

A tribute to Isabelle Grillo



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Talks

Self-assembly in di-alkyl chain surfactants and the role of co-surfactants and additives: impact upon product formulation and functionality.

Speaker: Jeffrey Penfold¹

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Home and personal care products, such as fabric and hair conditioners and shampoos, are often mixtures of di-alkyl chain ionic / nonionic surfactant mixtures. Such formulations exhibit a complex array of microstructures which affect their functionality, formulation, stability, reproducibility, and adsorption properties. It will be shown how small angle neutron scattering, SANS, has made important contributions to the evaluation of these complex microstructures, and how co-surfactants, alcohols and model perfume molecules affect the microstructure. The results will illustrate in some specific model examples the potential impact upon product formulation, stability and reproducibility.

Self-assembled nanostructured material : Mechanism of formation

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In memory of Isabelle, I choose 4 projects realized with her to illustrate how SANS can be used to determine the structure and the kinetic evolution of self-assembled nanostructured hybrid materials. In mesostructured materials made of organic surfactant (CTAB) and inorganic materials (ZrO₂), SANS kinetic experiments (with a stopped-flow coupled to SANS) permitted to identify the role played by the micelles in the precipitation process.[1] In the nanoparticle field, SANS also appears as a technique of choice to characterize the 3.2 nm CTAB bilayer around gold nanorods.[2] Probing the organic part of hybrid materials helps to understand the structure and mechanisms of formation of nanomaterials.

For the case of self-assembling squalene based nanoparticles used for nanomedicine,[3] SANS revealed 1) that particles size is controlled by the solvent composition (ethanol-water) after nanoprecipitation process[4] and 2) the key role of the organic solvent used in the nanoprecipitation process of nanoparticles formulation.[5] For squalene-adenosine (SqAd)[6] and Sq-SiRNA PM22 bioconjugates,[7] SANS coupled with different technics (Cryo-TEM, circular dichroism, steady-state fluorescence spectroscopy and isothermal titration calorimetry) helps to identify the specific interaction between the nanoparticles and fetal bovine serum (FBS) or bovine serum albumin (BSA), the main protein of blood plasma. The SqAd nanoparticles disassembles with the formation of complex between BSA and SqAd monomers extracted from the nanoparticles.[8] The Sq-SiRNA nanoparticles exhibit a colloidal stability in the presence of BSA or LDL which could be related to their particular structure.[9]

In each of these examples, SANS is a key technique to probe the transformation of the organic part in self-assembling nanostructured hybrid materials, allowing an access to the mechanisms of formation, disassembly and activity.

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2. Gomez-Grana, S., Hubert, F., Testard, F., Guerrero-Martinez, A., Grillo, I., Liz-Marzan, L.M., Spalla, O. "Surfactant (bi)layer on Gold Nanorods" *Langmuir* (2012), 28, 1453-1459.
3. Desmaële, D., Gref, R., & Couvreur, P. (2012). "Squalenoylation: a generic platform for nanoparticulate drug delivery". *Journal of controlled release* (2012), 161(2), 609-618.
4. Saha, D., Testard, F., Grillo, I., Zouhiri, F., Desmaële, D., Radulescu, A., Desert, S., Brulet, A., Couvreur, P., Spalla, O. "The role of solvent swelling in the self-assembly of squalene based nanomedicines" *Soft Matter* (2015), 1, 4173-4179.
5. Elodie Marret, "Nanoprecipitation de dérivés squalénés en milieu aqueux : Influence de la formulation sur la distribution de taille et structure interne des nanoparticules obtenues", thèse soutenue à l'Université Paris Saclay, (2019).
6. Gaudin, A., Yemisci, M., Eroglu, H., Lepetre-Mouelhi, S., Turkoglu, O. F., Dönmez-Demir, B., Caban, S., Sargon, M. F., Garcia-Argote, S., Pieters, G., et al. "Squalenoyl Adenosine Nanoparticles Provide Neuroprotection after Stroke and Spinal Cord Injury" *Nat. Nanotechnol.* (2014), 9, (12), 1054-1062.
7. Boutary, S., Caillaud, M., El Madani, M., Vallat, J. M., Loisel-Duwattez, J., Rouyer, A., ... & Massaad-Massade, L. (2021). "Squalenoyl siRNA PMP22 nanoparticles are effective in treating mouse models of Charcot-Marie-Tooth disease type 1 A". *Communications biology* (2021), 4(1), 1-14.
8. Gobeaux, F., Bizeau, J., Samson, F., Marichal, L., Grillo, I., Wien, F., Yesylevsky, S. O., Ramseyer, C., Rouquette, M., Lepêtre-Mouelhi, S., Desmaële, D., Couvreur, P., Guenoun, P., Renault, J-P., Testard, F. "Albumin-driven disassembly of lipidic nanoparticles: the specific case of the squaleneadenosine nanodrug" *Nanoscale* (2020), 12, 2793-2809.
9. Caillaud, M., Gobeaux, F., Hémadi, M., Boutary, S., Guenoun, P., Desmaële, D., Couvreur P., Wien, F., Testard, F., Massaad-Massade, L. (2021). "Supramolecular organization and biological interaction of squalenoyl siRNA nanoparticles". *Int. J. Pharm.* (2021), 609, 121117.

