello, G.; Irace, C.; Santamaria, R.; Colonna, A.; Angelico, R.; Radulescu, A.; D'Errico, G.; Montesarchio, D.; Paduano, L., *Biomacromolecules* (2013), 14(8), 2549-2.

Mangiapia, G.; D'Errico, G.; Simeone, L.; Irace, C.; Radulescu, A.I.; Di Pascale, A.; Colonna, A.; Montesarchio, D.; Paduano, L., *Biomaterials* (2012), 33(14), 3770-3782

Simeone, L.; Mangiapia, G.; Vitiello, Giuseppe; Irace, C.; Colonna, A.; Ortona, O.; Montesarchio, D.; Paduano, L., *Bioconjugate Chemistry* (2012), 23(4), 758-770.

Alessandra Luchini, Giuseppe Vitiello, Francesca Rossi, Odia Ruiz De Ballesteros, Aurel Radulescu, Gerardino D'Errico, Daniela Montesarchio, Cesar de Julian Fernandez and Luigi Paduano: *Phys. Chem. Chem. Phys.*, 2015, 17, 6087--6097

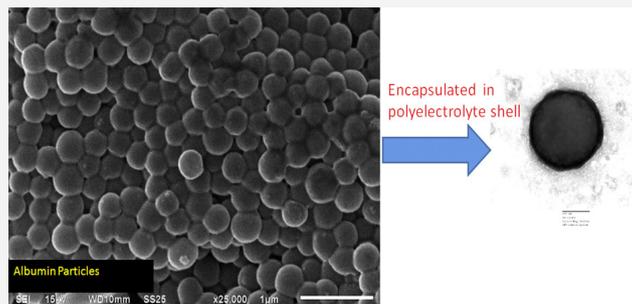
Encapsulation and surface charge manipulation of organic and inorganic colloidal substrates by multilayered polyelectrolyte films

C. Márquez-Beltrán^a

^a*Instituto de Fisica de la Benemerita Universidad Autonoma de Puebla, Mexico*

cmarquez@ifuap.buap.mx

Employing layer-by-layer (LbL) technique we could encapsulate both organic and inorganic nano- and microparticulate substrates by multilayer polyelectrolyte films of variable thicknesses. It has been observed that the uniformity of the polyelectrolyte multilayer does not depend severely on the chemical nature of particulate substrate; rather it depends on the initial surface charge density or potential of their bare surface. Higher potential of organic albumin nanoparticles helps to keep the polyelectrolyte chains unfolded. On the other hand, a lower potential of inorganic microparticles such as SiO₂ induces a folding of dangling polyelectrolyte chains, forming domains of their aggregates or complexes at the particle surface, making the encapsulating multilayer inhomogeneous.



Investigation of biocatalytic growth of gold nanoparticles using atomic force microscopy and dynamic light scattering

A. Ramanaviciene,^{a,b*} J. Voronovic,^a A. Popov,^b R. Drevinskas,^b A. Ramanavicius^{a,b}

^a *SRI Center for Physical and Technological Sciences, A. Gostauto 11, Vilnius, Lithuania*

^b *Faculty of Chemistry, Vilnius University, Naugarduko 24, Vilnius, Lithuania*

*almira.ramanaviciene@chf.vu.lt

Recently scientific and industrial impact of nanoscience and nanotechnology in analytical chemistry has been growing. Some challenging problems, such as sensitivity, reproducibility, duration and cost of analysis can be resolved by applying different nanostructures. Gold nanoparticles (AuNPs) could be synthesized of different shape and size using various techniques. AuNPs might be enlarged in the solution containing tetrachloroauric acid (HAuCl₄) and H₂O₂ [1]. Application of enzymes for the growth of metallic nanoparticles and enhancement of analytical signal is a very promising field in analytical chemistry [2,3].

In our study biocatalytic growth of 13 nm AuNPs in the presence of glucose oxidase (GOx) and different concentrations of glucose was investigated using Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS) methods. The 13 nm diameter AuNPs were synthesized by the reduction of HAuCl₄ with sodium citrate in the presence of tannic acid [4,5]. GOx in the presence of oxygen catalysed oxidation of glucose to gluconolactone and H₂O₂, followed by the reduction of AuCl₄ on AuNPs by the H₂O₂. The appropriate ratio of AuNPs and components needed for the growth of AuNPs was determined using UV-vis spectroscopy. The results obtained using DLS showed that hydrodynamic radius of enlarged AuNPs depended on the glucose concentration in the solution. The enlargement of immobilized AuNPs after 60 and 90 min of biocatalytic growth was determined by AFM using different glucose concentrations. Therefore, glucose biosensors based on biocatalytic growth of AuNPs using AFM and DLS methods can be developed.

Acknowledgement

This research was funded by the European Social Fund under the Global Grant measure.

References

1. M. Zayats, R. Baron, I. Popov, I. Willner. *Nano Letters* 5, 21-25 (2005)
2. Y.M. Yan, R. Tel-Vered, O. Yehezkeli, Z. Cheglakov, I. Willner. *Advanced Materials* 20, 2365-2370 (2008)
3. N. Zhou, J. Wang, T. Chen, Z. Yu, G. Li, *Analytical Chemistry* 78, 5227-5230 (2006)
4. H. Muhlfordt, *Experientia* 38, 1127-1128 (1982)
5. A. Ramanaviciene, G. Nastajute, V. Snitka, A. Kausaite, N. German, D. Barauskas-Memena, A. Ramanavicius. *Sensors and Actuators: B. Chemical* 137, 483-489 (2009)

Synthesis and Structural Characterization of Metals-Loaded TiO₂ Capsules with Bactericidal and Photocatalytic Activities

W. J. Tseng, H.-M. Wu

Department of Materials Science and Engineering, National Chung Hsing University, Taichung, Taiwan

wenjea@dragon.nchu.edu.tw

Ag and Ni nanoparticles encapsulated in anatase TiO₂ particles with a multi-cores@shell rattle-structure have been prepared by a facile chemical route using SiO₂ as the sacrificial template. Monodispersed SiO₂ beads prepared by the Stöber method were first modified by cationic polydiallyldimethylammonium chloride and anionic PdCl₄²⁻ molecules sequentially via electrostatic interactions. SiO₂@Ni particles with a raspberry-like structure were accordingly synthesized by an aqueous electroless deposition of Ni nanoparticles on the surface-modified SiO₂ beads using NiCl₂ as the Ni precursor and NaH₂PO₂ as the reducing agent. A SiO₂ shell was then coated uniformly on the SiO₂@Ni particles via a modified Stöber method, before being coated by titanium(IV) butoxide precursor in solution. The composite particles were calcined at 450°C and the sacrificial SiO₂ template was removed by hydrofluoric acid to form Ni@TiO₂ rattle-structured composites. Finally, the particles were mixed with AgNO₃ solution so that the Ni atoms were replaced by the Ag⁺ ions in the aqueous solution through redox-transmetalation reactions. The resultant Ag-Ni/TiO₂ nanocomposite capsules were tested for their photocatalytic activity under UV irradiation. In addition, bactericidal activity of the composite colloids was also examined using the gram-negative *E. Coli*.

From screening to overcharging: colloid stability in ionic liquid/water binary mixtures

T. Oncsik, T. Gregor, I. Szilágyi, M. Borkovec

*Department of Inorganic and Analytical Chemistry, Sciences II, University of Geneva
1205 Geneva, Quai Ernest Ansermet 30*

tamas.oncsik@unige.ch

Ionic liquids (ILs), due to their tuneable physical properties by varying the constituent anions and cations, are excellent candidates for many applications in different areas such as electrochemistry, catalysis as well as synthesis and dispersion of nanoparticles [1,2]. In the latter case the interaction between the nanoparticle surface and the IL constituents is crucial.

In the present study, aggregation of negatively charged sulphate functionalized polystyrene latex particles was investigated in IL/water binary mixtures. The IL cations were systematically varied tuning their hydrophobicity by changing the length of the alkyl chains. Time-resolved dynamic light scattering (DLS) and electrophoresis were used as experimental techniques.

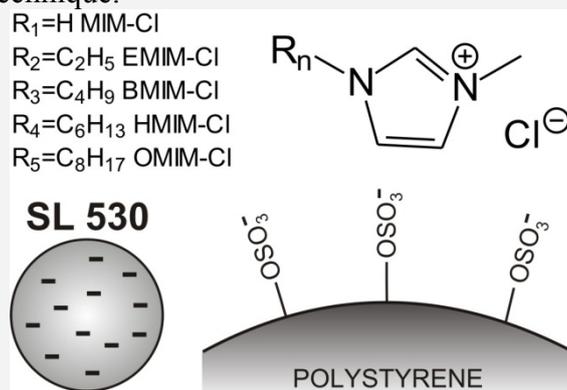


Figure 1. Systems investigated in this study (ILs above, functionalized latex particle below)

In all the systems investigated, at sufficiently low concentrations the particle suspensions are stable. At lower chain lengths (R_{1-3}) the suspensions can be destabilized by screening and charge neutralization. In systems containing HMIM-Cl and OMIM-Cl at intermediate IL concentrations, the dispersions are restabilized due to overcharging. At higher concentrations the charge-reversed particles are destabilized again due to screening by the IL constituent anions. In general, increasing the hydrophobic character of the IL cations, the coagulating power can be increased. This is reflected by the shifts in the corresponding critical coagulation concentration values as well.

[1] K. Ueno et al., *Phys. Chem. Chem. Phys.*, **2010**, 12, 1649-1658.

[2] T. L. Greaves et al., *Chem. Rev.*, **2008**, 108, 206-237.

Surface modification and colloidal stability of nano-carriers in physiological media

Alexandra Karasová¹, Denisa Lizoňová¹, Nina Sarvašová¹, Vlatimil Král¹, and František Štěpánek¹

¹ *University of Chemistry and Technology, Prague, Department of Chemical Engineering, Technická 3, Prague 6, 166 28, Czech Republic. E-mail: Frantisek.stepanek@vscht.cz; Tel: +420 220 443 236*

¹ *Laboratory of Structural Biology, Institute of Molecular Genetics, Academy of Sciences of the Czech Republic, v.v.i., Vídeňská 1083, Prague 4, 142 20, Czech Republic*

Alexandra.Karasova@vscht.cz

The efficiency of cancer treatment can be enhanced by using targeted drug delivery systems. This work focuses on the development of chemical robots - multifunctional antibody surface modified submicron particles capable of targeting solid tumours via antigen-antibody interactions and respond to external radiofrequency signals. The chemical robots are supposed to carry the encapsulated active substance or its precursor to the tumour and release the cargo as a response to the external stimuli. IgG-M75, monoclonal antibody against the Carbonic Anhydrase IX (CA IX, overexpressed in hypoxic colorectal carcinoma (Zavada et al., 2000)) antigen was used for the surface modification of model silica nanoparticles (60-100 nm), which serve as a tool for exploring the ability of binding CA IX, finding the appropriate way of antibody-nanoparticle coupling and studying the influence of particle size and surface coverage on the biodistribution *in vivo*.

The properties of fluorescently labelled IgG-M75 modified silica nanoparticles have been already published by Tokarova et al. (2013). Our latest results evaluating the biodistribution intravenous administration in Nu/Nu Nude mice indicate that physically adsorbed antibodies can desorb during the circulation thus leaving uncovered surface where opsonins can bind and redirect these particles to the RES (Reticulo-Endothelial System) organs.

The successful covalent coupling can be performed by forming peptide bonds between the particle and antibody and verified by ELISA-like test or flow cytometry. Using the poly (ethylene glycol) (PEG) or N-(2-hydroxypropyl) methacrylamide (HPMA) as surface coverage might provide "stealth" properties to the nanoparticles, prolong their systemic circulation and allow the covalent coupling of the antibody to the nanoparticles surface. The present work will report on the synthesis and colloidal stability of such nanoparticles. The results of zeta potential measurement, stability against aggregation, and adsorption of plasma proteins will be presented.

Gelatin-stabilized polyaniline–silver colloids

Patrycja Bober^a, Petr Humpolicek^b, Jaroslav Stejskal^a

^a *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,*

162 06 Prague, Czech Republic

^b *Centre of Polymer Systems, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic*

Polyaniline colloids are produced by the oxidation of aniline in the presence of suitable water-soluble polymers, e.g., poly(*N*-vinylpyrrolidone) [1], poly(vinyl alcohol) [1], gelatin [2] or more complex and tailor-made stabilizers. The oxidation of aniline with ammonium peroxydisulfate in gelatine solutions yields rice-grain colloidal polyaniline particles having the particle size between 200–350 nm as determined by dynamic light scattering. The similar oxidation of aniline with silver nitrate (Figure 1) yields hybrid composite polyaniline–silver nanoparticles with more complex morphology. The composites were characterized by transmission electron microscopy, dynamic light scattering and UV-visible spectroscopy. The biological properties have also been investigated. The gelatin-stabilized polyaniline colloids with or without silver thus may find uses in medicine, i.e. in devices monitoring or stimulating the processes in living tissues.

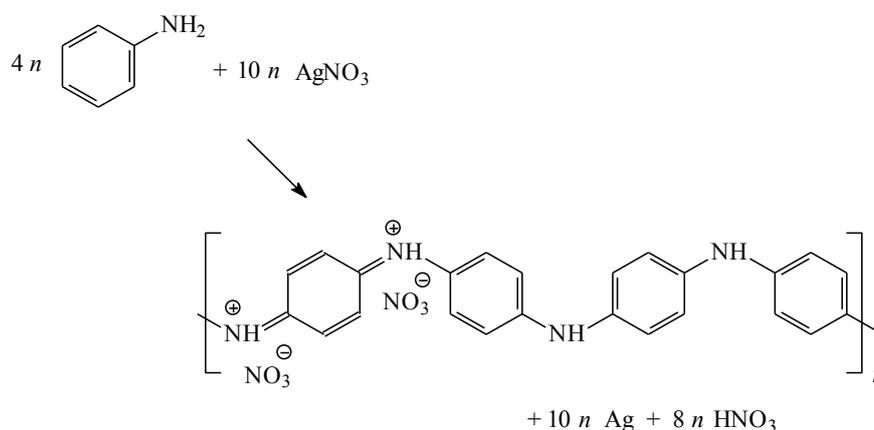


Figure 1. Aniline is oxidized with silver nitrate to polyaniline. Metallic silver and nitric acid are by-products

References:

1. Stejskal, J., Kratochvíl, P., Helmstedt, M. *Langmuir* 1996, 12, 3389–3392.
2. Ptschelin W., *Kolloid-Z* 1935, 70, 306–311.

Acknowledgment

The authors wish to thank the Czech Science Foundation (14-05568P) for the financial support.

E-mail: bober@imc.cas.cz

Hybrid nano-helix: from the organic self-assembly to the design of functional nanostructures

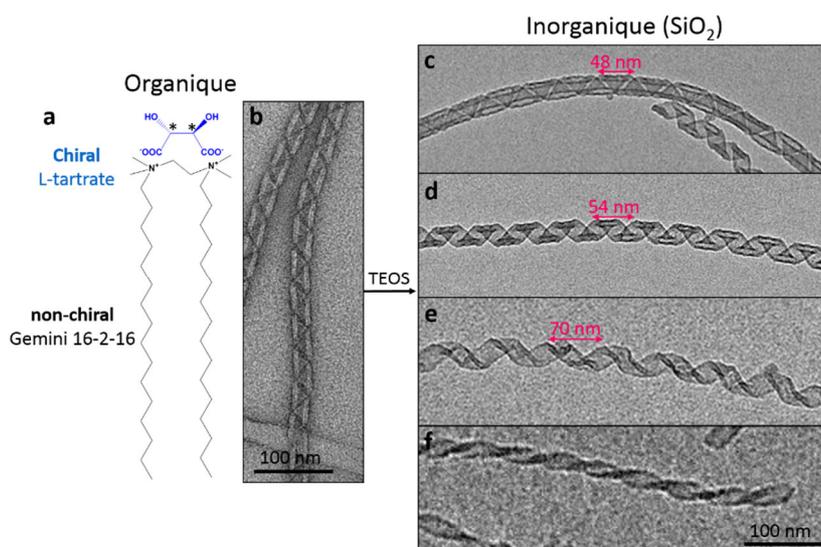
Emilie Pouget and Reiko Oda

Chimie et Biologie des Membranes et des Nano-objets, allée de St Hilaire, 33600 Pessac, France ;

**e-mail: e.pouget@cbmn.u-bordeaux.fr*

In the field of functional nano-materials, the chiral structures like helices or twisted ribbons are of great interest because of their optical and mechanical properties. In the present work, functional hybrid nano-helices are synthesized by use of organic chiral self-assemblies forming very well defined helix or ribbon structures as templates. A bio-inspired mineralization of these self-assemblies allows creating silica nano-helices with very well controlled morphologies in term of diameter and pitches (Figure 1). We focus particularly on the formation of short helices (length control), individualized and well-dispersed in solution.

These nanohelices are then used as functional materials for different applications currently developed in our lab as the conception of semiconductor helices for NanoElectroMechanical Systems (NEMS), the formation of nano-helices decorated with gold nanoparticles to create systems efficient for the Surface Enhanced Raman Spectroscopy (SERS) or in the metamaterials field, the creation of enantioselective catalylists or the use of these chiral structures as base for the stem cells differentiation in the tissue engineering field.



Synthesis of silica nanohelices. a) Helices formed by self-assembly of Gemini/L-tartrate complex. (b) Controlled silica transcription giving rise to pure silica nanohelices more or less opened (c, d and e) and twisted nanoribbons (f).