The D33 SANS instrument: Conception, Commissioning and Performance

Speaker: Charles Dewhurst¹
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In 2005, pressure from the scientific user community and strategic planning for instrumentation at ILL determined that additional Small-Angle Neutron Scattering (SANS) capacity and capability were required. Demand for SANS beamtime was (and still is!) skyrocketing being the neutron technique with the most diverse scientific community from soft-matter, biology, physics, materials science and magnetism. Shortfalls in SANS capability was also becoming apparent with restrictions in the use of high-magnetic fields and capabilities in polarisation and analysis techniques. At the same time, the rise in high-performance SANS instrumentation at spallation neutron sources gave users a taste of how the wide wavelength band gives access to the full dynamic q -range ($q_{\max}/q_{\min}$) without the need for several measurements on a monochromatic instrument.

The scientific case and instrument specification arrived from consideration of the factors mentioned above. D33 would be the third Small-Angle Neutron Scattering instrument at the ILL with particular emphasis on modern trends in materials science, physics, magnetism and nano-structured materials. D33 would provide high resolution and wide dynamic q -range options in both monochromatic and time-of-flight (TOF) modes of operation. Two large multi-tube detectors would extend the dynamic q -range further giving $q_{\max}/q_{\min} \approx 20$ in monochromatic mode and a massive $q_{\max}/q_{\min} > 1000$ in TOF mode. Beam polarisation and ^3He spin analysis would facilitate and expand studies of magnetism. The position of D33 would be such as to allow high magnetic fields at the sample position.



On the 20th June 2012 the neutron beam was opened for the first time on D33. After a sejour of several years as responsible for the ILL's chemistry laboratories Isabelle and I were a team once again on a SANS instrument. Isabelle's experience, hard work, meticulous attention to detail and (sometimes unknowingly!) brilliant ideas gave us both some of the happiest and satisfying times in commissioning and establishing the user programme on D33. Together, and within one week, D33 was configured, calibrated and commissioned in monochromatic mode producing high quality data comparable to that of D22 and D11. In the weeks and months that followed the full capabilities of D33 were commissioned and characterised with the instrument entering full user operation in early 2013. Isabelle took good care of D33 from its first neutrons in 2012 until her final day in 2019.

The beauty of contrast variation in SANS for soft matter : playing beyond classical studies in 4-components systems

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We all learn in textbooks that contrast variation is a unique possibility that makes SANS so powerful to probe the “extraordinary structure of ordinary things” in soft matter. But there is a clear difference between reading it and experiencing it by itself. As for my part, I discovered it the very first time I came in Grenoble during my PhD when I tried to probe the structural organization of a few spherical magnetic particles dispersed in a sea of clay nanoparticles that I contrast-matched [1]. It was an unforgettable souvenir and this is in great part because I had the chance to have a young, very efficient and very friendly local contact that arrived just some months ago before at ILL: Isabelle! We did not know at that time that we’ll become good friends later and that we’ll meet so often, when either she was coming in Saclay, when I was coming in Grenoble and during schools we organized together.

Thus, later during my academic career, I tried to push the contrast variation method up to its limit by considering four-components systems. I will show that playing with contrast in such systems remains possible if the system is craftily designed with respect to neutrons, with three of the components having a close SLD, very different from those of the component to be characterized, or if two pairs of components have the same contrast. I will illustrate it by examples taken from representative systems of soft matter : nanocomposites made of polymeric melts reinforced by nanoparticles [2], colloidal suspensions of complexes polyelectrolyte and proteins of opposite charges [3,4], and foams [5].

1. F.Cousin et al, V, *Langmuir*, 2002, 18(5), 1466-1473; F.Cousin et al, *Langmuir*, 2008, 24(20), 11422-11430
2. A.-S. Robbes et al, *Macromolecules*, 2018, 51 (6), 2216–2226
3. J. Gummel et al, *Macromolecules*, 2008, 41(8), 2898-2907
4. J. Gummel et al, *J. Am. Chem. Soc.*, 2007, 129(18), 5806-5807
5. A. Mikhailovskaya et al, *Adv. in Coll. and Int. Science*, 2017, 247, 444-453.

Deuterated Aerosol OT: My favourite molecule for neutron scattering

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The surfactant sodium dioctylsulfosuccinate (Aerosol OT or AOT) is used widely, due to its versatility. It is soluble in water and in oils, and it is surface active and can act as an emulsifier. There are hundreds of papers and patents every year that feature it. This amount of research provides ample opportunities to study AOT-containing formulations using scattering. Aerosol OT is hydrocarbon, so isotopic contrast from neutron scattering is ideal for studying it. It often appears in complex formulations where it is valuable to differentiate between the surfactant and other components. These are the times where the deuterated analogue of AOT, in particular, is useful for gaining information through neutron scattering experiments.

My interest in Aerosol OT is as a charging agent for colloids in nonpolar solvents. This is due to its dual ability to form inverse micelles, which act as a charge screening background electrolyte, and also to interact with colloids, which introduces an ionisable species to an otherwise uncharged particle. Over the last decade, small-angle neutron scattering (SANS) measurements of the binary system of deuterated AOT and hard-sphere PMMA latexes in latex contrast-matched alkane solvent have helped reveal how AOT charges particles in nonpolar media. The best mechanism to consistently explain these data is that the deuterated AOT surfactant is located throughout the whole of the latexes, absorbing inside the particle rather than adsorbing at the interface.

The key measurements to demonstrate this were performed with Isabelle Grillo on D11 at the ILL. Since we first reported this absorption model, I have used deuterated AOT and PMMA latexes to address other questions about the system. Is the distribution of AOT surfactant different to other colloids in nonpolar solvents? How can we modify the surfactant to make it a more effective charging agent? Can the surfactant reservoir be depleted if the particle concentration is increased? I will discuss how I have used deuterated AOT and give my perspective on future plans for using it in the areas of colloid and soft matter science.

Vesicular structure of amphiphilic block copolymers studied by SANS

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Amphiphilic diblock copolymers self-assemble in water solution in stable and robust polymersomes (vesicles), which combined to a chemical design flexibility make them excellent candidates as drug or imaging agent carriers. The introduction of actuator in polymersomes and the engineering of their targeted cell adhesion are critical issues for the applications of disease imaging and therapy. Functionalized polymersomes may respond to physical or chemical stimuli by permeability change, bursting or by other structural modifications of the membrane or of the whole polymersome. Stimuli can be temperature or pH changes, magnetic field application, light irradiation or osmotic shocks...

Small Angle Neutron Scattering (SANS) is perfectly suited to the determinations of the vesicles size and of the thickness and membrane structure of polymersomes. The first example concerns polymersomes with photo-responsive Liquid Crystalline (LC) polymers as hydrophilic block. External stimuli (heating or UV irradiation) have been applied to induce modifications of the LC polymersomes membrane at the molecular level [1,2]. Polymersomes prepared for biological applications could be prepared via osmHybrid vesicles resulting from the self-assembly of amphiphilic copolymers (P) and phospholipids (L) could integrate the bio-functionality of lipids and the improved stability and various coupling chemistries of polymers in a single hybrid vesicular structure. Composition (Polymer/Lipid ratio) and polymer architecture (graft copolymer vs. diblock or triblock) can be varied to obtain either homogeneous or nanostructured membranes. By varying the block length of the hydrophobic polymer, we can tune the thickness mismatch between lipid polymer membranes and play with the conformational constraints of the polymer chains at the L/P boundary. Using the contrast matching method, we could determine the homogeneous or nanostructured character [3] within the membranes of hybrid vesicles.

1. Structural changes induced by temperature variation and magnetic field in liquid crystal polymer vesicle S. Hocine, A. Brûlet, L. Jia, J. Yang, A. Di Cicco, L. Bouteiller, M.H. Li *Soft Matter*, 2011, 7 (6), 2613 – 2623.
2. Polymersomes with PEG Corona: Structural Changes and Controlled Release Induced by Temperature Variation. S.Hocine, D. Cui, M.-N. Rager, A. Di Cicco, J.-M. Liu, Wdzieczak-Bakala, A. Brûlet, and M.-H. Li. *Langmuir*, 2013, 29, 1356-1369.
3. Mixing Block Copolymers with Phospholipids at the Nanoscale: From Hybrid Polymer/Lipid Wormlike Micelles to Vesicles Presenting Lipid Nanodomains, Dao, TPT. ; Brûlet A.; Fernandes, F ; Er-Rafik, M ; Ferji, K ; Schweins, R ; Chapel, JP ; Schmutz, FM ; Prieto, M Sandre, O *Langmuir* 33,7 (2017) 1705-1715. Phase Separation and Nanodomain Formation in Hybrid Polymer/Lipid Vesicles, T. P. Tuyen Dao, F. Fernandes, M. Er-Rafik, R. Salva, M. Schmutz, A. Brûlet, M. Prieto, O. Sandre and J.-F. Le Meins, *ACS Macro Lett.* 2015, 4, 182-186.