Characterization of a liposomal drug carrier using continuous contrast variation SAXS

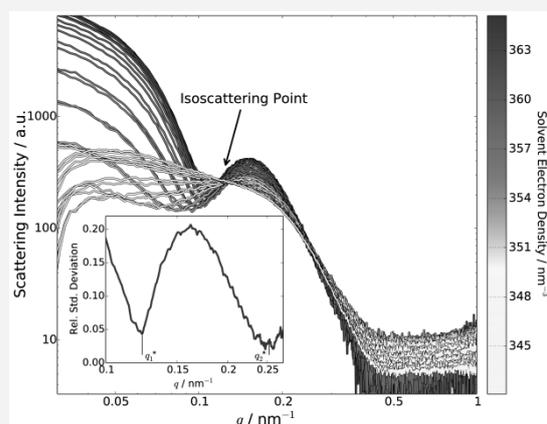
C Gollwitzer,^a R Garcia-Diez,^a Z Varga,^b M Krumrey^a

^aPhysikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, 10587 Berlin, Germany

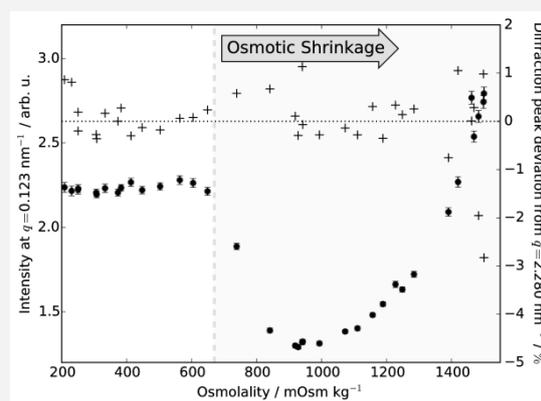
^bInstitute of Materials and Environmental Chemistry, Research Centre for Natural Sciences Magyar, Tudosok korutja 2, H-1117, Budapest, Hungary

christian.gollwitzer@ptb.de

Doxorubicin is an anticancer drug known for its high cardiotoxicity, though a liposomal formulation can reduce this side-effect significantly and improve the pharmacokinetics of the drug. In this work, the mean size and average density of pegylated liposomal doxorubicin (Caelyx®¹) was determined by continuous contrast variation in small-angle X-ray scattering (SAXS) with iodixanol, an iso-osmolar suspending medium. The study is focused on the isoscattering point position and the model-free analysis of the Guinier region of the scattering curves recorded at different solvent densities at the four-crystal monochromator beamline of PTB at the synchrotron radiation facility BESSY II². The response of the liposome to increasing solvent osmolality and the structure of the liposome-encapsulated doxorubicin fiber after the osmotic shrinkage of the liposome are evaluated with sucrose contrast variation in SAXS/WAXS³.



Scattering curves at different solvent densities obtained with a iodixanol density gradient. The inset shows the position of the isoscattering points.



The isoscattering point intensity (circles) and the shift of the doxorubicin-aggregate diffraction peak (crosses) as a function of the solution osmolality.

[1] Y. Barenholz, *Journal of Controlled Release* **160** (2012) 117–134

[2] R. Garcia-Diez, C. Gollwitzer, M. Krumrey, *J. Appl. Cryst.* **48** (2015) 20–28

[3] R. Garcia-Diez, C. Gollwitzer, M. Krumrey, Z. Varga, *Int. J. Nanomedicine* (subm.)

Mean size and dispersibility determination in real and concentrated liquid dispersions with Static-Multiple Light Scattering

Giovanni Brambilla, Christelle Tisserand, Pascal Bru, Gérard Meunier

Formulaction, 10 impasse Borde Basse, 31240 L'Union, France

Nano and micro suspensions are widely used in the industry but their real dispersion state remains unknown or not well characterized in their native and concentrated form (slurries, vaccines...). Indeed common measurement techniques may alter the dispersed phase or the apparent particle size due to the principle of measurement (microscopy, centrifugation, FFF, sieving, filtration) or the sample dilution (DLS, PTA, laser diffraction). This is especially the case for samples containing agglomerates which may breakdown because of measurement conditions such as shear stress (pumping, flowing, filtration, and centrifugation) or heavy dilutions. Because the industry requires particles analysis in the native suspension form for product development, regulatory compliance or health and safety tests, here we propose a method to assess the mean particles size and agglomeration state in concentrated media.

A technique based on Static Multiple Light Scattering is proposed to measure mean particles size in a large range of concentration between 0.0001 and 95%, for sizes between 10 nm and 100 μm by Turbiscan LAB technology. This technique has the advantage to measure in one click, without sample preparation or dilution, the mean particles size and so the dispersibility efficiency particularly for concentrated suspensions. Other optical techniques such as DLS or PTA can perform this measurement but only at a very high dilution which denatures the agglomerates and give an erroneous size of the native particles. The measurements presented here were performed with well-calibrated polystyrene and titanium dioxide particles.

Composite silica sols for strengthening of quartz ceramics

V.M. Volynkin¹, Yu. A. Gatchin², K.V. Dukelskiy^{2,3}, S.K. Evstropiev^{1,2}, A.G. Korobeynikov²

1 - JVC "Vavilov State Optical Institute", Saint-Petersburg, Kadetskaya linya, 12, Russia.

2 - National Research University of Information Technologies, Mechanics and Optics, Saint-Petersburg,
Kronversky pr., 49, Russia.

3 - The Bonch-Bruевич Saint-Petersburg State University of Telecommunications, Saint-Petersburg,
Moika 61, Russia.

Quartz ceramics is well-known material widely used in different applications. In many cases it's necessary that this material has very high mechanical strength and corrosion resistance.

In this work we present new strengthening method which is based on the impregnation of porous ceramics by special colloidal solution at room temperature with followed drying and thermal treatment of the material.

Initial samples were prepared by slip casting in gypsum molds, had size 65x8x8 mm and their porosity was about 25%. Composite colloidal solutions containing tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$), propanol-2, water and aluminum nitrate were used for impregnation of porous ceramics. Volatile components were removed from impregnated materials during drying. Thermal treatment of the samples led to the decomposition of aluminum nitrate and to the formation of bonding chains of colloidal silica particles inside ceramic body.

Measurements of bending strength of ceramic samples showed that significant strengthening effect was observed after impregnation even before thermal treatment. Thermal treatment additionally increased the strength of impregnated samples. Experimental results showed that new strengthening method allows increasing the mechanical strength of quartz ceramic samples (+200 %). The results of SEM investigations demonstrated the formation of some chains of silica nanoparticles that additionally bonded together ceramic particles.

Self-Organization of Rod-Like Viruses into Colloidal Membranes and Bundles by Depletion Interaction

Baeckkyoung Sung, Alexis de la Cotte, and Eric Grelet*
Centre de Recherche Paul-Pascal, CNRS, Pessac, France
sung@crpp-bordeaux.cnrs.fr

Spontaneous organization of anisotropic nanoparticles into highly ordered mesoscopic assemblies is a ubiquitous phenomenon in soft matter and biological systems [1-2]. Among such nanoparticles, filamentous *fd* viruses have been highlighted as a model system because of their high monodispersity in size and their ability to act as chiral building blocks [3-5]. These properties enable them to self-organize into well-defined liquid crystalline phases which are in quantitative agreement with theories and computer simulations for hard rods [6-7]. In this presentation, we explore the phase behavior of the *fd* rods self-organized into colloidal mesoscopic structures in presence of attractive interaction stemming from non-adsorbing polymers. Controlled assembly of hexagonal membranes and bundles is demonstrated to depend on both rod and polymer concentrations. An analysis of the membrane structure is performed, emphasizing the existence of intrinsic screw dislocation whose handedness is related to the rod chirality and the kinetics of growth.

- [1] G. M. Whitesides et al., *Science* 1991, **254**, 1312.
- [2] S. C. Glotzer, M. J. Solomon, *Nature Mater.* 2007, **6**, 557.
- [3] Z. Dogic, S. Fraden, *Curr. Opin. Colloid Interface Sci.* 2006, **11**, 47.
- [4] E. Barry, Z. Dogic, *Proc. Natl. Acad. Sci.* 2010, **107**, 10348.
- [5] P. Sharma et al., *Nature* 2014, **513**, 77.
- [6] E. Grelet, *Phys. Rev. Lett.* 2008, **100**, 168301.
- [7] E. Grelet, *Phys. Rev. X* 2014, **4**, 021053.

Recent advances in modulated light scattering

N.B.Brauer,^a M. Priebe,^a A.C.Voelker,^a
^aLS Instruments, Fribourg, Switzerland

nils.brauer@lsinstruments.ch

Dynamic light scattering (DLS) is a popular technique to analyse particles of nanometer to micrometer size in solution. It can be applied to a variety of systems including nanoparticles, polymers, proteins, peptides as well as emulsions. The principle of this technique is based on the analysis of the intensity fluctuations of scattered light caused by the random movement (Brownian motion) of the particles. With the intensity correlation function of the scattered light one can determine the Diffusion Coefficient of the particles. Furthermore if the temperature and the viscosity of the sample are known, one can obtain the particle size and size distribution. Since the theory of DLS is based on the assumption that only single scattered light is detected, multiple scattering results in a false particle size typically leading to an underestimate of the true hydrodynamic radius. In practice, this means that samples should be sufficiently diluted in order to avoid multiple scattering, thus severely limiting the application range of DLS. Two approaches can be adopted to extend the application of DLS to higher sample concentrations. First, multiple scattering can be minimized by reducing the optical path. Second, multiple scattered light can be suppressed. The combination of both approaches gives access to the highest concentrations.

Today the most frequently used suppression technique is the so called "3D cross-correlation" technology, which was further improved by the modulated 3D technology. Recently we have further extended the performance of this technique and combined it with path length reduction techniques. This has resulted in increased efficiency and a further extended range of particle sizes and concentrations. Here we present first results and give an outlook to further developments.

[1] Patent EP2365313 A1

[2] Modulated 3D cross-correlation light scattering: Improving turbid sample characterization, Ian D. Block and Frank Scheffold, Rev. Sci. Instrum. 81, 123107 (2010).

First Normal Stress Difference and Microstructure in Concentrated Kaolin Suspensions

H.-J. Mögel, P. Schiller, M. Bombrowski, M. Wahab
TU Bergakademie Freiberg, Institute of Physical Chemistry, 09599 Freiberg, Germany

hans-joerg.moegel@chemie.tu-freiberg.de

Aqueous suspensions of kaolin show negative first normal stress differences N_1 as nonlinear response to steady shear. The magnitude of N_1 depends on shear rate, kaolin volume fraction, pH and ionic strength. Thereby, the zeta potential and thus the particle interactions are adjustable. For flocculated suspensions with a volume fraction of 0.2, the shear rate dependence of N_1 is characterized by a minimum of -200Pa at intermediate shear rates. This unusual viscoelastic behavior is caused by shear induced changes of the microstructure of the suspension. In order to gain insight into the suspension microstructure after steady shear, an experimental cryo-technique has been developed. The method comprises shear load, sample freezing and ex-situ X-ray diffraction of frozen suspensions. Using the intensity ratios of the characteristic 001 and 060 X-ray reflections of kaolin, the average orientation order is described as function of the previously applied shear rate. A minimum of N_1 corresponds to a minimum of the intensity ratio. The microstructure with the lowest order causes a maximum of $-N_1$. To understand the shear induced change of the suspension microstructure, we calculated a phase diagram for interacting thin platelets based on pairwise interactions. There are regions with preferred parallel arrangement of the platelets and other ones with a typical card-house structure. In the framework of this theory, shear induced structure change can induce nonlinear viscoelastic response, including negative first normal stress differences due to nonanalytic functional behavior.

Phase-Transition Kinetics in Thermo- and Field-Responsive Microgel Suspensions

S. Nöjd^a, P. S. Mohanty^b, P. Bagheri^c, A. Yethiraj^c and P. Schurtenberger^a.

^a*Division of Physical Chemistry, Lund University, Lund, Sweden*

^b*School of Applied Sciences, KIIT University, Bhubaneswar, India*

^c*Department of Physics and Physical Oceanography, Memorial University, St. John's, Canada*

Sofi.Nojd@fkem1.lu.se

Due to the intrinsic and tuneable softness of ionic poly(N-isopropyl-acrylamide) (PNIPAM) microgels they are ideally suited to study the complex phase behavior found for particles interacting via a soft potential. Subjecting the particles to an alternating electric field results in an additional dipolar contribution to the interaction potential, which strongly depends on the strength and frequency of the applied field. We use confocal laser scanning microscopy (CLSM) to observe

the new phases that are forming as the dipolar interactions are increased (Fig. 1) [1]. At high densities, a face-centred cubic (FCC) crystal diffusively transforms into a body-centred tetragonal (BCT) crystal via nucleation and growth. However, in the reverse direction, the BCT phase transforms cooperatively into a body-centred orthorhombic (BCO) phase, which only relaxes back to the FCC phase as the temperature is increased. The kinetics is consequently either diffusive or martensitic depending on the path, and we believe that this is the first real-space insight of diffusive and martensitic transitions, respectively, in a single system [2].

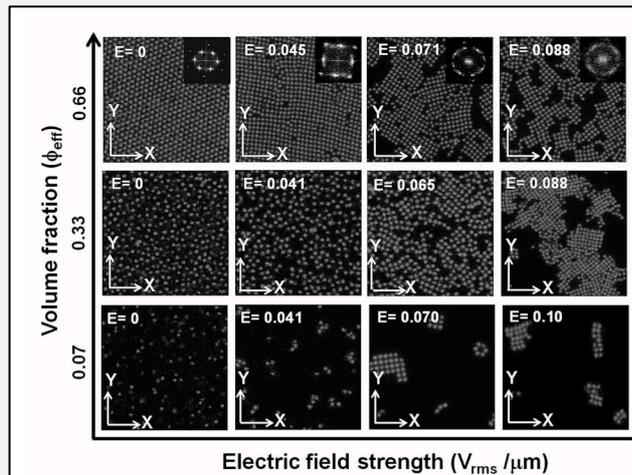


Figure 1. Examples of field-induced structures.

[1] S. Nöjd, P. S. Mohanty, P. Bagheri, A. Yethiraj and P. Schurtenberger, *Soft Matter*, 9 (2013) 9199

[2] P. S. Mohanty, P. Bagheri, S. Nöjd, A. Yethiraj and P. Schurtenberger, *Phys. Rev. X* 5 (2015) 011030

Pigment Dispersions for UV-Curable Inkjet Inks

L. Petton, G. Van Baelen
Agfa-Gevaert NV, Mortsel, Belgium

lionel.petton@agfa.com

The trend towards digitalisation in the printing industry is growing at a fast pace. The advantage of digital printing lies in its flexibility so that one must only print what is required when it is needed, hereby greatly reducing wastes and minimising costs. Particularly, wide format media can be printed using inkjet with UV-curable inks. Upon jetting of the ink onto the substrate, UV radiation is applied, which will induce a photopolymerisation of the ink and subsequent hardening of the ink. The great advantage is that such UV-curable inks can be printed on versatile media without the need for further substrate preparation.

The main challenge in the preparation of UV-curable inks is that they must have a low viscosity for a good jetting performance and that pigment particles are preferred over soluble dyes for a better lightfastness. Thus, with a required shelf life of up to 18 months, it is important to achieve a very good colloidal stability.

An ink is usually produced in two steps. First a dispersion is prepared where the pigment is finely dispersed into a main monomer as continuous phase. This is followed by the manufacture of the ink itself, where the dispersion is diluted with additives and other monomers to enhance adhesion or curing speed for example. Only the combination of energy-intensive processes such as bead milling with a good wetting and stabilisation of the dispersed pigment particles can achieve the desired colloidal properties for the dispersion and then the ink. Wetting and steric stabilisation of the dispersion is obtained by carefully choosing the right polymer dispersant and, sometimes, synergist [1]. Finally, care must be given to avoid incompatibility between the additives present in the dispersion and the products added to form the final ink composition.

Literature:

[1] X. André, European Patent EP2684922, 2014.

Preparation of Novel Antimicrobial Polymeric System Based on (+)-Usnic Acid and Poly(vinylbenzyl chloride) Colloids

R. Bengü Karabacak,^a Turgay Tay,^a Merih Kıvanç^b

^aAnadolu University, Department of Chemistry, 26470 Eskişehir, Turkey

^bAnadolu University, Department of Biology, 26470 Eskişehir, Turkey

rbkarabacak@yahoo.com

Antimicrobial colloids have received considerable attention because of their high stability and environmentally friendly properties [1-2]. In this study we prepared a novel antimicrobial colloidal system based on (+)-usnic acid, an important natural antimicrobial molecule, and poly(vinylbenzyl chloride) (PVBC) colloids (Image 1). For this purpose, PVBC colloids were treated with (+)-usnic acid in triethylamine. The antimicrobial activity of the (+)-usnic acid loaded colloidal particles (PVBC/Us/Us) was tested against various microorganisms such as *Listeria monocytogenes*, *Staphylococcus aureus*, *Enterococcus faecalis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhimurium*, and *Klebsiella pneumonia*, *Candida albicans* and *Candida glabrata* [3]. *P. aeruginosa* and *Escherichia coli* appeared to be the most sensitive microorganism compared to the others. The minimum inhibitory concentration (MIC) was determined using different colloid concentrations. The resultant (+)-usnic acid loaded colloids showed high antimicrobial activity against many microorganisms with MIC values down to 0.12 mg colloid/mL. Furthermore, this colloidal system had bactericidal effect against *P. aeruginosa* and *Escherichia coli* with minimum bactericidal concentration (MBC) values of 0.94 and 3.75 mg colloid/mL, respectively. In contrast, (+)-usnic acid had no activity on its own. Owing to the small and uniform sizes and high surface areas, (+)-usnic acid loaded colloids afforded greater contact area with the bacterial cell.

References

1. Sharma, V. K., Yngard, R. A., Lin, Y., 2009. *Adv. Colloid Interfac.* 145, 83–96.
2. Kralova, I., Sjöblom, J. 2009. *J. Disper. Sci. Technol.* 30, 1363–1383.
3. Karabacak, R.B., Tay, T., Kıvanç, M. 2014. *React. Funct. Polym.* 83, 7–13.

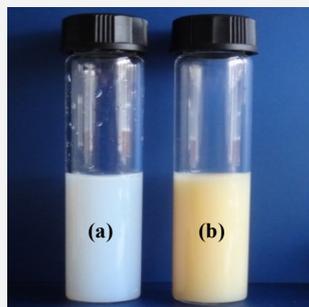


Image 1. Digital images of polymer colloids in water: (a) without (+)-usnic acid (PVBC), and (b) with usnic acid (PVBC/Us/Us).

Emulsions prepared using polysaccharide-based stabilizers as precursors of polylactide particles with controlled delivery applications

Asma Chebil,^{a,b} Michèle Léonard,^{a,b} Cécile Nouvel,^{a,b} Jean-Luc Six,^{a,b} Alain Durand,^{a,b}

^a Université de Lorraine, Laboratoire de Chimie Physique Macromoléculaire LCPM, UMR 7375, Nancy F-54000, France

^b CNRS, Laboratoire de Chimie Physique Macromoléculaire LCPM, UMR 7375, Nancy F-54000, France

asma.chebil@univ-lorraine.fr

Polysaccharide-covered polyester particles were prepared by two procedures: emulsion/solvent evaporation in batch^{1,2} and emulsion/solvent diffusion in microfluidics. The core of particles was made of polylactic acid (PLA) while their surface was covered by dextran chains thanks to the use of water-soluble randomly hydrophobized dextran which acted as a polymeric stabilizer (Fig. 1).

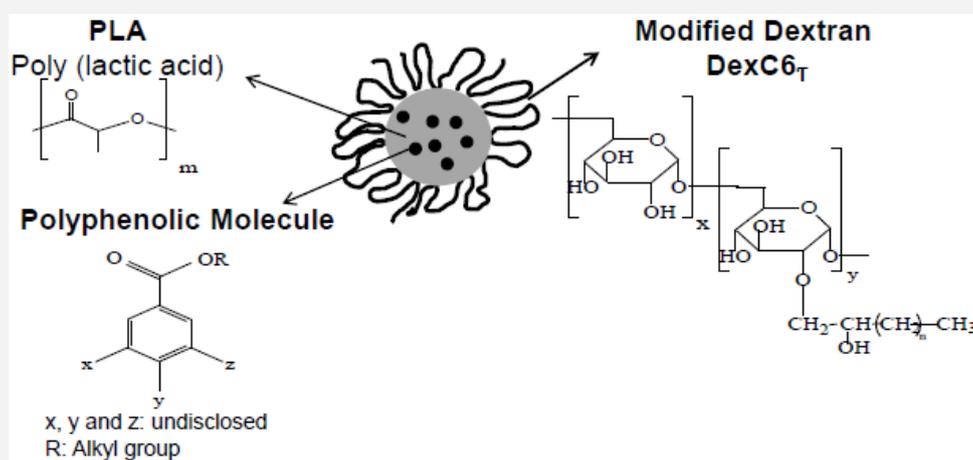


Figure 1. Dextran-covered PLA particles.

Hydrophobized dextrans were efficient stabilizers in both processes and limited aggregate formation. Emulsification process and conditions were varied in order to obtain nano- and microparticles covering a wide range of diameters (between 0.1 and 500 μm) with reproducible and narrow size distributions. Encapsulation and release of polyphenolic molecules (PM, undisclosed substances) were examined with a focus on the effects of fabrication process and PM structure (alkyl group R, Fig. 1). The effect of the presence of PM on particle formation was detailed. Loaded particles elaborated by both processes were characterized and compared regarding their size distribution, surface coverage, and thickness of polysaccharide superficial layer. We demonstrated that the use of dextran-based stabilizers ensured colloidal stability over a wide range of ionic strength (up to 4 mol/L NaCl) and allowed re-dispersion after freeze-drying. Drug release was followed and correlated to the process of preparation of particles.

References

1. Gavory, C.; Durand, A.; Six, J.-L.; Nouvel, C.; Marie, E.; Léonard, M. *Carbohydr. Polym.* **2011**, *84*, 133-140.
2. Rouzes, C.; Léonard, M.; Durand, A.; Dellacherie, E. *Colloids Surf. B-Biointerfaces* **2003**, *32*, 125-135.

Mixed Micelle Based Doxorubicin Delivery System From Modified Pluronics

T. Pettersson, S. Hassanzadeh, Z. Feng, M. Hakkarainen

Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

torbj@kth.se

Doxorubicin (DOX) is a potent cytotoxic, antineoplastic, anthracycline antibiotic agent with a range of antitumor activities. That can lead to death of cancerous cells in the tumor as well as normal cells at other parts of the body. By clever control of the delivery system the effect on normal cells can be minimized. Delivery systems of pluronic are FDA approved, but their applications are limited by low drug encapsulation capacity and low stability due to high cmc.

Pluronic based mixed micelles were designed from PEG-PPO-PEG (F127, Mn=12500 g/mol) and the reverse pluronic PPO-PEG-PPO (P10R5, Mn=2000) that were chemically modified with folic acid (F127-FA) and quercetin (P-Q), respectively, to work as multifunctional micelle system. The successful synthesis of modified pluronics was evidenced by several standard analysis. Quercetin as a hydrophobic flavonoid was included in P-Q with the aim to boost DOX interactions with the hydrophobic core of the micelles. Colloidal probe AFM displayed almost doubled adhesion forces between DOX coated probe and pluronic when quercetin was incorporated in the mixed micelle system. The use of quercetin increased the amount of encapsulated DOX from 19% for mixed micelles without quercetin (FF/PL) to 43% for mixed micelles with anchored quercetin (FF/PQ).

The quercetin as a combinatorial drug with DOX could also decrease the side effects for normal cells. In combination with the folate tagging of the hydrophilic shells the prepared mixed micelles are anticipated to combine several advantages for targeted delivery with enhanced drug loading capacity that can reduce side effects like cardiocytotoxicity of DOX therapy regimes.

Nanohybrid polymer brushes on silica for bioseparation

L.D. Jiang,^a H.B. Navarro,^a T. Kamra,^{a,b} T.C. Zhou,^a and L. Ye^{*,a}
^a*Division of Pure and Applied Biochemistry, Lund University, Lund, Sweden*
^b*Division of Synchrotron Radiation Research, Lund University, Lund, Sweden*

lingdong.jiang@gmail.com

Boronic acid based affinity materials are of great importance for effective enrichment of biomolecules containing a cis-diol structure, for example glycoproteins. In this work, a nanohybrid composed of silica core and flexible polymer brushes, denoted as Si@poly(NIPAm-co-GMA)@APBA, was prepared via surface-initiated atom transfer radical polymerization (SI-ATRP) in combination with Cu (I)-catalyzed azide-alkyne cycloaddition (CuAAC) 'click' reaction. The size, morphology and composition of the obtained nanohybrid are characterized by dynamic light scattering (DLS), SEM, FT-IR, elemental analysis and thermogravimetric analysis (TGA). The NIPAm and GMA in the Si@poly(NIPAm-co-GMA) were determined to be 1.52 mmol/g and 2.49 mmol/g, respectively. The glycoprotein binding experiments show that the maximum binding capacities of the nanohybrid for ovalbumin (OVA) and horseradish peroxidase (HRP) are 87.6 mg/g and 22.8 mg/g, respectively. The glycoprotein binding can be controlled by varying the pH of the binding buffer. By increasing the temperature from 20 °C to 35 °C, the glycoprotein binding to the nanohybrid was decreased. This new pH and temperature responsive nanohybrid will be useful for biotechnology and biomedical applications, for example for drug delivery and theranostics of diseases.

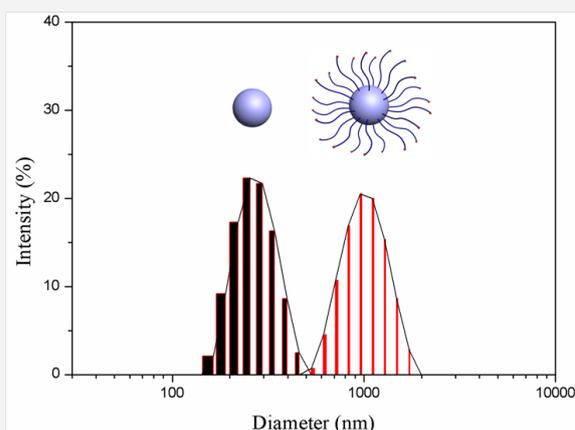


Fig.1 The hydrodynamic diameter of silica core and silica with polymer brushes.

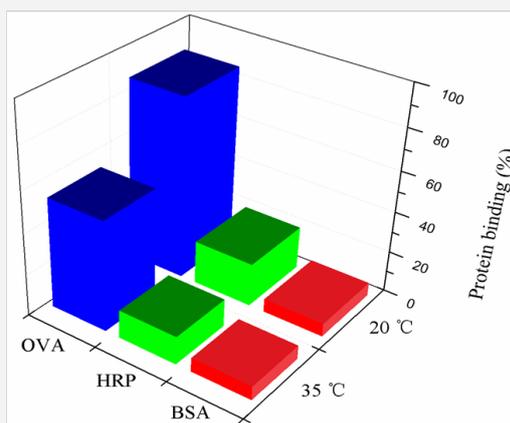


Fig.2 The adsorption of proteins at different temperatures by the nanohybrid particles.

Systematic Study of Human Fibrinogen Adsorption on Negatively Charged Colloidal Particles

A. Bratek-Skicki^{a*}, P. Żeliszewska^a, Z. Adamczyk^a

^a*J.Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences
30-239 Cracow, Poland*

*e-mail: ncbratek@cyf-kr.edu.pl

Fibrinogen is a key structural 340 kDa plasma glycoprotein that is converted by thrombin into fibrin during blood clot formation. It plays an important role in angiogenesis, thrombosis, fouling of artificial organs. In our work we focused on determining the amount and orientation of fibrinogen on negatively charged latex particles using the microelectrophoretic method, and the concentration depletion method combined with AFM. Measurements were performed at pH 7.4 and in the range of ionic strength of 10^{-3} -0.15M NaCl. Systematic experiments were conducted to determine the dependencies of the electrophoretic mobility of latex on the amount of adsorbed fibrinogen. Electrophoretic mobility increased upon fibrinogen adsorption. The maximum coverage of fibrinogen on latex particles determined via the concentration depletion method varied between 1.9 mg m^{-2} and 3.2 mg m^{-2} for 10^{-3} and 0.15M NaCl respectively. The experimental results were interpreted in terms of a heterogeneous charge distribution confirmed by the 3D electrokinetic model [1]. These measurements proved the side-on adsorption mechanism of fibrinogen. Additionally, the stability of latex covered by fibrinogen was determined. It was proven that cyclic changes of ionic strength from 10^{-3} to 0.15M NaCl did not change electrophoretic mobility. Therefore, it was concluded that there were no conformational changes within adsorbed fibrinogen molecules.

Acknowledgements

This work was financially supported by the KNOW Grant "Revealing adsorption mechanism of proteins on latex particles" and the POIG Grant: 01.01.02-12-028/09, FUNANO.

[1] A. Bratek-Skicki, P. Żeliszewska, z. Adamczyk, *Current Topics in Med. Chem.*, 2014, 14, 640-648.

Interaction of cobalt bis(dicarbollide) anion with PEG and glucose-PEG derivatives

V. Dordovic,^a P. Matejcek,^a D. Vrbata,^a A. Zhigunov,^b J. Ruokolainen^c

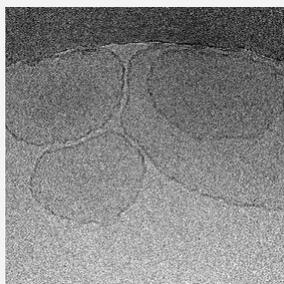
^a *Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic,*

^b *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic*

^c *Department of Applied Physics Nanotalo, Aalto University, Espoo, Finland*

vladimir.dordovic@natur.cuni.cz

Sodium cobalt bis(dicarbollide) COSAN gives many potential applications, mainly in medical field, as an inhibitor of important enzymes. After discovering COSAN interacts with poly(ethylene oxide) (PEO) via specific interactions, many complexes of polymer-COSAN have been prepared. We studied an influence of PEO length on freezing of PEO segments after addition of COSAN. These solutions in most cases precipitate. Thus we synthesized glucose-PEO derivative, in which glucose is linked via triazol group to short PEO chain ($M = 2000$) or to PEO chain with another glucose unit respectively. Hydrophylic glucose was supposed to stabilize nanoparticles with COSAN-PEO core in water solution. Titration with COSAN was carried out and we observed unexpected forming of vesicles and nanosheets. In addition, glucose part gives a variety of biomedical applications and also a potential of derivatization of its structure. Presented results were obtained by means of light scattering, NMR, SAXS and cryo-TEM. Acknowledgment: GACR P205/14-14608S; GAUK 512214.



Cryo-TEM micrograph of glucose-PEG-glucose/COSAN nanoparticles.

Synthesis of Polyacid-functionalized Diblock Copolymer Nano-Objects via Polymerisation-Induced Self-Assembly

Lee A. Fielding and Steven P. Armes
The University of Sheffield, Sheffield, UK

l.a.fielding@shef.ac.uk

Well-defined diblock copolymer nanoparticles can be prepared in a wide range of solvents via reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization.¹ During this process, a soluble stabilizer block is chain-extended using a solvent-miscible monomer. Initially, a soluble diblock copolymer is obtained, but at some critical degree of polymerization the growing second block becomes insoluble, which causes in situ self-assembly. Depending on the precise conditions, the initially-formed spheres can evolve to form worm-like or vesicular nanoparticles. Thus this approach is a powerful and versatile technique for the preparation of a wide range of bespoke organic diblock copolymer nano-objects of controllable size, morphology, and surface functionality at relatively high concentrations. In this talk, a binary mixture of anionic and non-ionic macromolecular chain transfer agents (macro-CTAs) is used to design novel polyacid-functionalized spherical, worm-like or vesicular nanoparticles with controllable anionic character and morphology. The molar ratio and degree of polymerization of the stabilizer macro-CTAs, and the mean degree of polymerization of the core-forming block are all important in determining the final morphology of the nanoparticles. The nanoparticles are characterized by electron microscopy, aqueous electrophoresis and small-angle X-ray scattering. Particular attention is paid to rheological properties of the worm-like micelles, which form free-standing gels of varying gel strengths depending on their composition.

- (1) Warren, N. J.; Armes, S. P. J. Am. Chem. Soc. 2014, 136, 10174.

Colloidal Surface PEGylation via Multivalent Host-Guest Interactions: PNIPAM Microgels Stabilization

I. Antoniuk,^a D. Kaczmarek,^b V. Wintgens,^a G. Volet,^a T.T. Nielsen,^c I. Varga,^b C. Amiel,^a

^a*Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS and University Paris-Est, Thiais, France*

^b*Eötvös Loránd University, Budapest, Hungary*

^c*Department of Chemistry and Bioscience, Aalborg University, Aalborg Ø, Denmark*

antoniuk@icmpe.cnrs.fr

High colloid stability and robust protection from uptake by the blood mononuclear phagocyte system are among the major requirements to polymer particles used in biomedical field. One of the well-established ways to meet them consists in decorating the surface of nanoparticles with polyethylene glycol (PEG), often referred as PEGylation¹. On the other hand impregnation of drug carriers with cyclodextrin-containing materials was proved to be efficient in suppressing the “burst release” of hydrophobic therapeutic agents². In this work we present a possible path for combining the benefits of PEGylation and β CD-containing materials.

We report the synthesis of novel bifunctional (PEG, adamantane)-grafted dextrans by copper-catalyzed azide-alkyne cycloaddition (CuAAC). Their affinities towards native β -cyclodextrin and β -cyclodextrin polymers (p β CD) were evaluated by ITC and SPR; the strength of interpolymer interactions was strongly dependent on the degrees of substitution by PEG and adamantyl groups. Then, (PEG, adamantane)-grafted dextrans were applied for sterical stabilization of pNIPAM-100%AAc core-shell microgels, covered by positively charged p β CD⁺. The total charge of these core-shell microgels may be tuned from negative to positive depending on the p β CD⁺ content. The formation of a PEG corona via multivalent host-guest interactions between p β CD⁺ and (PEG, adamantane)-dextrans allowed to avoid the precipitation of the microgels even at zero-charge point, where their colloidal stability is lost otherwise. Given the above, (PEG, Ada)-grafted dextrans should be auspicious candidates for biomedical applications where fast and reversible PEGylation is required.

1. Gaucher, G.; Dufresne, M. H.; Sant, V. P.; Maysinger, D.; Leroux, J. C. *J. Controlled Release* **2005**, 109, (1-3), 169-188.

2. Quaglia, F.; De Rosa, G.; Granata, E.; Ungaro, F.; Fattal, E.; La Rotonda, M. I. *J. Controlled Release* **2003**, 86, (2-3), 267-278.

π -Conjugated Polymer Nanoparticles synthesized by Nanoagglomeration via Polyion Association

H. Yao,^a C. Fukui^a

^a Graduate School of Material Science, University of Hyogo, Hyogo 678-1297, Japan

yao@sci.u-hyogo.ac.jp

Currently available fluorescent nanoparticles include semiconductor quantum dots such as CdSe and/or dye-doped silica/polymer colloids; however, cytotoxicity can be a critical problem for the heavy metal-containing quantum dots, and there are also a number of limitations with the dye-loaded beads such as self-quenching. An unexplored alternative is the use of fluorescent π -conjugated polymer nanoparticles, so there is growing interest in their synthesis and applications.

In the present study, we demonstrate a new and facile method for obtaining fluorescent π -conjugated polymer nanoparticles based on ion association. The polymer we chose was anionic MPS-PPV. The synthesis utilizes NanoAgglomeration via Polyion Association (called NAPA method) that includes polyion complex formation between MPS-PPV and cationic polyammonium (PDDA) and subsequent globulization to fabricate nanoarchitectures. In the synthesis, typically, rapid addition of aqueous MPS-PPV solution containing PDDA into 2-propanol/water (p/w) mixtures produced almost clear suspension of MPS-PPV-based nanoparticles (see microscopy images in Fig. 1a). In the nanoparticles, interestingly, the fluorescence properties changed dramatically as compared to those in the pure aqueous phase, although absorption spectra were almost unchanged. In contrast to a common observation that hydrophobic conjugated polymer nanoparticles made by a “reprecipitation method” show a blue shift in their absorption, the NAPA-based approach exhibited no spectral shift during the nanoparticle formation, suggesting the absence of further bending or kinking of the polymer backbone in the polyion complexes. The fluorescence peak was particle size dependent (Fig. 1b). We found that blue-site (red-site) fluorescence should be associated with the surface site (inner site) of the polymer nanoparticles, respectively. We believe that the present nano-engineering methodology for functional polymers will play a fundamental role in an entire new class of fluorescent nanoparticles.