Adventures in surfactant wonderland, with Dr Grillo

Speaker: Julian Eastoe¹

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Isabelle and I worked together for 20 years. In that time, we published 51 papers that have been cited over 1800 times. The talk will cover highlights from this collaboration including magnetic surfactants, ionic liquid microemulsions and the search for the Holy Grail in the field of surfactants.

- **Ionic liquid-in-oil microemulsions**
J. Eastoe*, S. Gold, S.E. Rogers, A. Paul, T. Welton, R.K. Heenan and I. Grillo, *J.Am.Chem.Soc.*, 2005, 217, 7302-7303. (333 citations)
- **What is so special about Aerosol-OT? 2. Microemulsion systems.**
J.Eastoe*, S.Nave, R.K.Heenan, D.C.Steytler and I.Grillo, *Langmuir*, 2000, 16, 8741-8748. (178 citations)
- **Anionic surfactant ionic liquids with 1-butyl-3-methylimidazolium cations: characterization and applications**
Paul Brown, Craig Butts, Julian Eastoe*, David Fermin, Isabelle Grillo, HuaiChin Lee, David Parker, Daniela Plana, Robert Richardson, *Langmuir*, 2012, 28 2502–2509. (127 citations)
- **Magnetic Control over Liquid Surface Properties with Responsive Surfactants**
Paul Brown, Alexey Bushmelev, Craig Butts, Jing Cheng, Julian Eastoe*, Isabelle Grillo, Richard K. Heenan, Annette Schmidt, *Angewandte Chemie*, 2012, 51, 2414-2416. (122 citations)

Magnetic disorder in ferrite nanoparticles: a neutron view beyond the classical picture

Speaker: Dirk Honecker¹

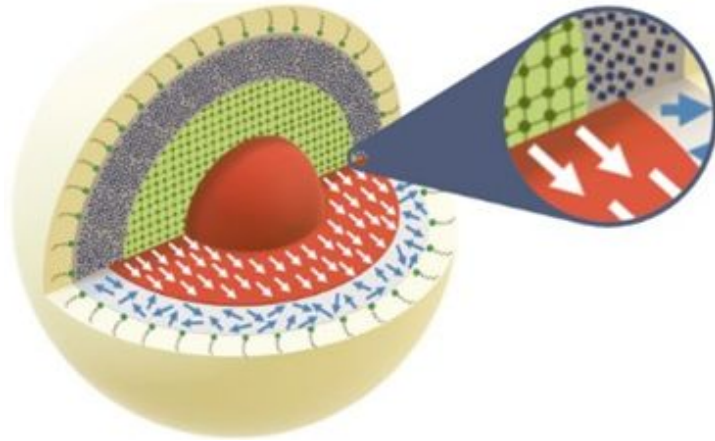
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Magnetic iron oxide nanoparticles offer unique magnetic properties attractive for data storage, spintronics, and biomedical applications. Disorder effects are ubiquitous for nanostructured materials and they crucially influence relevant parameters, like the relaxation dynamics and magnetic hyperthermia performance. Despite the technological relevance, a quantitative interpretation of these perturbances of the spin structure remains a key challenge.

Small-angle neutron scattering is a powerful technique to investigate the structure and dynamics of magnetic materials on length scales between about 1 – 100 nm [1]. Typical investigated systems cover bulk material like chiral magnets and skyrmion hosting materials, shape-memory alloys, Nd-Fe-B based permanent magnets. For magnetic nanocrystals in ferrofluidic dispersion or assembled in densely packed powders, SANS can help to resolve characteristic spin arrangements e.g. reveal the transition from a single-domain to a multidomain state in iron oxide nanoparticles [2].

In this contribution, I will demonstrate how magnetic-field-dependent SANS allows accessing more quantitative information on the spin structure of magnetic nanoparticles. With nm resolution and employing a micromagnetic description of the magnetic structure, neutrons allow distinguishing surface spin disorder from intra-particle disorder contributions in ferrite nanoparticles [3]. Analysis of the data indicates that the total magnetic moment of the particle is strongly field-dependent as the thickness of the magnetically disordered shell reduces with magnetic field.



Representation of the structure (vertical cut) and magnetic (horizontal) morphology of Co ferrite NP [3]. Blue arrows indicate surface spin disorder.

1. S. Mühlbauer, D. Honecker, E. A. Périgo, F. Bergner, S. Disch, A. Heinemann, S. Erokhin, D. Berkov, C. Leighton, M. Eskildsen, A. Michels, *Rev. Mod. Phys.* 91, 015004 (2019).
2. L. G. Vivas, R. Yanes, D. Berkov, S. Erokhin, M. Bersweiler, D. Honecker, P. Bender, and A. Michels, *PRL* 125, 117201 (2020).
3. D. Základná, D. Nížňanský, L.C. Barnsley, E. Babcock, Z. Salhi, A. Feoktystov, D. Honecker, S. Disch, *PRX* 10, 031019 (2020).