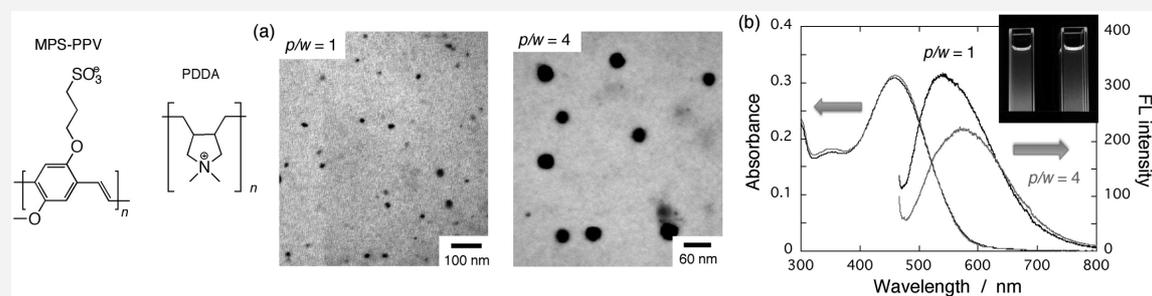


Fig.1. (a) Typical electron microscopy images of the MPS-PPV polymer nanoparticle samples prepared at $p/w = 1$ and 4. (b) Absorption and fluorescence spectra of MPS-PPV nano-particles synthesized on the basis of ion association in water and in mixed p/w solvents. Chemical structures of MPS-PPV and PDDA are also shown.

Encapsulation of co-solvent and ionic liquid in polymer particles synthesized via dispersion polymerisation in non-polar solvents

Calum T.J. Ferguson,^a Alexandre P. Richez,^{ab} Louise Farrand,^b Mark Goulding,^b
Jonathan H. Wilson,^b Simon Lawson,^b Simon Biggs,^a and Olivier J. Cayre^a

^a*Institute of Particle Science and Engineering, University of Leeds, Leeds, LS2 9JT, UK*

^b*Merck Chemicals Ltd, Southampton, SO16 7QD, UK*

bsctjf@leeds.ac.uk

Dispersion polymerisation can be utilised to create polymer particles with controlled sizes and polydispersities. The use of these controlled polymer particles spans a number of industries, including therapeutics and the displays industry. We have investigated the possibility of modifying these particles by altering their properties for different uses. Each of the following modifications exploits the preferential wetting of a polar species to the growing polymer rather than to the oil continuous phase. As a result, we are able to incorporate various species within the polymer particles. We have adapted the polymer particles in the following ways for specific uses:

- We have incorporated polar solvents (water and acetonitrile), allowing particle density to be tuned.
- By loading the polar solvents with pigments, we have been able to create coloured and fluorescent particles.
- The incorporation of small ionic molecules has been achieved to demonstrate the potential for active ingredient encapsulation. Furthermore, we have synthesised the particle out of a responsive polymer to enable the release of encapsulated species.

Preparation and Characterisation of Colloidal Inkjet Inks

M.A. Mulla,^a H.N. Yow,^b S.R. Biggs^c and O.J. Cayre,^a

^a*Institute of Particle Science and Engineering, School of Chemical and Process Engineering,
University of Leeds, Leeds, LS2 9JT, U.K*

^b*Briggs of Burton PLC, Briggs House, Derby St., Burton-on-Trent DE14 2LH, U.K*

^c*Faculty of Engineering, Architecture and Information Technology, University of Queensland,
Brisbane, QLD 4072, Australia.*

pmmam@leeds.ac.uk

Nanoparticles are widely used in ink formulations as they offer some very desirable advantages, including a long shelf life due to the high stability of the dispersions, and controllable jetting behaviour. The aim of this project is to produce high solids content, sub 100 nm monodisperse latex particles to be used as model inkjet inks.

Highly concentrated (up to 45 wt% solids content) stable PMMA latex particle dispersions have been prepared via emulsion polymerisation. More specifically a chain transfer agent has been utilised to enhance particle nucleation efficiency, aiding the preparation of polymer particles with a narrow weight distribution and increased monodispersity. Our initial work has found that high nanolatex concentration can be achieved with a relatively low emulsifier concentration, without sacrificing the colloidal stability of the dispersions. Waterborne nanoparticles around 50 nm have been obtained with a 45 wt % solids content.

These dispersions do not require any lengthy processing to perform rheological experiments in regions where the particle suspensions show clear shear thinning behaviour. We also examine the depletion flocculation behavior, exhibited upon addition of free polymer to these systems. This flocculation behavior is advantageous during droplet drying as particle motion is restricted once the particles have concentrated in the center of the droplet. This then means the readily observed coffee ring effect, which occurs due to the convective transport of particles to the contact line, can be effectively overcome.

In this study, we systematically study the effect of the emulsifier, initiator and chain transfer agent concentration on final particle size and polydispersity of the synthesised particles. In addition we also study the stability, deposition and jetting behavior of the prepared dispersions at various particle concentrations, in ethylene glycol as a co-solvent and at various concentrations of non-adsorbing polymer (to induce depletion flocculation).

Effects of protonation on foaming properties of dodecyldimethylamine oxide solutions: a pH study

Kathrin Schellmann¹, Natalie Preisig¹, Per Claesson², Cosima Stubenrauch^{1*}

¹Universität Stuttgart, Institut für Physikalische Chemie, Pfaffenwaldring 55, 70569 Stuttgart, Germany; ²KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Division of Surface and Corrosion Science, Drottning Kristinas väg 51, Stockholm, SE-100 44 Sweden

The critical micelle concentration (cmc), the surface excess (Γ), as well as the micelle aggregation number (m) of the surfactant dodecyldimethylamine oxide (C₁₂DMAO) are reported to strongly depend on the pH-value of the aqueous surfactant solution [1-5]. At high ionic strength, the cmc displays a minimum, while both Γ and m have a maximum at a pH-value close to the pK_a of the surfactant [1-5]. These experimental observations are explained with specific hydrogen bonds between the head groups, which are formed once the surfactant is partly or fully protonated. We went one step further and addressed the question of whether the pH also affects the foaming properties of C₁₂DMAO solutions [6]. To answer this question we measured the foamability and the foam stability of C₁₂DMAO solutions at a fixed C₁₂DMAO concentration of 5 cmc for five different pH-values (pH = 2, 3, 5, 8, and 10) using the commercially available *FoamScan* apparatus [7]. It was found that the foamability is hardly affected by the pH-value, while the foam stability strongly depends on the pH. As is the case for the above mentioned properties, the foam stability also displays an extremum in the studied pH-range, namely a maximum at pH = 5 [6]. We discuss our results in terms of the hydrogen bond hypothesis and show that this hypothesis indeed is in line with the observed trend for the foam stability [6]. Moreover, we discuss that hydrogen bond formation may rationalize how the molecular structure of a surfactant affects foam stability.

References

- [1] H. Maeda, J. Colloid Interface Sci. 1995, 175, 497.
- [2] H. Maeda, Colloids and Surfaces A 1996, 109, 263.
- [3] H. Maeda, R. Kakehashi, Advances in Colloid and Interface Sci. 2000, 88, 275.
- [4] V. Lair, S. Bouguerra, Turmine, M., Letellier, P., Langmuir 2004, 20, 8490.
- [5] V. Peyre, S. Baillet, P. Letellier, Anal. Chem. 2000, 72, 2377.
- [6] K. Schellmann, N. Preisig, P. Claesson, C. Stubenrauch, Soft Matter 2015, 11, 561.
- [7] J. Boos, W. Drenckhan, C. Stubenrauch, J. Surf. Det. 2013, 16, 1.

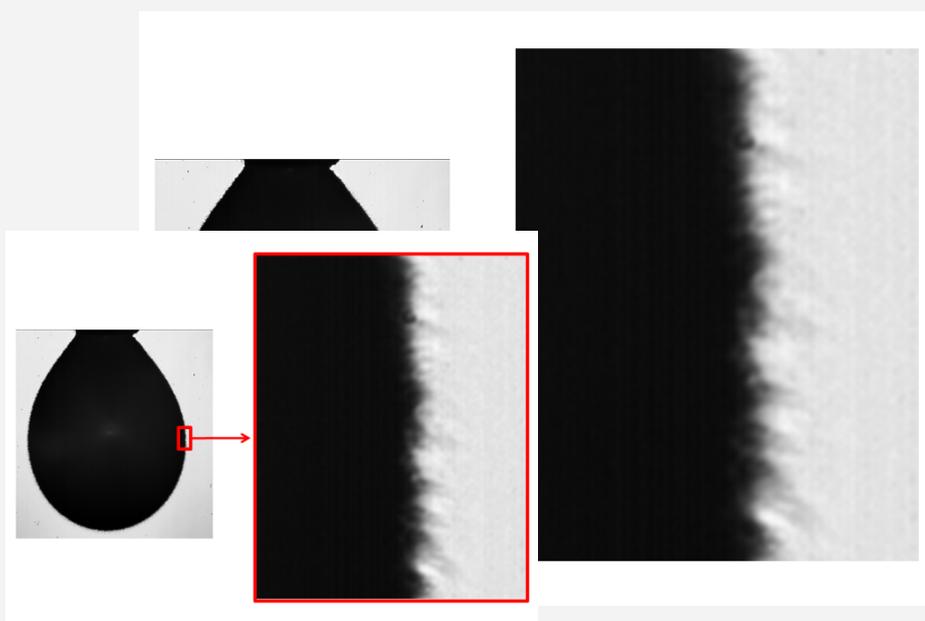
Microstructure formation at water paraffin oil interfaces

M. Schmitt, R. Denoyel, M. Antoni
Aix-Marseille Université, UMR/CNRS 7246 MADIREL
Centre Scientifique de St. Jérôme, 13397 – Marseille Cedex 20
m.antoni@univ-amu.fr

SPAN80 is a hydrophobic surfactant commonly used for the stabilization of emulsions. When adding SPAN80 to water in paraffin oil emulsions, the continuous paraffin oil phase becomes opaque over time indicating the presence of micrometer sized objects. Microscopy observations suggest that a spontaneous process promotes the appearance of water microstructures. These latter are transported into paraffin oil and contribute to the increasing opacity of the emulsions.

The present work aims to better understand this phenomenon by investigating the exchanges taking place in the neighborhood of water/paraffin oil interfaces. A simplified system consisting in a water droplet pending at the end of a capillary tip (see below left image) in SPAN80 loaded paraffin oil is studied. A darkening of the drop with time is evidenced. This phenomenon is the consequence of the appearance of microstructures that progressively cover the complete water paraffin oil interface. Its kinetics indicates two regimes with characteristic times that strongly depend on the concentration of SPAN80 and temperature.

Long term evolution shows an increasing roughness of the interface (right image). The drop becomes elongated indicating a decrease of interfacial tension as microstructures are generated. These latter slowly drift along the interface towards the bottom of the drop from which they finally detach. This phenomenon progressively removes water from the drop that, at the end of the process, behaves as a hollow vesicle.



Enhanced active motion of Janus colloids at the water surface

X. Wang, M. In, C. Blanc, M. Nobili and A. Stocco

*Soft Matter Group, Laboratoire Charles Coulomb, Université Montpellier et CNRS,
Montpellier, France*

xiaolu.wang@univ-montp2.fr

Active colloids are an emerging and promising class of colloidal particles, which are designed to perform autonomous motion by transforming chemical or other form of energies into work and propulsion.

Here, we have investigated the active motion of self-propelled colloids confined at the air-water interface. The two dimensional motion of micron-sized Silica-Platinum Janus colloids has been experimentally measured by particle tracking video-microscopy under increasing concentration of the catalytic fuel, i.e. H₂O₂. Comparing to the motion in bulk, a dramatic enhancement of both the persistence length of trajectories and the speed has been observed. The interplay of colloid self-propulsion, due to an asymmetric catalytic reaction occurring on the colloid, and interfacial frictions controls the enhancement of the directional movement. The slowing down of the rotational diffusion at the interface, also measured experimentally, plays a pivotal role in the control and enhancement of active motion.

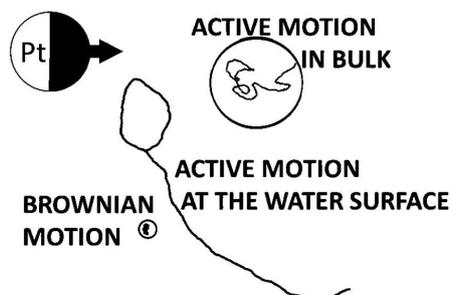


Figure. Trajectories of Brownian motion, active motions in bulk and at water surface.

Phase behaviour around the HLB temperature: microemulsion characterization in a technical grade nonionic surfactant system

M. Homs, D. Morales, C. Solans

*Institute of Advanced Chemistry of Catalonia-Spanish National Research Council (IQAC-CSIC)
and Biomedical Research Networking center in Bioengineering, Biomaterials and
Nanomedicine (CIBER-BBN), Barcelona, Spain*

maria.homs@iqac.csic.es

The phase behaviour of water/poly(oxyethylene) nonionic surfactant/oil systems and its dependence towards temperature changes have been systematically studied and at present are fairly well understood [1,2]. At low temperatures the poly(oxyethylene) chains of these surfactants are hydrated and the surfactant monolayer has a positive spontaneous curvature, consequently the surfactant is hydrophilic. When the temperature is increased there is a dehydration of the polyoxyethylene chains and the spontaneous curvature of the surfactant becomes negative, thus, the surfactant becomes lipophilic. At intermediate temperatures, the so-called hydrophile-lipophile balance temperature (HLB temperature), the hydrophilic and lipophilic properties of the surfactant are balanced [3] and the mean spontaneous curvature of the surfactant is zero. The phase behaviour around the HLB temperature has been studied in detail in systems with pure surfactants. However, there is a lack of knowledge of the phase changes produced in technical grade surfactant systems around this temperature. Therefore, the objective of this work was to study the phase behaviour of a water/technical grade nonionic surfactant/oil system around the HLB temperature. First, HLB temperature values of samples with a constant oil-surfactant ratio were determined by conductivity measurements and Fourier Transform Pulsed-Gradient Spin-Echo NMR. Phase behaviour studies by means of phase diagram determinations allowed to identify single isotropic and shear birefringent liquid phases below and above the HLB temperature curve. Characterization by FT-PGSE NMR and dynamic light-scattering (DLS) techniques showed the presence of different microemulsion structures around the HLB temperature.

References:

- [1] H. Kunieda and N. Ishikawa, "Evaluation of the Hydrophile-Lipophile Balance (HLB) of Nonionic Surfactants," *J. Colloid Interface Sci.*, vol. 107, no. 1, 1985.
- [2] H. Kunieda and K. Shinoda, "Phase Behavior in Systems of Nonionic Surfactant / Water / Oil around the Hydrophile - Lipophile - Balance - Temperature," *J. Dispers. Sci. Technol.*, vol. 3, no. 3, pp. 233–244, 1982.
- [3] K. Shinoda and H. Saito, "The Effect of Temperature on the Phase Equilibria and the Types of Dispersions of the Ternary System Composed of Water, Cyclohexane, and Nonionic Surfactant," *J. Colloid Interface Sci.*, vol. 26, pp. 70–74, 1968.

Biological activity of saponins correlates with their interaction with model lipid membranes

Marta Orczyk, Kamil Wojciechowski

Warsaw University of Technology, Department of Chemistry, Warsaw, Poland

kamil.wojciechowski@ch.pw.edu.pl

Saponins are secondary plant metabolites belonging to glucosides. Their main biological activity seems to be related with the plant's defence mechanism through their strong interaction with biological membranes. We have chosen three model triterpenoid saponins: α -hederin, hederacoside C and glycyrrhizic acid (ammonium salt). The first two originate from the same plant (*Hedera helix*) and differ in the extent of sugar substitution, and the third is extracted from *Glycyrrhiza glabra* (Licorice).

The saponin-lipid interactions were studied in a confined environment of Langmuir monolayers of DPPC and DPPC/cholesterol (10:9 mol/mol) with the saponins present in the subphase. A combined monolayer relaxation, surface dilational rheology, fluorescence microscopy and neutron reflectivity (NR) study showed that all three saponins are able to penetrate pure DPPC and mixed DPPC/cholesterol monolayers. Penetration of bare DPPC monolayers by hederacoside C and ammonium glycyrrhizate resulted in formation of an additional thin layer, most likely comprising the hydrated glycone part of the respective saponins, and the remainder triterpene part inserted into the DPPC's hydrophobic region. The most striking results were obtained for α -hederin in contact with the mixed DPPC/Cholesterol monolayer, where an additional 34 Å additional layer developed, consisting probably of a α -hederin-cholesterol complex. Overall, the effect of the saponins on the model lipid monolayers correlates well with the lipid-saponin complex formation in the homogeneous solution (except for hederacoside C) and their membranolytic activity. The combined bulk and monolayer results will be discussed in view of the role of confinement in modulating the saponin-lipid interactions.

Stern layer of uniformly charged spherical colloids

K. Bohinc^a, G. Volpe Bossa^b, S. May^b, S. Gavryushov^c

^aFaculty of Health Sciences, University of Ljubljana, Ljubljana, Slovenia,

^bDepartment of Physics, North Dakota State University, Fargo, North Dakota, USA

^cEngelhardt Institute of Molecular Biology Russian Academy of Sciences, Moscow, Russia

klemen.bohinc@zf.uni-lj.si

Electrostatic interactions are omnipresent in biological and biotechnological systems and are of fundamental importance to understand interactions between colloids and charged surfaces in electrolyte solutions. The colloids have spatially extended charge instead of being point-like. The charge distribution of colloids influences the properties of interfacial electric layers. The problem can be described within the mean-field Poisson-Boltzmann framework if the charge distribution within the spatially extended colloids is accounted for [1, 2]. In our work, we consider an electrolyte solution that is composed of multivalent colloidal spherical particles with uniformly charge distribution for which the excluded volume with the charged wall is taken into account. Minimization of the mean-field free energy yields an integral-differential equation for the electrostatic potential that we solve numerically. Our results emphasize the importance of the charge distribution within the colloids on the charge profiles with the interfacial electric layer. The theoretical results were compared with Monte Carlo simulations and a good agreement was observed.

[1] Bohinc, K., May, S., 2011. Attraction between Like Charged Surfaces Mediated by Uniformly Charged Spherical Colloids in a Salt Solution, *Croat. Chem. Acta* 84 (2): 251.

[2] Bohinc, K., May, S., Mean-Field Electrostatics of Stiff Rod-Like Ions, in *Electrostatics of Soft and Disordered Matter*, Pan Stanford Publishing, Singapore 2014, editors D. Dean, J. Dobnikar, A. Naji and R. Podgornik, ch. 23, p. 335-346.