Monitoring of protein aggregation by levitation techniques on D33

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The sample environment is a critical component of research programs in advanced materials, geological systems, biology, and energy-related applications.

Over the past ten years, an increasing number of studies on liquid materials have been carried out thanks to container-free sample handling methods. Techniques based on aerodynamics or electromagnetic levitation have created new opportunities for investigating the structure of high-temperature liquids (up to 3000K) and during their glass transition with a very high degree of temperature and chemical composition control.

In this talk, I will present the technique we have implemented to monitor the aggregation of proteins in solution using a Single-axis Acoustic Levitator (SAL) device available at ILL.

Isabelle accompanied me from my first step with the levitator experience. She shared with me the long SANS experiments helping me to solve problems and to find the best solutions to obtain the best results with such a complex set-up.

This will be my way to commemorate her and to thank her for being my ‘shoulder’ during our 10 years of friendship.

From vesicles to nanocomposites, from Saclay to Grenoble and Montpellier, a scientific journey with Isabelle Grillo

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A few examples of experimental studies of soft matter systems will be presented to illustrate some aspects of the personal and scientific journey of Isabelle Grillo. I have met Isabelle for the first time almost twenty-five years ago in the Bombannes school, and since then a combination of geographic coincidence, common scientific topics – from surfactant systems to polymer nanocomposites –, and a shared interest in a technique, neutron scattering, made us walk some steps of this journey together. While the extra-ordinary structure of many of the systems Isabelle took interest in will be presented by world-leading experts in this symposium, my presentation will shortly highlight vesicular structures, and then bridge the gap between PhD work supervised by us on nanocomposites to our current understanding of the structure of such nanomaterials.

How to produce responsive aqueous foams based on green surfactants?

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Soft materials, such as foam and emulsion systems, which respond to external stimuli, are on the leading edge of materials research and have recently been of interest to many scientists, such as Isabelle Grillo. The macroscopic responsivity relies on the ability to react at microscopic or mesoscopic scales. Stimuli-responsive surfactants that can change their structure in response to a trigger such as pH, temperature or light have attracted great attention due to their versatile applications in various fields. A change in the molecular structure of the surfactant activated by stimuli can affect the self-assembled structure in water and the interfacial activity, which can in turn tune the properties at the macroscopic scale such as emulsion and foam stability. Responsive foams correspond to foams for which stability can be reversibly tuned between ultrahigh stability and immediate destabilization under stimuli [1].

Fatty acids are anionic surfactants of particular interest since they can be extracted from agricultural resources and are available in large amount in nature. These biomolecules can be qualified as green surfactant with both biodegradability and low toxicity. Fatty acid molecules can self-assemble under various shapes in aqueous solution [2]. These self-assembled structures can respond to stimuli such as pH and temperature due to changes occurring at the molecular level [2]. These specificities make them green surfactants of special interest to tune the foam stability.

Our approach to produce responsive foams from fatty acid self-assemblies is to use the links between the microscopic, mesoscopic and macroscopic scales. The prerequisite to produce these smart foams is a perfect understanding of the mechanisms leading to changes of self-assembled structures both in bulk and at the air/water interface under stimuli. These structural changes are determined by neutron scattering. We developed a green formulation: 12-hydroxystearic acid (12-HSA) mixed with counterions (alkanolamine) of different chain lengths, and at different molar ratio R between 12-HSA and the counterions [3-4]. We will illustrate how both SANS and neutron reflectivity are fundamental techniques to obtain the key information to produce thermoresponsive foams based on this system [5]. We will also discuss how these systems can be made to be photo- as well as magneto responsive [6-7]. Systems, such as those presented here, could find application in a wide range of industrial and environmental processes that require controlled, non-contact and on-demand defoaming.

1. Fameau et al., *ChemPhysChem*, 2015, 16, 66.
2. Fameau et al., *Advances in Colloid and Interface Science*, 2014, 207, 43.
3. Fameau et al., *Langmuir*, 2017, 33, 12943.
4. Fameau et al., *SoftMatter*, 2018, 14, 2578.
5. Fameau et al., *Angewandte Chemie International Edition*, 2011, 50, 8264.
6. Fameau et al., *Chemical Science*, 2013, 10, 3874.
7. Fameau et al., *Chemical Communications*, 2015, 51, 2907.