The Thermodynamic Study of Interpolyelectrolyte and Protein-Polyelectrolyte Complexation

J. Požar, L. Štajner, T. Kremer, D. Kovačević

^aDivision of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, 10000 Zagreb, Croatia

davor.kovacevic@chem.pmf.hr

In order to systematically examine and interpret the thermodynamics of formation of polyelectrolyte complexes we investigated the complexation of sodium poly(allylammonium) chloride (PAH) with sodium poly(styrenesulfonate) (PSS) and with poly(acrylic acid) (PAA). Additionally, the interactions between lysozyme and PSS were studied as an example of protein-polyelectrolyte complexation processes. The heat effects of abovementioned processes were determined by isothermal titration microcalorimetry. Electrophoretic mobility and particle size measurements were also applied. The influence of electrolyte type, ionic strength, pH, reactant concentration and titration direction (addition order) on complexation was investigated at $t = 25\text{ }^{\circ}\text{C}$

In all examined cases complexation was found to be predominantly entropically driven, irrespectively of the type of reaction products formed (polyelectrolyte complexes, precipitates), electrolyte type, addition order and concentration. For PAH-PSS complexation the correlation between obtained reaction enthalpies for complex and precipitate formation with anion hydration enthalpies was observed and the product formation was the least enthalpically favorable in solutions containing weakly hydrated NO_3^- and ClO_4^- anions. For lysozyme-PSS complexation the process is notably more exothermic at $\text{pH} = 3.1$ than at $\text{pH} = 7.5$. It seems that the formation of protein-polyelectrolyte complexes is more favorable than that of PSS-PAH. The cumulative enthalpy changes per monomer of PSS for lysozyme-PSS complexation were found to be somehow higher than in the case of almost isoenthalpic pairing of PAH with PSS. Such differences are most likely caused by the more pronounced counterion condensation in solution of two strongly charged polyelectrolytes, than in solution of lysozyme and PSS.

Presenting author's email: davor.kovacevic@chem.pmf.hr
COST CM1101 Workgroup 2

Splitting of Surface Immobilized Polymeric Micelles into Clusters upon Charge Inversion

I. Dewald^{a}, J. Gensel^a, E. Betthausen^b, A.H.E. Müller^{b,c}, A. Fery^a*

^a*University of Bayreuth, Physical Chemistry II, D-95440 Bayreuth*

^b*University of Bayreuth, Macromolecular Chemistry II, D-95440 Bayreuth*

^c*Johannes Gutenberg University Mainz, Institute of Organic Chemistry, D-55128 Mainz*

* *inna.dewald@uni-bayreuth.de*

Smart coatings made from macromolecular building blocks continue to be an innovative area in research and technology with the aim to meet a high demand for intelligent surface solutions. Especially polymeric micelles are an interesting type of material with versatile properties depending on their structure and composition. Furthermore, using micelles as coating material enables the transfer of their bulk properties to the surface or even introduces new functionality.[1,2]

In our work, we investigate multicompartment micelles formed from amphiphilic ABC triblock terpolymers as building blocks for responsive coatings. The application of such colloidal units for thin films has several advantages from a material-science perspective, *e.g.* stimulus-responsivity and multi-functionality on a single particle level and simple preparation of coatings by physisorption. Furthermore, the presence of pH-sensitive ionic blocks enables formation of interfaces with nano-scale structural (re-)organization tunable by external stimuli.[2] The focus of this contribution is the investigation of the impact of external triggers on properties of these coatings. Especially the pH-induced charge inversion of surface immobilized micelles and the accompanying morphological changes - the splitting of micelles into clusters - were studied in more detail using *in-situ* ellipsometry and *quasi in-situ* atomic force microscopy.

[1] J. Gensel, I. Dewald, J. Erath, E. Betthausen, A.H. E. Müller, A. Fery, *Chem. Sci.*, **2013**, 4, 325-334.

[2] J. Gensel, E. Betthausen, C. Hasenöhr, K. Trenkenschuh, M. Hund, F. Boulmedais, P. Schaaf, A.H. E. Müller and A. Fery, *Soft Matter*, **2011**, 7, 11144-11153.

Specific ion effect at micellization of anionic surfactants: A thermodynamic approach

M. Bešter-Rogač, Ž. Medoš, B. Šarac

*Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-1000 Ljubljana,
Slovenia*

marija.bester@fkkt.uni-lj.si

Interactions between anions and cationic surfactants have been widely studied, whereas less attention has been devoted to the influence of cations on the micellization of anionic surfactants [1]. Despite sodium dodecylsulfate (SDS) belongs to one of the most studied surfactants, there is only one systematic investigation of the counter ion influence on the thermodynamics of micellization of lithium, sodium, potassium and caesium decyl- and dodecyl sulphates, carried out by Ropers and co-workers [2].

In this contribution, first the influence of alkali metal cations on the micellization process of carboxylate surfactants in aqueous solution will be shown. Next, the parameters for micellization process of SDS in the presence of short chain ionic liquids, differing in hydrophobicity of cation, will be presented. New results for anionic surfactants will be compared with already reported values for cationic surfactants in salt solutions [3-5].

Finally, the effect of salt addition and nature of counterions on the thermodynamic parameters of the micellization of ionic surfactants in water will be discussed.

[1] A. Kroflič, B. Šarac, M. Bešter-Rogač, Thermodynamics and Specific Ion Effects in Connection with Micellization of Ionic Surfactants. In *Colloid and Interface Chemistry for Nanotechnology*; Kralchevsky, P.; Miller, R.; Ravera, F., Eds.; CRC Press Taylor&Francis Group, 2014, pp 475–502.

[2] M. H. Ropers, G. Czichocki, G. Brezesinski, J. Phys. Chem. B, 107 (2003) 5281-5288.

[3] A. Kroflič, B. Šarac, M. Bešter-Rogač, J. Chem. Thermodynamics, 43 (2011) 1557-1563.

[4] B. Šarac, G. Mériquet, B. Ancian, M. Bešter-Rogač, Langmuir, 29 (2013) 4460-4469.

[5] A. Kroflič, B. Šarac, J. Cerkovnik, M. Bešter-Rogač, Colloid Surface A, 460 (2014) 108–117.

Sphingosine *Versus* Sphingosine-1-Phosphate: A Possible Regulator of Amyloid-beta / Membrane Interactions

C. Watanabe¹, G. Staneva³, N. Puff^{1,2}, M. Seigneuret¹, M. I. Angelova^{1,2}

¹*Matiere et Systemes Complexes, Univ. Paris-Diderot-Paris 7 UMR 7057 CNRS, Paris, France,*

²*UFR925-Physics Dept, Univ. Pierre et Marie Curie-Paris 6, Paris, France,*

³*Institute of Biophysics and Biomedical Engineering, Bulgarian Acad. of Sci., Sofia, Bulgaria*

chiho.watanabe@univ-paris-diderot.fr

Sphingosine (Sph⁺) and Sphingosine-1-Phosphate (S1P⁻) are single chained bioactive lipids known to regulate cell fate together with ceramide through changing their balance. The system is called “sphingolipid rheostat” [1]. The metabolic pathway of the three lipid is enzymatically interconnected. Recent studies found relatively low S1P⁻/Sph⁺ ratio in certain brain regions of Alzheimer’s disease (AD) patients compared to controls [2, 3]. AD is a neurodegenerative disease and the most common form of dementia. One of the characteristic pathogenesis of AD is accumulation of Amyloid-beta (Ab) aggregates or fibrils in extra- and intra-cellular space. It may be that S1P⁻ and Sph⁺ regulate membrane physico-chemical properties through their local ratio (apart from their signalling roles as second messengers) and thus regulating Ab/membrane interactions. Our previous study of model membranes shows that S1P⁻/Sph⁺ ratio regulates membrane electrostatic properties packing and phase separation behaviour [4]. In the present work, we focus on Ab/membrane interactions in the case of lipid membranes containing different S1P⁻/Sph⁺ ratios and the fluorescent makers LAURDAN and di-8-ANEPPS that detect lipid packing and membrane dipolar potential respectively. Our results show that the increased level of membrane Sph⁺ (but not of S1P⁻) intensifies significantly Ab/membrane interactions and the Ab effect on both membrane packing and membrane dipolar potential. Curiously, when both sphingolipids are incorporated into the model membrane at ratio S1P⁻/Sph⁺ 1:1 Ab modifies lipid packing rather than membrane dipolar potential. These results suggest the role of S1P as a protector against Ab. The result underscores the specific lipid role in the pathogenesis of AD.

1. Newton, J. et al., *Exp Cell Res* (2015) *in press*.
2. Ceccom, J. et al., *Acta Neuropathol Commun* (2014) 2:12.
3. Couttas, T. et al., *Acta Neuropathol Commun* (2014) 2:9.
4. Watanabe, C. et al., *Langmuir* (2014) 30:13956.

COST WG1 (Interfacial phenomena – fundamentals, modelling and analytical methods)

Nonequilibrium Complexation of Oppositely Charged Polyelectrolytes and Surfactants in the Presence of Nonionic Amphiphiles

R. Meszaros^{a,b}, E. Fegyver^a

^a*Institute of Chemistry, Eotvos Lorand University, 1117, Pazmany Peter setany 1/A, Budapest, Hungary*

^b*SDepartment of Chemistry, University J. Selyeho, 945 01 Komárno, Slovakia*

meszaros@chem.elte.hu

The various commercial applications of oppositely charged polyelectrolytes (P) and ionic surfactants (S) with added nonionic amphiphiles initiated intensive research on the polyion/mixed surfactant interaction. A large group of earlier studies revealed that one of the major effects of the nonionic cosurfactants is the suppression of the associative phase separation of P/S systems. In contrast, recent studies indicated that in the dilute surfactant concentration range the added uncharged surfactant could enhance the precipitation concentration range. In order to rationalize these observations, the impact of dodecyl maltoside on the properties of different polyanion/cationic surfactant and polycation/anionic surfactant mixtures was investigated using a variety of experimental methods. It was shown that the nonionic cosurfactant has two distinct and competing impacts on the mixed surfactant binding onto the polyions. The composition dependent variation of the chemical potentials of the amphiphiles determines, which of these effects is the dominant one, explaining the seemingly diverse earlier observations and their interpretations.

We also demonstrate that the nonionic amphiphile affects considerably the nonequilibrium features of polyion/ionic surfactant complexation. Namely, the presence of the uncharged cosurfactant could either enhance or suppress the kinetic stability of the colloidal dispersion of P/S nanoparticles formed in the two-phase composition range. Furthermore, depending on the applied mixing procedures, precipitation, the formation of large aggregates or stable dispersion of small P/S nanoparticles can be equally achieved at the same concentration of the components. These results clearly indicate that the nonionic surfactant additives can be successfully used to tune the nonequilibrium association of oppositely charged macromolecules and amphiphiles.

Preparation of Gadolinium-alginate nanogels for theranostic application

K. Szczepanowicz¹, K. Podgórna¹, W. Węglarz², E. Bielańska¹, P. Warszyński¹

¹*Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences,
Niezapominajek 8, 30-239 Cracow, Poland*

²*Institute of Nuclear Physics Polish Academy of Sciences, ul. Radzikowskiego 152
31-342 Cracow, Poland*

ncszczep@cyf-kr.edu.pl

Alginate hydrogels are very promising materials for biomedical applications. Due to their properties like softness, elasticity, high water content, they are one of the most favorable materials for drug carriers. Physically crosslinking alginate with divalent cations for example Ca^{2+} , Ba^{2+} , Fe^{2+} allow to form stable three dimensional networks. Moreover, alginate forms gels also in the presence of trivalent cations such as Gd^{3+} . Gadolinium is interesting because of its paramagnetic properties. It is commonly used as a contrast agents in Magnetic Resonance imaging MRI. However, free gadolinium ions are highly toxic, it is essential to use it in complex form.

The aim of our study was synthesis of Gadolinium-alginate drug carriers. Gadolinium-alginate nanobeads were prepared using water in oil (W/O) microemulsions. Prepared beads were purified from free gadolinium ions. The size and stability of obtained nanobeads were investigated by Dynamic Light Scattering measurements (DLS) and Nanoparticle Tracking Analysis (NTA). Additionally, morphology of gadolinium alginate nanocapsules were analyzed by Scanning Electron Microscopy. Using T_2 and T_1 NMR relaxation measurements as well as relaxation time weighted images at 9.4T preclinical MRI scanner we demonstrated that prepared drug carriers are sensitive to magnetic field, which thus can be detected due to locally altered contrast in the MR image. Our nanobeads may be promising candidate for future theranostic application.

Janus dumbbells and their functionalization as magnetically guided self-propelled particles

Florian Guignard, Marco Lattuada
Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland
marco.lattuada@unifr.ch

Janus nanoparticles have unique properties and self-assembling behaviour when compared to their isotropic counterparts, thanks to the presence of multiple segregated functionalities.

In the work, we developed a flexible procedure for the preparation of polymeric Janus dumbbells, and studied their functionalization to obtain a unique system. Dumbbells of different size and aspect ratio have been synthesized using a two-step swelling procedure starting from various polystyrene seeds. During a first swelling step, a polymerizable silane has been used, which brings silane groups to the surface of the nanoparticles. After one additional swelling and polymerization step, dumbbell nanoparticles bearing silane groups on the surface of the first hemisphere and not on the second one are obtained. Silane coupling chemistry can be then performed selectively on one hemisphere. By using a silane with an amino group, positive charges are brought to the first hemisphere, while the second remains negatively charged due to the presence of (SDS) used as surfactant. The resulting dumbbells are then dipolar under the right pH condition. These dumbbells have been asymmetrically functionalized by binding negatively-charged Pt nanocrystals on the positively-charged hemisphere. In this manner, self-propelled dumbbells have been prepared when dispersed in an aqueous solutions containing hydrogen peroxide. When the dumbbell preparation procedure was carried out by starting with a hybrid polystyrene colloid containing magnetite nanocrystals, magnetically-guided self-propelled dumbbells were prepared. Dynamic light scattering and optical microscopy have been used to characterize their behaviour.

Investigation of Mixed Fluorinated and Triblock Copolymers system for the Design of Mesostructured Bimodal Silica

J.L. Blin^a, K. Assaker^a, A. May-Masnou^{a,b}, M.J. Stébé^a

^a UMR SRSMC N° 7565 Université de Lorraine/CNRS, Faculté des Sciences, BP 70239, F-54506 Vandoeuvre-les-Nancy cedex, France

^b Chemical Engineering Department, Chemistry Faculty, Universitat de Barcelona, Martí i Franquès 1-11, 08028, Barcelona, Catalonia, Spain

jean-luc.blin@univ-lorraine.fr

Mixtures of hydrogenated and fluorinated surfactants are excellent candidates to design bimodal mesostructures on the condition that the two surfactants have hydrophobic chains with different sizes. The mesoporous materials can be synthesized either through the cooperative mechanism (CTM) or by the liquid crystal mechanism (LCT). In this study, we have investigated the ability of a mixture of a polyoxyethylene fluoroalkyl ether [$R^F_8(EO)_9$] and a triblock copolymer (Pluronic P123) to be used as template to prepare bimodal mesoporous silica through both the CTM and the LCT mechanisms.

First we have characterized in detail the $R^F_8(EO)_9$ /P123/ water system to better address the synthesis of the bimodal materials. A micellar solution, composed of two kinds of micelles is detected for total surfactant concentration until at least 30 wt.%. A liquid crystal domain appears beyond 50 wt.% of total surfactant. Thanks to the determination of the structural parameters we have shown that the hexagonal region is mainly composed of a biphasic mixture of one fluorocarbon-rich H^F_1 hexagonal phase in equilibrium with one hydrocarbon-rich H^H_1 hexagonal phase. Each phase can incorporate only a weak fraction of the second surfactant.

Then the mixed micelles and the liquid crystal mixtures have been respectively used as building blocks for the design of bimodal mesostructured silica via the CTM and the LCT pathway. Starting with micelles bimodal mesoporous silica (3.6 and 9.4 nm) are obtained and have two ordered interconnected pore networks. [1]. When the LCT is used, our results evidence that the proportion of the two liquid crystals types (H^F_1 and H^H_1) affects the two mesopores populations[2].

Literature:

[1] A. May, M. J. Stébé, J. M. Gutiérrez and J. L. Blin, *Langmuir* 2011, 27, 14000.

[2] K. Assaker, I. Naboulsi, M. Stébé, M. Emo and J.L. Blin, *J. Colloid and Interface Sci.* 2015,446, 170.

COST member

preferred working group : WG4

Electrokinetic and Dielectric Properties of Poly(3-aminophenylboronic acid) in Aqueous and Non-aqueous Media

Seyma OZKAN, Omer Yunus GUMUS and Halil Ibrahim UNAL

Smart Materials Research Lab. Chemistry Department, Science Faculty, Gazi University, Ankara, Turkiye

In recent years, conducting polymers, besides their remarkable optical and electronic properties, have been used for the production of durable and functional materials by combining with boric acid derivatives. In this study, semiconducting poly(3-aminophenylboronic acid), PABA was synthesized with the expectations of controlled size and shape, enhanced colloidal and electrorheological properties. Structural, morphological and surface characterizations of PABA nanoparticles were carried by various techniques. Particle size of PABA nanoparticles was measured to be 254 nm by DLS. Electrokinetic properties of PABA_(aq) dispersions were determined by zeta(ζ)-potential measurements by taking the effects of various electrolytes, surfactants and temperature. The highest ζ -potential values were observed for NaCl as -45.4 mV at pH 6, and for CTAB as 26.3 mV. Temperature increments from 20 °C to 70°C were observed to enhance the ζ -potentials of PABA(aq) dispersions from 7 mV to 26 mV. ζ -potential measurements of PABA nanoparticles in non-aqueous silicone oil (SO) medium was also carried out and a ζ -potential value of +33 mV was determined. Dielectric properties of PABA/SO/Triton-X dispersions was determined by an LCR meter equipped with a liquid test fixture and high relaxation peak was observed in the frequency range of 1×10^2 - 1×10^5 Hz. Electric field induced polarizability ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$) of PABA/SO system was observed to enhance from 3×10^{-3} to 65 when 1.25 V/V% Triton-X was added and indicated that this system could be a good candidate for potential electrorheological applications. Optical microscopy studies of PABA/SO/Triton X-100 system showed the strong fibrillar structure formations of dispersed PABA particles under the influence of externally applied electric field strengths and revealed the vibration damping potential of these particles in industrial applications.

Acknowledgements: The authors thanks to COST Action CM1101 and Turkish Scientific and Technological Research Council, TUBITAK (112T811) for the financial support of this work.

Mechanisms of silver ion and nanoparticle release from antibacterial coatings

Magdalena Oćwieja^a, Zbigniew Adamczyk^a, Maria Morga^a, Dawid Lupa^b

^a *Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Cracow, Poland.*

^b *Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland.
e-mail: ncocwiej@cyf.kr.edu*

The determination of nanoparticle desorption and the release of silver ions from antibacterial coatings is significant for understanding of their activity as well as production of environmental friendly materials. Therefore, the goal of this work was to reveal the influence of ionic strength, pH and temperature on the release kinetics of silver nanoparticles from well-defined monolayers deposited on polyelectrolyte-covered mica.

AAS was used for determining the concentration of silver ions in the solutions whereas a direct enumeration of particle coverage from the images obtained from AFM and SEM proved an efficient tool for studying nanoparticles release kinetics. Using the RSA theoretical approach to interpret experimental results, the equilibrium adsorption constants and the binding energy of nanoparticles (energy minimum depth) were calculated.

It was shown that the decrease of pH and the increase in the temperature caused an significant increase in the ion release rate, although for longer desorption times this process was inhibited by the formation of silver oxide layers around nanoparticles.

The next series of experiments, which concerned the stability of silver monolayers, showed that for particles of the average size of 15 nm, the energy varied between -16.9 kT for ionic strength 0.1 M and -18.8 kT for ionic strength 10^{-4} M. For the largest nanoparticles (54 nm) the energy varied between -17.7 kT for ionic strength 0.1 M and -20.8 kT for ionic strength 10^{-4} M. In contrast to predictions of the mean-field DLVO theory, the kinetics of this process was governed by electrostatic interactions treated as discrete interactions among ion pairs rather than in terms of continuous theories of the electrical double layer.

Acknowledgments: This work was supported by UMO-2012/07/B/ST4/00559 grant.

Silica nanocarrier controlled delivery of antibiotics for acrylic bone cement applications

S. Perni,^a P. Prokopovich,^a

^a *School of Pharmacy and Pharmaceutical Sciences, Cardiff University, Cardiff, UK*

pernis@cardiff.ac.uk

Bone cement is routinely used in orthopaedic applications and antibiotics are added in order to prevent infections offset. Uneven distribution and uncontrolled release of the antibiotic are drawbacks associated with the mixing of such drug in the bone cement dough. Particularly, the antibiotic is released in the first weeks after implantation and, therefore, does not offer protection against infection that can occur months after the surgery. In order to control the antibiotic release and consequently extend the antimicrobial activity, silica nanocarriers containing gentamicin have been prepared through various synthetic routes.

The antibiotic has been conjugated directly to amino functionalised or to succinylated amino functionalised particles and through direct entrapment of gentamicin in the nanoparticles during synthesis. The antibiotic content was determined using TGA; whilst gentamicin release from all prepared nanocarriers was quantified as function of time and pH of solution using the ortho-phthalaldehyde. The direct entrapment provided the highest antibiotic load but the release was completed after 4 hours. For all other conjugated nanocarriers, gentamicin was released over a period of at least 2 days without significant differences among the synthetic route and pH.

In order to extend the period over gentamicin is released, the antibiotic (positively charged) has been deposited on the silica nanoparticles using the Layer-by-layer technique, sandwiching the drug between alginate layers. Using this approach the released has been sustained for at least a 2 week.

Our results therefore, show that silica nanocarriers of antibiotics can prepared and, depending on the preparation route, the release can be controlled. For a prolonged (many weeks) time, the coating of silica nanoparticles with antibiotic through LbL apper the most promising technique.

Advanced Nanocomposite Based on Silica Nanohelices Decorated with Gold Nanoparticles for Chiroptical Properties

J. Cheng,^a M-H. Delville,^b P. Barois,^c E. Pouget^a and R. Oda^a

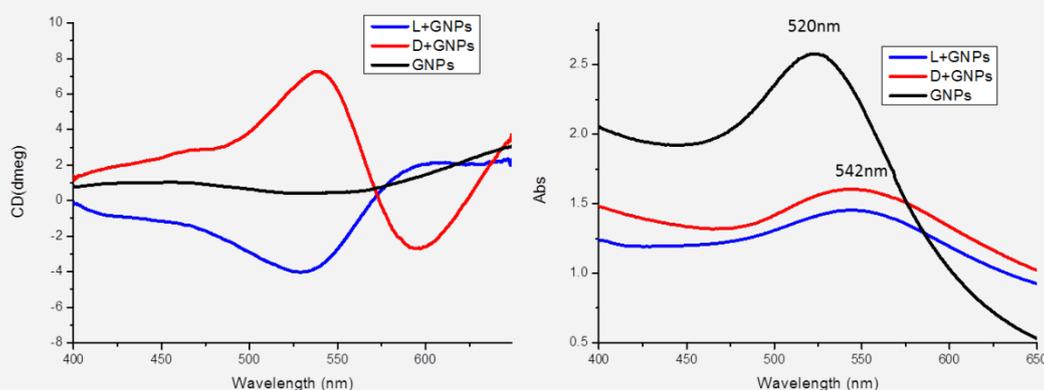
^a Chimie Biologie des Membranes et Nanoobjets, Université Bordeaux 1-CNRS UMR 5248, Allée St Hilaire, Bat B14, 33607 Pessac, France

^b CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France

^c CRPP, Centre de Recherche Paul Pascal, 115 Avenue Schweitzer, 33600 Pessac

j.cheng@iecb.u-bordeaux.fr

Silica nanomaterials have been widely employed as basic three-dimensional templates or scaffolds in biomedical and optical applications due to their great biocompatibility and optical properties. Via sol gel chemistry, they can be easily fabricated, fashioned and functionalized as bases for alignment of nanoparticles, however, to rationally fabricate the self-assembly of nanoparticles into silica templates exhibiting specific optical properties still remains challenging. Herein, we utilize a template-based methodology to prepare a diverse collection of helical gold nanoparticle (GNPs) superstructures having controllable handedness and structural metrics by using GNPs as the building blocks, and the silica nanohelices as the template matrix. The synthesized materials exhibit well-defined chiral arrangement of GNPs following the helicity of silica nanohelices by electrostatic interactions. The plasmon chiroptical activity is observed in circular dichroism (CD) spectrometer in the wavelength of surface plasmon resonance of the GNPs (as shown below). Further observations and simulations prove this plasmon CD comes from the chiral arrangement of GNPs and this effect is highly scale dependent. We expect that this assembly strategy will pave a way to rationally design a variety of superstructures based on nanoparticles to discover a better view towards metamaterials and spark the view towards “bottom-up” approaches in nanoscience.



Polyelectrolyte nanocapsules for hyperthermia

Luigi Cristofolini^a, Krzysztof Szczepanowicz^b, Davide Orsi^a, Tiziano Rimoldi^a, Franca Albertini^c, Piotr Warszynski^b

^a *DiFeST- Parma University, Parma , Italy*

^b *J. Haber Institute of Catalysis and Surface Chemistry PAS, Krakow, Poland*

^c *IMEM-CNR, Parma, Italy*

luigi.cristofolini@unipr.it

Hyperthermia means a body temperature that is higher than normal. Higher body temperatures are often caused by illnesses, such as fever or heat stroke, but hyperthermia can also refer to heat treatment – the carefully controlled use of heat for medical purposes [1]. When cells are exposed to higher temperatures, changes take place inside the cells. Warmer temperatures can make the cells more sensitive to other treatments e.g. to radiation therapy or to chemotherapy. “Very high” temperatures can kill cancer cells, but they also can damage or kill normal cells. Local hyperthermia (or thermal ablation) is used to heat a small area like a tumor. High temperatures can be used to kill the cancer cells by coagulating proteins inside them and destroying nearby blood vessels. The use of nanoparticles and the induction heating of magnetic materials that are implanted into tumors are some new types of hyperthermia that are under study. The aim of our work was to develop the method of formation polyelectrolyte nanocapsules containing magnetic nanoparticles for combining hyperthermia and drug delivery. The method is based on a liquid core encapsulation by polyelectrolyte (PE) multilayer adsorption. Magnetically responsive nanocapsules were prepared by the sequential adsorption of biocompatible polyelectrolytes: (Poly L-lysine as the polycation and Poly Glutamic acid as the polyanion) and Fe₃O₄ nanoparticles. The hyperthermia effects was demonstrated by applying a radio frequency (rf) magnetic field with maximum fields H up to 0.025 T and frequencies up to 430 kHz. We observed increase of local temperature depending on the concentration of capsules and amount of nanoparticles in the shell. Changes to the capsules morphologies could be observed after irradiation.

[1] www.cancer.org

This work was supported by JUVENTUS IP2012 058972 project and COST CM1101 Action.

Fabrication of SPR nanosensor Using Gold Nanoparticles and Self-Assembled Monolayer Technique for Detection of Cu^{2+} In an Aqueous Solution

Eid M. S. Azzam^{a*}, Ail A. Abd El-aal^a, Osama Shekhah^b, Hasan Arslan^b and Christof Wöll^b

^a*Applied surfactants laboratory, Petrochemicals Department, Egyptian petroleum research institute, 11727 Nasr City, Cairo, Egypt*

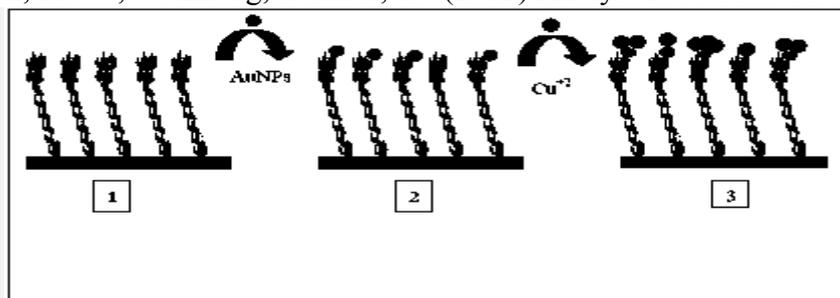
^b*Institut für Funktionelle Grenzflächen (IFG), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

eazzamep@yahoo.com

In this work we investigated the fabrication of surface Plasmon resonance (SPR) nanosensor using gold nanoparticles (AuNPs) chemisorbed onto self assembled monolayer of 10-(3-amino phenoxy) decane-1-thiol on gold substrate. The fabrication process of SPR nanosensor was characterized using different techniques such as infrared reflection-absorption spectra (IRRAS), X-ray photoelectron spectroscopy (XPS) and Atomic force microscope (AFM). The fabricated SPR nanosensor was used for detection of Cu^{2+} in an aqueous solution using Surface Plasmon Resonance Refractometer. The results confirm the fabrication of new SPR nanosensor. The fabricated SPR nanosensor showed a good activity toward the detection of Cu^{2+} . The detection of Cu^{2+} in an aqueous solution using the fabricated SPR nanosensor was enhanced in the presence of gold nanoparticles.

References

1. Azzam , E.M.S. Bashir , A. Shekhah , O. Alawady , A.R.E. Birkner , A. Grunwald , Ch. Wöll, Ch. (2009) *Thin Solid Films* 518: 387-391.
2. Forzani, E. S. Foley, K. Westerhoff, P. Tao, N. (2007) *Sensors and Actuators B: Chem* 123: 82-88.
3. Ye, S. Shi, X. Gu, W. Zhang, Y. Xian, Y. (2012) *Analyst* 137: 3365-3371.



Schematic illustrating the fabrication process of the SPR nanosensor.

Step 1: Formation of C10/SAM on gold. Step 2: Chemosorption of AuNPs onto C10-SAM. Step 3: Immobilization of Cu^{2+} on C10-SAM and AuNPs.

Temperature Controlled Fluorescence on Au@Ag@PNIPAM-PTEBS Microgels: Effect of the Metal Core Size on the MEF Extension

D. Mendez-Gonzalez,^a R. Contreras-Caceres,^b P. Alonso-Cristobal,^a M. Laurenti,^a A. Maldonado-Valdivia,^c F. Garcia-Blanco,^a E. López Cabarcos,^a A. Fernandez-Barbero,^c J. M. Lopez-Romero,^b and J. Rubio-Retama^a

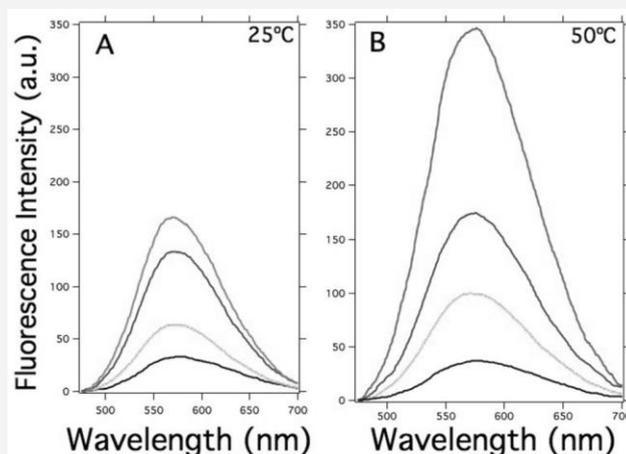
^aDepartment of Physical-Chemistry II, Faculty of Pharmacy, Complutense University of Madrid, Madrid, Spain

^bDepartment of Organic Chemistry, Science Faculty, Malaga University, Malaga, Spain

^cDepartment of Physical-Chemistry, Almeria University, Almeria, Spain

diegomen@ucm.es

In this work, we present a novel method to produce thermoresponsive, monodisperse microgels which display temperature-dependent photoluminescence.¹ The system is based on bimetallic cores of Au@Ag encapsulated within thermoresponsive poly(N-isopropylacrylamide) microgels and coated with a photoluminescent polymer (poly[2-(3-thienyl)ethoxy-4-butylsulfonate] (PTEBS) using the Layer-by-Layer technique. The electromagnetic radiation used to excite the PTEBS induces a local electromagnetic field on the surface of the bimetallic cores that enhances the excitation and emission rates of the PTEBS, yielding a metal enhanced fluorescence (MEF). This effect was studied as a function of the bimetallic core size and the separation distance between the PTEBS and the bimetallic cores. Our results permit to evaluate the effect that the metallic core size of colloidal particles exerts on the MEF for the first time, and prove the relevance of the metallic cores to extend the effect far away from the metallic surface.



Fluorescence intensity of the synthesized microgels; From the bottom up: PS@PNIPAM-PTEBS (control), Au@Ag(6 nm)@PNIPAM-PTEBS, Au@Ag(17 nm)@PNIPAM-PTEBS, and Au@Ag(28 nm)@PNIPAM-PTEBS at (A) 25 °C and (B) 50 °C, respectively. Excitation wavelength 405 nm.

[1] R. Contreras-Caceres; P. Alonso-Cristobal; D. Mendez-Gonzalez; M. Laurenti; A. Maldonado-Valdivia; F. Garcia-Blanco; E. López Cabarcos; A. Fernandez-Barbero; J. M. Lopez-Romero; J. Rubio-Retama *Langmuir* 2014, 30(51), 15560-15567

Interfacial and Emulsifying Properties of Pumpkin (*Cucurbita pepo*) Seed Protein Isolate and Hydrolysates

J. Katona, S. Bučko, Lj. Popović, Ž. Vaštag, L. Petrović, J. Fraj, J. Milinković
Faculty of Technology, University of Novi Sad, Novi Sad, Serbia

jkatona@uns.ac.rs

Pumpkin (*Cucurbita sp.*) belongs to a group of oilseed plants whose seeds are known for high oil and protein content. After the oil extraction from pumpkin seeds, protein content in an oil cake, which is a by-product of the extraction process, can exceed 60 % what makes it a valuable source of plant proteins. Pumpkin seed proteins are desirable ingredients in food products from a nutritional standpoint but they can play a functional role as well. The aim of this work was to investigate solubility, interfacial activity and emulsifying properties of pumpkin seed protein isolate (PSPI) as a function of pH (3–8) and ionic strength (0–1 M NaCl) in comparison to the performance of two PSPI hydrolysates, H1 and H2 obtained by enzymatic PSPI hydrolysis by alcalase and pepsin, respectively. The hydrolysis improved solubility of PSPI, especially at the isoelectric point of PSPI (pH 5). Both salting-in and salting-out of PSPI were observed, depending on pH of a solution, while ionic strength has little effect on solubility of H1 and H2. PSPI, H1, and H2 decrease surface/interfacial tension of solutions indicating protein adsorption at gas-liquid and liquid-liquid interfaces. 20 % wt. emulsions of sunflower oil in 1 % v/w PSPI, H1 or H2 solutions were prepared by Ultraturrax T-25 at 10000 rpm. Stable PSPI emulsions were obtained only at pH 3 and 8 at 0 M ionic strength. Both H1 and H2 effectively stabilize the emulsions at all pH tested even at increased ionic strength (0.5 M).

This work was financially supported by Ministry of Education, Science and Technological Development of Republic of Serbia, Grant No III 46010. It was done within COST CM1101 and MP1106 action framework.

WG 5

Study of β -galactosidase – nanostructured silica interactions by vibrational spectroscopy

Sofia Prazeres^a; Ileana Pavel^b; Andreea Pasc^b; Nadia Canilho^b; Carmen García-Ruiz^a; Gemma Montalvo^a.

^a*Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, University of Alcalá, and University Institute of Research in Police Sciences, Ctra. Madrid-Barcelona Km. 33.6, 28871, Alcalá de Henares (Madrid), Spain*

^b*NANO Group, Faculty of Sciences and Technology, University of Lorraine, Bvd des Aiguillettes, 54506 Vandoeuvre les Nancy, France*

Lactase, an enzyme of the β -galactosidase family, is responsible for the hydrolysis of lactose, the predominant sugar in milk.¹ An appropriate amount and a good activity of this enzyme are required in the small intestine in order to prevent the passage of the indigested lactose into the colon, and consequently the lactose intolerance.

One way to treat this disorder consists in using exogeneous β -galactosidase. However, upon administration, the enzyme needs to be encapsulated into a carrier in order to protect it from (1) the acidic pH of the stomach, and from (2) the deactivating environment in the small intestine because of the presence of inhibitors and proteases.