Nano-ions in solution

Speaker: Olivier Diat¹

Co-author(s): Pierre Bauduin¹ ; Luc Girard¹ ; Alban Jonchère¹ ; Coralie Pasquier¹

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Beyond electrostatic, the interaction of ions with their close environment depends on their hydration shell and the water dynamic in this environment. Non-negligible water mediated effects can indeed influence many physical chemistry processes such as cloud point, protein salting-in or out, bubble coalescence, the topology of bilayers... They are thus qualified of “ion specific”. During the last 10 years, we have shown that these effects can be exalted with nanometric ions. These latter can indeed bind to electrically neutral matter in solution although highly charged but always characterized by low charge density. This nano-ion specific effect, called superchaotropic effect in referring to an extension of the Hofmeister series, arises from the partial dehydration of both the nano-ion and the solute or surface in interaction that lead to a significant gain in enthalpy of the system. The characterization of this effect is strongly supported by scattering experiments, neutron and x-ray, always in a very complementary manner and also by other spectral techniques that allow to precisely defined the predominant chemical functions in interaction with the nano-ions that can vary depending on their supramolecular environment. Some examples and perspectives of these studies will be presented in this paper.

Spontaneous Ouzo emulsions co-exist with pre-Ouzo ultra-flexible microemulsions

Speaker: Sylvain Prévost¹

Co-author(s) Isabelle Grillo¹ ; Olivier Diat² ; Thomas Zemb² ; Werner Kunz³

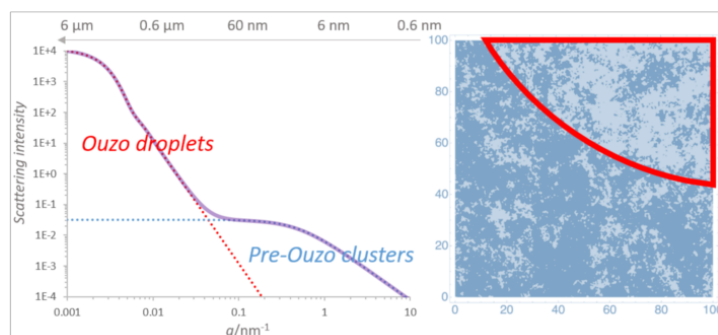
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In 2003, Isabelle Grillo published a highly publicized article on *Le Pastis*, analyzing with SANS the large-scale structure of droplets responsible for the famous milky appearance of this Mediterranean drink. At the same time, the seminal article of Vitale and Katz on the “Ouzo effect” appeared. These two references kindled an ever-growing field of applied and fundamental research. Isabelle recently worked with Leonardo Chiappisi on a South-Italian drink, “*Limoncello*”, where droplets are formed whose size remains much smaller than for Ouzo. With her continuous interest in such common and (only) seemingly simple systems, Isabelle and I joined the team led by Thomas Zemb and Werner Kunz on “*pre-Ouzo*”: nanoscale fluctuations of concentrations in mixtures of liquids, otherwise known as UltraFlexible MicroEmulsions or Surfactant-Free MicroEmulsions, to understand their relation to the Ouzo phenomenon. SAXS data on ID02 and SANS data on D11 and D33 at ILL demonstrated that Ouzo is in fact a metastable equilibrium between **two fluids with nanoscale organization**. I will show the current results of our work and the future steps we will undertake to reveal the complexity of these ordinary fluid mixtures.



Co-existence of Ouzo and pre-Ouzo as seen by by Small-Angle Scattering

Galenic-on-chip, Emulsions and micelles along the flow

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Isabelle was deeply fascinated by the beauty of many simple things, including unspoiled natural landscapes and the beauty of the self-assembly of amphiphilic molecules. To honor her memory and send her a wink, I will tell you a short light-hearted story where these two passions once met.

But before that, I would like to share with you some recent results that illustrate how self-assembly and scattering experiments, two domains where her contribution is outstanding, can contribute to new routes to produce and test nanomedicine.

1. N. Rolley, M. Bonnin, G. Lefebvre, S. Verron, S. Bargiel, L. Robert, J. Riou, C. Simonsson, T. Bizien, J.-C. Gimel, J.-P. Benoit, G. Brotons and B. Calvignac, "Galenic Lab-on-a-Chip concept for lipid nanocapsules production". *Nanoscale*, 2021, 27
<https://doi.org/10.1039/D1NR00879J>

Tuning Ionic Liquids – a Small-Angle Scattering Study

Speaker: Sarah Rogers¹

Co-author(s) Christopher Cabry² ; Duncan Bruce³ ; Isabelle Grillo⁴ ; John Slattery³ ; Julian Eastoe⁵

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Ionic liquids (ILs) are molten salts that are liquid at relatively low temperatures. They are composed of sterically mismatched ions that hinder crystal formation and are often defined as salts with melting temperatures below 100 °C, though many are liquid at room temperature and below [1].

Recently, there has been great interest in ILs as their unusual combination of properties, such as, low vapour pressures, wide electrochemical windows, good thermal stabilities, and the ability to dissolve a wide range of solutes, has led to their use in a wide range of areas. These include, but are not limited to, as reaction media for sustainable chemistry, in the electrochemical deposition of metals and semiconductors, catalysis [2], nanoscience [3], biomass processing [4], carbon capture and storage [5], and analytical chemistry [6].

One of the advantages of ILs is that their physicochemical properties can be tuned by changing the anion, cation, or both. For this reason, ILs are often described as “designer solvents”. Recent studies have shown that a library of liquids with a range of properties can be produced by mixing two or more ILs [7]. However, whilst many studies on pure ILs have been performed [8], comparatively little is known about the fundamental properties of IL mixtures and how these relate to their composition.

The structure of ILs in the bulk are critical to many of their applications. In the bulk, the amphiphilic nature of many IL ions results in nanosegregation of the liquid into polar and nonpolar domains [9], leading to the development of nanostructures that have been studied using a range of experimental and computational approaches [8]. Much less is known about the nanostructures formed within mixed IL systems and how these effect their physicochemical properties [10].

Alongside laboratory-based techniques such as rheology and surface tension, we have used the complementary techniques of small-angle neutron and X-ray scattering (SANS and SAXS) to study the bulk structure of mixed IL systems in a systematic fashion. The systems of interest are mixtures of [C_nMIM][Tf₂N] – varying the chain length, *n*, of the cation between 2 to 12.

Selective deuteration of the chain on the cation has been utilised during the SANS measurements and has allowed us to gain a detailed view of the nanosegregation within the systems under study. This has moved us one-step further in determining how different the chain lengths need to be in order for aggregation to occur.

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Unlocking the properties and dynamics of commercial oil additives using SANS

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Additives are used in lubricant systems to minimise destructive processes in the engine (e.g. wear and corrosion) and to confer beneficial properties (e.g. more uniformed viscosity with temperature and improved fuel economy). Lubricant formulations typically up to 10 ingredients, comprising mixtures of amphiphilic species: surfactants, polymers, sols and inorganic salts dispersed in non-aqueous media. Producing stable formulations with the requisite performance properties is vital to successful product development. In collaboration with Isabelle, the D22 Small Angle Neutron Scattering (SANS) instrument at ILL has been used to investigate the mechanism and dynamics of product performance and stability.

- **Mechanism of Product Performance:** Overbased detergents are an integral element of additive systems, comprising surfactant stabilised calcium carbonate particles. Such particles represent “model” hard-sphere systems with narrow polydispersity and mean core radius in the range 2 – 5 nm. They are used to neutralise acid species introduced into the lubricant through acidic blow-by gases. In addition, the detergent helps maintain piston cleanliness. With the increased use of exhaust gas recirculation in diesel engines (used to reduce the level of NO_x by reducing combustion temperature), there is increased interest in the factors affecting acid neutralisation kinetics. The mechanism of acid neutralisation for small, acid-containing microemulsion droplets and for larger (acid containing) emulsion droplets the SANS measurements have been performed as a function of percentage neutralisation.
- **Surfactant Competition influencing stability:** Interaction/ competitive adsorption between lubricant additives can result in product instability. Stopped flow SANS has been performed on specially deuterated commercial additives to investigate the mechanism and dynamics of such interactions.

The elucidation of microemulsion properties – my scientific journey with Isabelle

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The journey together with Isabelle started 20 years ago in February 2000 at D22. The goal of these studies was to find the mechanism behind the dramatic enhancement of the solubilisation efficiency of ordinary surfactants obtained by adding only traces of amphiphilic diblock copolymers. Performing high-precision two-dimensional contrast variation SANS measurements [1] we could demonstrate that the polymer is distributed uniformly in the surfactant membrane where it influences its bending rigidity, saddle-splay modulus and curvature. Although being highly relevant for washing, tertiary oil recovery, etc. the efficiency boosting effect is so far only rarely used in technical application. One drawback is the difficult large-scale synthesis of the originally applied polyethyleneoxide–polyethylpropylene polymers. To circumvent this drawback we very recently applied a new class of poly(ethylene oxide)-b-poly(alkyl glycidyl ether) block copolymers [2], which excel by an easy scalable synthesis, to microemulsions containing long chain n-alkanes and technical relevant waxes [3]. Interestingly, only by the use of this new class of polymers an efficient solubilization of these large oil molecules is obtained [4]. As friendly users, Isabelle in 2012 gave us the chance to study the formation of kinetics of polymer-free microemulsion shortly after the commissioning of D33, which turned out to be of the order of a few milliseconds [5]. In future we plan to study the influence of these polymers on the formations kinetics of microemulsions using Isabelle’s favored spectrometer.