Recently, silica materials were proposed as carriers for food delivery applications, as being biocompatible, biodegradable, resistant to microbial attack and exhibiting good mechanical strength and thermal stability.²

The main aim of this work is to study the interactions between the enzyme and host nanostructured silica by vibrational spectroscopy. Different host matrixes have been considered, according to our previous experiences^b, either mesostructured or meso-macrostructured, with various pore sizes and in which the enzyme is physisorbed, chemisorbed or physically entrapped. For the system β -galactosidase and silica SBA-15, preliminary results by IR spectroscopy have shown intensity differences in the characteristic silica group bands. Besides, a new band characteristic of aromatic rings appears in the Raman spectra. Both spectral characteristics are attributed to the immobilization of the β -galactosidase on the silica carrier. As main conclusion, from both spectroscopic techniques, Raman are highly promising for a non-invasive and easy-to-interpret study of β -galactosidase – nanostructure silica interactions.

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 606713 – BIBAFOODS.

¹ Contesini, F. et al, *International Journal of Molecular Sciences*, **2013**, vol 14, 1335-1369.

² Bernal, C. et al, *Engineering in Life Sciences*, **2013**, vol 00, 1-10.

Colloidal, Viscoelastic and Antibacterial Properties of Polythiophene-graft-Chitosan Copolymer Particles

Mehmet CABUK^{1,*}, Mustafa YAVUZ¹, Halil Ibrahim UNAL²

¹Department of Chemistry, Faculty of Arts and Sciences, S. Demirel University, Isparta, Turkey

²Gazi University, Chemistry Department, Smart Materials Research Lab. Ankara, Turkey

*mehmetcabuk@sdu.edu.tr

Colloidal, viscoelastic and antibacterial properties of copolymers have gained much interest since they give vulnerable information on the surface properties, colloidal stabilities, viscoelastic behaviors under external electric fields and antibacterial characteristics of the particles [1,2].

Present study describes the synthesis, characterization, colloidal, viscoelastic and antibacterial properties of polythiophene-graft-chitosan (PT-g-CS) copolymer, as a new hybrid material. For this purpose, PT-g-CS colloidal particles were synthesized by chemical oxidation method using FeCl_3 as initiator and their structural and morphological properties were characterized by using FTIR, $^1\text{H-NMR}$, SEM, XRD and TGA techniques. Some physical properties such as grafting yield, grafting efficiency, particle size and distribution, dielectric constant, conductivity and apparent density of the particles were also determined. The characterization results confirmed the introduction of conducting PT chains onto CS back-bones after the graft copolymerization process.

To determine the colloidal properties of PT-g-CS copolymer, effects of time, pH, various electrolytes, surfactants, and temperature onto ζ -potentials of the particles dispersed in water were examined. The ζ -potential of pure PT observed to enhance from +36 mV to +52 mV after grafting with CS (Fig. 1). Concomitantly, the isoelectric point of the pure PT shifted from 6.5 to 8.4. The presence of monovalent (NaCl) electrolyte had no impact on ζ -potentials of the copolymer whereas; divalent (BaCl_2) and trivalent (AlCl_3) electrolytes caused the ζ -potentials to shift to more positive regions.

In order to characterize the dynamic viscoelastic properties of PT-g-CS particles dispersed in silicone oil (SO), the frequency is an important parameter. For this reason, relationship between storage modulus (G') and loss modulus (G'') in the whole frequency range was measured under externally applied electric field strengths. The overwhelming magnitudes of G' to G'' values under electric field induced frequency sweeps revealed the solid-like viscoelastic structure formation of PT-g-CS/SO dispersion system and classified as smart material.

Further, the PT-g-CS copolymer was tested against various bacterial strains (*Klebsiella pneumoniae*, *Escherichia coli*, *Bacillus megaterium*, *Enterococcus faecalis*, *Staphylococcus aureus*) at various concentrations. All the antibacterial results were compared with both untreated polythiophene and chitosan. PT-g-CS copolymer showed relatively higher or equipotent antibacterial activities against the microorganisms compared with the reference antibiotics.

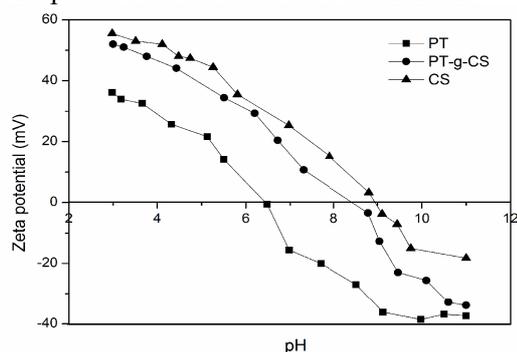


Fig. 1 ζ -potential of the dispersions as a function pH, $c_{\text{samples}} = 0.1 \text{ g/L}$, $T = 25 \text{ }^\circ\text{C}$

Literature:

1. Gumus, O.Y., Unal, H.I., Erol, O., Sari, B., 2011. *Polym. Composite* 32: 418-426.
2. Cabuk, M., Yavuz, M., Unal, H.I., 2015. *J. Intell. Mater. Syst. Str.* DOI: 10.1177/1045389X15577652.

Acknowledgements:

The authors thanks to COST Action CM1101 and TUBITAK (111T637 and 214Z199) for the financial support of this work.

Structure-Activity Relationships of Delivery Agents in a Series of Self-Assembling Pyridines as NAD/NADH Analogues

O.Petrichenko^{a,b}, A.Vezane^c, K.Pajuste^a, M.Rucins^a, I.Timofejeva^c, M.Gosteva^a,
B.Cekavicus^a, Kl.Pajuste^a, M.Plotniece^{a,d}, V.Ose^c, B.Vigante^a,
A.Sobolev^a, T.Kozlovska^c, A.Plotniece^a

^aLatvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, LV-1006, Latvia

^bUniversity of Latvia, Zellu str. 8, Riga, LV-1002, Latvia

^cLatvian Biomedical Research and Study centre, Ratsupites str. 1, Riga, LV-1067, Latvia

^dRiga Stradiņš University, Dzirciema str. 16, Riga, LV-1007, Latvia

aiva@osi.lv

Polyfunctional pyridinium derivatives on the 1,4-dihydropyridine (1,4-DHP) scaffold possess self-assembling properties. 1,4-DHP **1** (Fig. 1B) forms liposomes and efficiently acts as gene delivery agent.^{1,2} The influence of lipid head-groups on gene transfection activity³ and properties of formed liposomes⁴ were reported previously.

The aim of the work is:

1. modification of an active linker of delivery agents – variations of 1,4-DHP structure and their oxidation to putative metabolites - pyridines **3**;
2. studies of biological activity and physical-chemical properties;
3. characterisation of nanoparticles formed by modified delivery agents;
4. clarification of the structure-activity relationships.

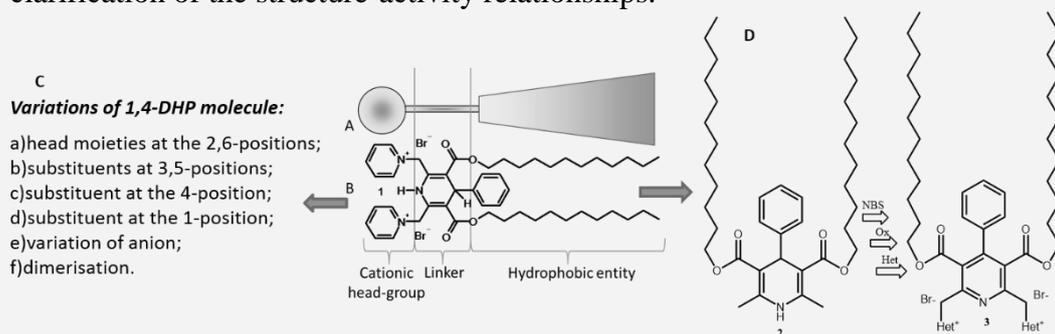


Figure 1. General structure of cationic lipids (A)⁷; structure of cationic 1,4-DHP amphiphile **1** (B); planned structure variations at the 1,4-DHP linker (C) and planned target structure **3** variations after oxidation of linker (D).

Two main groups of new amphiphiles – cationic 1,4-DHP with variations of substituents and fully aromatised amphiphiles with head-groups variations were synthesised (Fig.1 C and D). DTG analysis data of compounds **3** showed that these transition stages were related to phase transitions. Transfection ability of compounds to deliver pEGFP-C1 plasmid DNA into the BHK-21 cell line was studied. For some compounds delivery activity was comparable to 1,4-DHP **1**. The buffering capacity of studied 1,4-DHPs were in the pH range 6.8–8.8. According to TEM and DLS measurements all amphiphiles possessed self-assembling properties, formation of nanoparticles with the average size 79–532 nm; values of zeta-potentials for the nanoparticles were in the range of 48–89 mV.

Acknowledgements: Research was supported by the Latvian National Research Programme BIOMEDICINE and project InnovaBalt (for O.Petrichenko and travel grant for A.Plotniece).

[1] Hyvönen Z.; et al. *BBA*, 2000, 1509, 451; [2] Hyvönen Z.; et al. *J. Controll. Release*, 2004, 99, 177; [3] Pajuste K.; et al. *New J.Chem.*, 2013, 37, 3062; [4] Rucins M.; et al. *Adv.Mater. Research*, 2013, 787, 157; [5] Byk G.; et al. *J.Med.Chem.*, 1998, 41, 224.

ZrO₂ Nanoparticles with High Surface Area Synthesized Using Colloidal Chemistry Method

M.I. Čomor , M. Carević, Tatjana Novaković, Nadica Abazović

Laboratory for Radiation Chemistry and Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

A number of chemical methods have been explored to synthesize high-surface zirconia powders and to stabilize metastable tetragonal or cubic nanocrystals. While conventionally prepared zirconia shows a surface area of about 30 m²g⁻¹ after calcination at 600°C, the doping of zirconia with some metal ions (M) at a concentration of ≤ 5 at% can greatly improve active surface area, even after calcination. Usually rare earth ions are used for doping, especially Y³⁺ and La³⁺. Studies on new dopants capable of producing improved properties of zirconia are still of great interest [1].

Here we present a colloidal chemistry based hydrothermal method for preparation of zirconia nanoparticles doped with Si⁴⁺ ions. Extremely alkaline solutions of Zr⁴⁺ and Si⁴⁺ precursors were subjected to high temperatures (120-180° C) and pressure for 6h. After washing and drying, nanopowders were calcined at 600°C. Zirconia samples were characterized using XRD, SEM/EDX, UV/Vis spectroscopy. Obtained results were correlated with textural properties of samples. A stable, cubic crystalline phase nanoparticles with a diameters of about 8-10 nm, were reproducibly synthesized. All synthesized nanomaterials had specific surface areas of about 10² m²g⁻¹.

Acknowledgement: Financial support for this study was granted by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project 172056 and 45020) and as a part of COST CM1101 and MP1106 actions.

[1] S. Yin, B. Xu, CHEMPHYSICHEM 2003, No. 3, 277-281.

Acknowledgement: This work was financially supported by Ministry of Education, Science and Technological Development of Republic of Serbia and COST action CM1101.

CM 1101: "Colloidal aspects of Nanoscience for Innovative Processes and Materials"
WG3 "Synthesis of nano and bio-colloidal materials: development and up-scaling" and
WG4 "Kinetic and catalytic aspects of nano-colloids and nano-structured surfaces"

Food grade nanodispersions as replacements of oil and aqueous phase in macroemulsions

E. Mitsou^a, G. Tavantzis^b, V. Papadimitriou^a, A. Xenakis^a

^aInstitute of Biology Medicinal Chemistry & Biotechnology, National Hellenic Research Foundation, Athens, Greece

^bResearch, Innovation & Improvements of Food Operations Department, Yiotis S.A.-Nutritional Foods Industry, Peristeri, Greece

emitsou@eie.gr

During the last years there has been a great interest from food industry in the formulation of edible nanodispersions due to their stability and their ability to encapsulate biologically active substances (vitamins, antioxidants, etc.).

The application of nanodispersions in food products is limited due to the type of surfactants and oils which are used for their formulation.

The aim of this work was the preparation of stable nanodispersions, water-in-oil (w/o) and oil-in-water (o/w), in order to replace a part or the total volume of the oil or aqueous phase respectively, in confectionary products such as whipped creams and icings. With the addition of nanodispersions in such products we achieved the decrease of unsaturated fats, the decrease of the energy required for the formulation and the increase of the health benefits for the consumer. Bioactive compounds (such as vitamins) that increase the nutritional value of the final products were incorporated. The encapsulation of these compounds in nanodispersions is of great importance due to the avoidance of their oxidation.

The nanodispersions which have been developed consisted of biocompatible ingredients such as caprylic/capric triglyceride, sunflower oil, extra virgin olive oil, lecithin, mono and di-glycerides, water etc. No external energy was required for the formulation of such nanodispersions and as a result the cost for the product is reduced.

The replacement of parts of a confectionary product permitted the modification of characteristics such as texture, flavor, color, stability and as a result modified confectionary products came off. Structural characterization of the proposed systems regarding particle size distribution was obtained using Dynamic Light Scattering (DLS) technique. The interfacial properties were examined by Electron Paramagnetic Resonance (EPR) spectroscopy using the spin probing technique. [1]

Finally, the encapsulation of bioactive compounds such as vitamins, which can increase the nutritional value of the final products (whipped cream and icing), was examined.

[1] A. Kalaitzaki, M. Emo, M.J. Stebe, A. Xenakis, V. Papadimitriou, *Food Res. Int.*, 2013, 54, 1448

Acknowledgments

This work was funded within the frame of NSRF 2007-2013 program for development. We are also grateful to Yiotis S.A.- Nutritional Foods Industry for their support and for providing necessary guidance.

Oil-in-water microemulsions, as carriers for pharmaceutical substances: encapsulation of bioactives, structural study and *in vitro* cell lines testing

I.Theochari, M. Goulielmaki, P.Zoumpoulakis, V.Papadimitriou, A. Pintzas, A. Xenakis

Institute of Biology Medicinal Chemistry & Biotechnology, National Hellenic Research Foundation, Athens, Greece

jtheochari@eie.gr

The subject of the study is the development and characterization of biocompatible O/W microemulsion systems as matrixes for encapsulation of various pharmaceutical substances. O/W microemulsions composed of: PBS buffer 1X or water as the continuous aqueous phase, Tween 80 as the emulsifier and triacetin as the dispersed phase have been formulated and used for the encapsulation of bioactive molecules such as PLX 4720 and squalene. PLX 4720 is an anticancer drug for melanoma and squalene is an isoprenoid compound which is an intermediate metabolite in the synthesis of cholesterol and it has been studied for its potential antitumor activity.

The study of structural characteristics was performed by the technique of Dynamic Light Scattering (DLS), Cryogenic transmission electron microscopy (*cryo-TEM*) and Nuclear Magnetic Resonance (NMR). DLS technique was used to determine the diameter of the micelles and to evaluate the homogeneity by measuring the polydispersity index (PDI). The measurements were compared in absence and presence of PLX 4720 and squalene in the microemulsion. The measurements provided a homogenous dispersion, micelles diameter was 10nm approximately and polydispersity index values were measured in the range of 0.1-0.3. Cryo-TEM was applied to study the internal structure of nanoparticulate carrier systems as well as the overall colloidal composition of the corresponding dispersions. ^1H and 2D ^1H DOSY NMR techniques were applied to investigate the degree of encapsulation of the bioactive compounds in the microemulsion systems.

Furthermore, O/W microemulsions were examined in presence and absence of PLX 4720 and squalene *in vitro* test for cell viability and cell toxicity. RKO and Colo-205 cell cultures were used. Percentage of cell survival was measured in order to determine the effect of microemulsions' substances and the effective release of PLX 4720 and squalene in cell cultures.

Food grade Microemulsions as effective carriers of nisin

M.D. Chatzidaki^{a,b}, S. Alexandraki^c, V. Papadimitriou^a, A. Yaghmur^d, K. Papadimitriou^c, E. Tsakalidou^c, A. Xenakis^{a,b}

^a*Institute of Biology Medicinal Chemistry & Biotechnology, National Hellenic Research Foundation, Athens, Greece*

^b*MTM, Faculty of Science and Engineering, Örebro University, Sweden*

^c*Laboratory of Dairy Research, Department of FST, Agricultural University of Athens*

^d*Department of Pharmacy, Health and Medical Sciences, University of Copenhagen, Denmark*

mhatzidaki@eie.gr

Recently, there has been an increase of interest for the formulation of microemulsions for the encapsulation of bioactive molecules having application in the food industry. Another demand of food industry is the replacement of high energy methodologies for the use of bacteriocins, peptides with antimicrobial characteristics, and the enhancement of their effectiveness as food preservatives.

The aim of this study was the formulation of water-in-oil (W/O) microemulsions based on vegetable oils with nisin-vehicle applications. To this respect, vegetable oils such as olive oil and sunflower oil were selected. Mono and di- glycerides (DMG) were used as emulsifiers due to their amphiphilic character, while ethanol was used as co-surfactants. Nisin, a hydrophilic peptide, originating from *Lactococcus lactis* was solubilized in the aqueous phase and finally incorporated to the microemulsion in given concentrations.

A structural study and characterization of microemulsions was then applied, using techniques such as Dynamic Light Scattering (DLS), Small Angle X-Ray Scattering (SAXS) and Electronic Paramagnetic Resonance (EPR) spectroscopy in the absence and presence of the bioactive molecule. Also, a study concerning the addition of water and Ethanol was applied. Parameter changes resulted to significant alteration to the size and shape of the reversed micelles.

Finally, microemulsions were tested for their antimicrobial activity against *Lactococcus lactis* and *Staphylococcus aureus* using the well diffusion assay technique. Significant alterations were observed to the effectiveness of the encapsulated molecule at different parameter changes.

Literature:

1. Kalaitzaki, A., *et al.*, *Biocompatible nanodispersions as delivery systems of food additives: A structural study*. Food Res.Intern. 2013. **54** 1448.
2. M. Chatzidaki, *et al.*, *Microemulsion versus emulsion as effective carrier of Hydroxytyrosol*. Colloids Surf.B. (2015) DOI 10.1016/j.colsurfb.2015.04.053

Acknowledgments: This work was performed in the framework of STHENOS project within GSRT's KRIPIS action, funded by Greece and the European Regional Development Fund of the European Union under the O.P. Competitiveness and Entrepreneurship, NSRF 2007-2013 and the Regional Operational Program of Attica.

Corrosion and fouling protection by superhydrophobic coatings

M.Ferrari*, F.Cirisano, L.Liggieri,
F.Ravera, E.Santini, A.Benedetti
¹ CNR - IENI, Via De Marini, 6, 16149 -Genova, Italy
m.ferrari@ge.ieni.cnr.it

In sea environment the complex multi-specific biological community of bacteria, algae, fungi and ultimately higher organisms producing a biological phenomenon of accumulation and development on an interface is called biofouling. Severe problems in particular for the naval industry due to the deterioration of the surfaces, increased roughness lead to an increase of fuel consumption and, as a final result, increased material corrosion.

The limitations associated to the more recent Foul Release Coatings (FRCs) can be overcome by superhydrophobic surfaces (SHS) since in this type of surfaces the combination of low surface energy and the existence of a specific surface morphology (micro-nano roughness) coexist, lead to significantly less wettable surfaces than for FRCs with water contact angle (CA) higher than 150° and a hysteresis lower than 5°. Protection and friction reduction in marine environment where interactions with aqueous environment are usually strongly to be avoided like can efficiently benefit of such highly water repellent coatings.

Mixed organic-inorganic systems obtained by using nanoparticles and capsules to provide self-healing properties have been prepared and their aging resistance has been evaluated as a function of the coating features.

Surface characterization and on-field electrochemical studies have been carried out to test the performance in terms of fouling prevention and protection of metals in underwater conditions.

Acknowledgements:

The Authors acknowledge the RITMARE (La Ricerca Italiana per il Mare) Flagship Project for the financial support.

COST WG4

Gelatin-based nanoparticles for the efficient intracellular delivery of DNA

M. Carmen Morán^{1,2*}, Neus Rosell¹, Guillem Ruano¹, M. Antònia Busquets^{2,3}, M. Pilar Vinardell^{1,2}

¹ *Departament de Fisiologia; Facultat de Farmàcia, Universitat de Barcelona, Avda. Joan XXIII s/n, 08028-Barcelona-Spain*

² *Institut de Nanociència i Nanotecnologia-IN²UB, Universitat de Barcelona, Avda. Joan XXIII s/n, 08028-Barcelona-Spain*

³ *Departament de Fisicoquímica; Facultat de Farmàcia, Universitat de Barcelona, Avda. Joan XXIII s/n, 08028-Barcelona-Spain*

mcmoranb@ub.edu

The rapidly rising demand for therapeutic grade DNA molecules requires associated improvements in encapsulation and delivery technologies. One of the challenges for the efficient intracellular delivery of therapeutic biomolecules after their cell internalization by endocytosis is to manipulate the non-productive trafficking from endosomes to lysosomes, where degradation may occur. The combination of the endosomal acidity with the endosomolytic capability of the nanocarrier can increase the intracellular delivery of many drugs, genes and proteins, which, therefore, might enhance their therapeutic efficacy [1]. The gelification properties of gelatin as well as the strong dependence of gelatin ionization with pH makes this compound an interesting candidate to be used to the effective intracellular delivery of active biomacromolecules [2]. In the present work, gelatin (either high or low gel strength) and protamine sulfate has been selected to form particles by interaction of oppositely charged compounds. Particles in the absence of DNA (binary system) and in the presence of DNA (ternary system) have been prepared. The physicochemical characterization (particle size, polydispersity index and degree of DNA entrapment) have been evaluated. Cytotoxicity experiments have showed that the isolated systems and the resulting gelatin-based nanoparticles are essentially non-toxic. The pH-dependent hemolysis assay and the response of the nanoparticles co-incubated in buffers at defined pHs that mimic extracellular, early endosomal and late endo-lysosomal environments demonstrated that the nanoparticles tend to destabilize and DNA can be successfully released. It was found that, in addition to the imposed compositions, the gel strength of gelatin is a controlling parameter of the final properties of these nanoparticles. The results indicate that these gelatin-based nanoparticles have excellent properties as highly potent and non-toxic intracellular delivery systems, rendering them promising DNA vehicles to be used as non-viral gene delivery systems.

M.C. Morán acknowledges the support of the MICINN (Ramon y Cajal contract RyC 2009-04683). This study was financially supported by Project MAT2012-38047-C02-01 from the Spanish Ministry of Science and Innovation and FEDER, European Union. M.A. Busquets is grateful to the Spanish Ministry of Science and Innovation for financial support of the Project MAT2012-36270-C04-03. This work was conducted under the umbrella of COST CM1101 and MP1106 Actions.

- 1) A. K. Varkouhi et al., *J. Control. Release*, **151** (2011) 220.
- 2) A. O. Elzoghby, *J. Control. Release*, **172** (2013) 1075.

Glyco-biosensing of prostate specific antigen using surface plasmon resonance lectin-based assay

Pavel Damborský, Jaroslav Katrlík

Institute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9,

845 38 Bratislava, Slovakia

E-mail:katrlík@yahoo.com

One of the frontiers in cancer research aims at glycoprofiling of proteins and cells since altered glycosylation is a common feature of tumorigenesis. Hence the study of interactions of glycoproteins with glycan binding proteins attracts considerable attention due to their importance in glycoprofiling of glyco-biomarkers. Conventional assays for clinical diagnostic are mostly based on sandwich strategy involving a monoclonal or a polyclonal antibody. However, such approaches have several disadvantages including the reproducibility and the necessity of labelling. Furthermore, the biospecific interaction could not be observed in the real-time. Nowadays, surface plasmon resonance (SPR) is one of the most effective optical label-free biosensing techniques for both quantitative and qualitative parameters of the biosensing event. Prostate cancer diagnostics can be effectively addressed using sensor-based approaches. The objective of this study was to develop sandwich-based assay for glycoprofiling of the prostate cancer biomarker, prostate specific antigen (PSA), thus paving way for the personalized medicine. Experiments with capture antibody (anti-PSA) followed by glycoprofiling using glycan-binding proteins (lectins) were performed. A panel of lectins with complementary glycan specificity was used in the developed bioassays and PSA – lectin interactions were evaluated also by microarray assay.

Acknowledgements: This work is supported by the grants Marie Curie Initial Training Network PROSENSE (grant No. 317420, 2012-2016), European Commission; CMST COST Action CM1101 (WG6); VEGA 2/0162/14.

Electrokinetic and heavy metal adsorption properties of polypyrrole-graft-chitosan colloidal dispersions

Mehmet CABUK¹, Murat OZTAS¹, Mustafa YAVUZ¹, Halil Ibrahim UNAL², Fethiye GODE¹

¹*Süleyman Demirel University, Arts and Sciences Faculty, Chemistry Department, Isparta, Turkey*

²*Gazi University, Chemistry Department, Smart Materials Research Lab. Ankara, Turkey*

mehmetcabuk@sdu.edu.tr

Surface electric properties of a solid particle in an aqueous solution can be determined by ζ -potential measurements which are dependent on pH values and ionic strength of the media. The ζ -potential is one of the important tools to enlighten the colloidal stability of dispersions [1,2].

Polypyrrole-*graft*-chitosan (PPy-*g*-CS) colloidal particles were chemically synthesized and their structural and physical properties were characterized by using various techniques. To determine electrokinetic and colloidal properties of PPy-*g*-CS copolymer, effects of time, pH, various electrolytes, surfactants, and temperature onto ζ -potentials of the copolymer particles dispersed in water were examined. The adsorption of Cr(III) and Cr(VI) onto PPy-*g*-CS particles were also investigated by using a batch method at various temperatures.

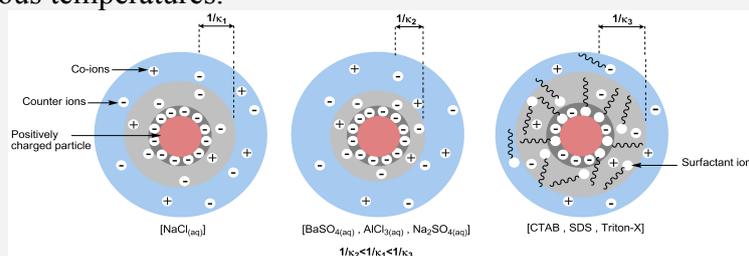


Fig. 1 Schematic representation of the particle surfaces in aqueous media at various conditions.

It was observed that the ζ -potential of PPy-*g*-CS dispersions shifted to more positive region and also its' IEP shifted to higher pH value with grafting. This shift can be attributed to the synergistic effect between positively charged $-NH_3^+$ groups on CS back-bone and PPy⁺ chains after grafting. These shifts in the ζ -potentials became dominant when the valencies of the cations increased from +1 to +2 and +3. Thickness of electric double layers, κ^{-1} were determined to change in the following order at $1 \times 10^{-3} M$ electrolytes concentrations: $\kappa^{-1}_{Al^{3+}} = 3 \text{ nm} < \kappa^{-1}_{Ba^{2+}} = \kappa^{-1}_{SO_4^{2-}} = 5 \text{ nm} < \kappa^{-1}_{Na^+} = \kappa^{-1}_{Cl^-} = 10 \text{ nm}$. When κ^{-1} was decreased, the electric double layer was compressed, its thickness reduced and as a result, the ζ -potential was decreased (Fig. 1). The heavy metal adsorption capacity of Cr(III) and Cr(VI) increased with initial metal concentration. PPy-*g*-CS particles can be used as good adsorbents for removal of Cr(III) and Cr(VI) ions in aqueous solutions.

References:

1. Cabuk, M., Yavuz, M., Unal, H.I., 2015. *J. Intell. Mater. Syst. Str.* DOI: 10.1177/1045389X15577652.
2. Lopez-Leon, T., Ortega-Vinuesa, J.L., Bastos-Gonzalez, D., et al. 2006. *J. Physical Chem. B* 110: 4629-4636.

Silica Nanoparticles - Fatty Acids Interaction at Fluid Interfaces and Stability of Emulsions and Foams

F. Ravera,^a E. Santini,^a S. Llamas,^a M. Ferrari,^a L. Liggieri,^a E. Guzmán,^b S.Y. Lin.^c

^a *CNR - Institute for Energetics and Interphases, Genoa, Italy*

^b *Complutense University of Madrid, Madrid, Spain*

^c *NSC-Taiwan National Science Council, Taipei, Taiwan*

Presenting author's email: f.ravera@ge.ieni.cnr.it

The modification of the degree of hydrophobicity of solid particles dispersed in aqueous phases by adding appropriate surfactants is widely used to favour the transfer to water/air or water/oil interfaces and, consequently, stabilize foams and emulsions.

In recent studies [1,2] it has been shown that associating palmitic acid to hydrophilic silica nanoparticles allows obtaining emulsions with enhanced stability due to the formation of surfactant-particle complexes segregating at water-oil interface.

Here the interfacial properties of systems containing silica NP and fatty acid with different length of the hydrophobic chain are systematically investigated and the results compared to the stability properties of the respective foams and emulsions.

These properties are importantly dependent on the length of the fatty acid hydrophobic chain. This is due to the fact that the processes occurring in the system, that are the formation of NP-fatty acid complexes, the attachment of these complexes to the fluid interface and their potential re-dispersion among the two bulk phases, are essentially driven by hydrophobic interactions between molecules, particles and interfaces and, for that, strongly dependent on the chain-length.

The results obtained show that fatty acids can be an interesting alternative to synthetic surfactants, for the wettability modification of particles because confer adequate and controlled physico-chemical characteristics to the particle-laden interfaces for the long-term stabilization of emulsions and foams

Moreover, the formation of mixed fatty acid – silica particle layers at fluid interfaces, in association with other suitable additives, may be utilized for the production of more complex systems, such as microcapsules.

[1] E. Santini, E. Guzmán, F. Ravera, M. Ferrari, L. Liggieri: Properties and structure of interfacial layers formed by hydrophilic silica dispersions and palmitic acid, *Phys. Chem. Chem. Phys.*, 14, 607–615, 2012.

[2] E. Santini, E. Guzmán, M. Ferrari, L. Liggieri: Emulsions stabilized by the interaction of silica nanoparticles and palmitic acid at the water–hexane interface, *Colloids and Surfaces A*, 460, 333-341, 2014..

The Neuroprotectant Loaded PCL Nanocarriers as Efficient Drug Delivery Across the Blood-Brain Barrier

M. Lapczynska^a, K. Szczepanowicz^a, S. Lukasiewicz^b, P. Warszynski^a

^a*Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Niezapominajek 8, 30-239 Krakow, Poland*

^b*Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Krakow Poland*

ncszczep@cyf-kr.edu.pl

Prevention and treatment of stroke and neurodegenerative diseases such as Alzheimer's and Parkinson's are major and unresolved problems of contemporary medicine. Despite of the progress in understanding of molecular mechanisms of neuronal injury and preventing them, only few neuroprotective substances are used in the clinic. However their efficiency in the treatment of stroke and neurodegeneration is not satisfactory. One of the major limitations is an inefficient delivery of neuroprotective drugs by the blood-brain barrier to the affected part of the brain. Therefore, The main aim of the research is to develop a new strategy of delivery of neuroprotectants by the nanocarriers, which are able to cross the blood-brain barrier without imposing side effect on its normal function.

In this research we were focused on synthesis of polycaprolactone (PCL) nanoparticles containing active neuroprotective substances (Polydatin and/or Resveratrol) as well as model drugs (Cumarin-6, Clozapine, Curcumin and/or Vitamin D₃). The drugs loaded PCL nanocarriers were synthesized from nanoemulsions by phase inversion emulsification method. All nanocarriers were characterized by size, size distribution, zeta potential, imaged by cryo-SEM, cytotoxicity assay and stability in the simulated body fluid (SBF) determination.

Acknowledgments: This study was supported by the Norwegian Financial Mechanism grant Pol-Nor/199523/64/2013 NanoNeucar.



Molecularly Imprinted Polypyrrole for Sensor Design

Ieva Baleviciute^{1,2}, Vilma Ratautaite¹, Lina Mikoliunaite¹, Inga Vilkonciene – Morkvenaite¹, Zigmantas Balevicius², Almira Ramanaviciene³, Arunas Ramanavicius^{1,2},
¹ Department of Physical Chemistry, Faculty of Chemistry, Vilnius University, Naugarduko 24, LT03225 Vilnius, Lithuania;
² Laboratory of BioNanotechnology, Center for Physical Sciences and Technology, Vilnius Lithuania;
³ NanoTechnas – Center of Nanotechnology and Materials Science, Department of Analytical and Environmental Chemistry, Faculty of Chemistry, Vilnius University, Naugarduko 24, LT03225 Vilnius, Lithuania.

Presenting author's email: arunas.ramanavicius@chf.vu.lt

Molecularly imprinted polymer (MIP) based sensors are interesting because of their relatively low costs and good selectivity towards imprinted analyte. Electrochemical [1] and chemical [2] polymerization enables deposition of thin layers of Ppy over electrodes, which could be applied in the design of sensors suitable for the determination of high molecular weight [3,4] and low molecular weight [5-8] analytes.

In this research affinity and dielectric properties of molecularly imprinted conducting polymer – polypyrrole (MIP-Ppy) based thin films were evaluated. Films of polypyrrole molecularly imprinted with theophylline, caffeine and some other compounds (MIP-Ppy) and non-imprinted polypyrrole (NIP-Ppy) were evaluated and the efficiency of Ppy to bind theophylline was determined. Electrochemical impedance spectroscopy was applied for the investigation of kinetics of analyte interaction with MIP-Ppy and NIP-Ppy. The sensitivity of molecularly imprinted and non-imprinted polymer films was analyzed by injection of different analyte concentrations. Assuming that Ppy film electrical capacitance change is a result of Ppy dielectric constant change induced by absorbed analyte molecules, the electrical capacitance change (ΔC) kinetics at different concentrations of analyte was analyzed using first pseudo order kinetic equation. The dissociation equilibrium constant K_D of MIP-Ppy/analyte complex at room temperature was calculated, and Gibbs free energy change (ΔG) of MIP-Ppy/analyte complex formation was estimated. It was concluded that molecularly imprinted polypyrrole thin film could be used for the detection of imprinted analytes.

References:

- [1] D. Plausinaitis, V. Ratautaite, L. Mikoliunaite, L. Sinkevicius, A. Ramanaviciene, A. Ramanavicius, Quartz crystal microbalance based evaluation of electrochemical formation of aggregated polypyrrole particle based layer. *Langmuir* 2015, 31 (10), 3186-3193.
- [2] K. Leonavicius, A. Ramanaviciene, A. Ramanavicius, Polymerization Model for Hydrogen Peroxide Initiated Synthesis of Polypyrrole Nanoparticles. *Langmuir* 2011, 17, 10970-10976.
- [3] V. Ratautaite, S.N. Topkaya, L. Mikoliunaite, M. Ozsoz, Y. Oztekin, A. Ramanaviciene, A. Ramanavicius, Molecularly Imprinted Polypyrrole for DNA Determination. *Electroanalysis* 2013 25, 1169-1177.
- [4] A. Ramanaviciene, A. Ramanavicius, Molecularly imprinted polypyrrole-based synthetic receptor for direct detection of bovine leukemia virus glycoproteins. *Biosensors and Bioelectronics* 2004, 20, 1076-1082.
- [5] V. Ratautaite, S.D. Janssens, K. Haenen, M. Nesládek, A. Ramanaviciene, I. Baleviciute, A. Ramanavicius, Molecularly Imprinted Polypyrrole Based Impedimetric Sensor for Theophylline Determination. *Electrochimica Acta* 2014 130, 361-367.
- [6] V. Ratautaite, D. Plausinaitis, I. Baleviciute, L. Mikoliunaite, A. Ramanaviciene, A. Ramanavicius, Characterization of Caffeine-Imprinted Polypyrrole by a Quartz Crystal Microbalance and Electrochemical Impedance Spectroscopy *Sensors and Actuators B* 2015, 212, 63-71.
- [7] V. Ratautaite, M. Nesládek, A. Ramanaviciene, I. Baleviciute, A. Ramanavicius, Evaluation of Histamine Imprinted Polypyrrole Deposited on Boron Doped Nanocrystalline Diamond. *Electroanalysis* 2014, 26, 2458-2464.
- [8] A. Ramanaviciene, A. Finkelsteinas, A. Ramanavicius, Basic electrochemistry meets nanotechnology: Electrochemical preparation of artificial receptors based on a nanostructured conducting polymer, polypyrrole. *Journal of Chemical Education* 2006, 83, 1212-1214.