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SANS and SAXS on pluronic and hyaluronic acid mixed with essential oils

or how to do a very elegant and simple hand cream

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To illustrate the title of Isa's tribute "the extraordinary structures of ordinary things", I will present Isa's latest personal research work in which I had the chance to participate. Her study focused on the structure of complex solutions obtained from essential oils, micelles of pluronic and from hyaluronic acid. Her goal was to make an elegant and simple hand cream. The birth, chronology and methodology of this work, as well as the quantity and quality of the SAXS and SANS measurements and fittings, perfectly define who Isabelle was. She loved science and art ; she practiced science as she created paintings, mosaics, statues... with perseverance and until she obtained the most aesthetic results. My wish today is to take a journey through both science and artworks, presenting both scattering curves and her artistic creations, for a time, make them or her live again.

Understanding the interfacial behaviour of bile salts, a key to their roles during fat digestion

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Regulating fat (dietary lipid) digestion to tackle the ongoing obesity crisis has become a pressing issue. Bile salts (BS) are biosurfactants produced in the liver and released into the small intestine, which play key roles in lipid digestion and absorption: they facilitate enzyme adsorption to fat droplet interfaces and remove insoluble lipolysis products from the interface, carrying them to the gut mucosa for absorption. It is suggested that BS structural diversity is responsible for these contrasting functionalities (1). Our objective is to correlate BS molecular structure with their interfacial properties to shed light on the mechanisms governing their different functions in lipolysis. Two BS constituting 15% of human bile were selected, sodium taurocholate (NaTC) and sodium taurodeoxycholate (NaTDC), which differ only by one hydroxyl group but display contrasting adsorption/desorption dynamics (1). Their adsorption behaviour at the air/water interface and their interaction with a phospholipid monolayer – a preliminary mimic of physiological fat interfaces – were assessed using a Langmuir trough and ellipsometer, and the interfacial film structure characterised by Brewster angle microscopy, X-ray and neutron reflectometry. NaTC was found to exhibit a high affinity for the interface, while NaTDC was shown to remove DPPC molecules from the interface, through a dynamic exchange (2). NaTC may thus facilitate enzyme adsorption onto fat droplet surfaces, whereas NaTDC may displace lipolysis products from the interface. BS micellisation was studied using pyrene fluorescence spectroscopy and small-angle neutron/X-ray scattering. NaTC was found to form smaller micelles from a higher critical micelle concentration (CMC), compared to NaTDC (3). Interestingly, BS interfacial properties correlate with their bulk aggregation: both BS preferentially adsorb at the interface below their CMC and desorb above that value.

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Engineered soft-matter nanosystems for large scale delivery of bioactive molecules

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Nanovectors are used for delivery purposes in many fields. First developed for biomedical and pharmaceutical applications, they have recently been extended to large scale processes and agriculture. Although soft matter materials such as lipids and polymers are generally considered biocompatible, in recent times concerns have been expressed regarding the sustainability of the whole process from preparation to final administration. In order to comply with these issues, different pathways can be followed. Here the possibility of obtaining nanovectors from sustainable and eco-friendly sources will be addressed. In particular, by-products from agriculture and biomasses obtained from algae are proposed as source to build up engineered soft matter nanosystems for delivering bioactive molecules to plants. The reuse of olive pomace, a lipid-rich waste material in the olive processing, is firstly discussed for delivery phyto-hormones that are scarcely bioavailable, due to low solubility in water media. This allows to combine cost-effectiveness and environmentally friendly procedures. The implementation provided by adjuvants, such as purified natural lipids which form more stable and well-defined nano-objects, is also discussed. Newly formulated lignin nanocapsules are then proposed as vectors for natural pesticides and fungicides, such as neem oil and capsaicin, in the framework of circular economy. Finally, algae grown in nitrogen-deprived culture media, that are known to provide biomasses with increased lipid content, are proposed as carriers for natural anti-oxidants with broad spectrum of action.

In all these systems the in depth physico-chemical characterization of plain and loaded vectors is a fundamental requirement to control stability and optimize the release of cargo molecules. We thus applied Dynamic Light Scattering, Zeta potential, Small Angle X-ray Scattering and Electron Microscopy to get a comprehensive picture of the overall nanoparticle size, surface charge and internal structuring.

Assays of cytotoxicity and cargo release were carried out in model plants and cell lines and in all cases a remarkable enhancement of the loaded principle activity could be evidenced with respect to conventional treatments, indicating that the new formulations here fabricated have strong potentiality for large-scale administration in the context of sustainable economy.

Dense solutions of polyelectrolytes and interpolyelectrolyte complexes

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The intrinsic stiffness of polyelectrolytes plays an essential role in the structure of their dense solutions and the ones of interpolyelectrolyte complexes.

First, we will report SAXS and SANS experiments performed on dense aqueous solutions of highly charged polyelectrolytes that reveal the existence of an Onsager transition preceded by a new regime, both depending on the intrinsic stiffness of the macroions as well as the ionic strength of the solutions. Four macroions with increasing non-electrostatic persistence length will be considered: poly(styrene sulfonate) (PSS); poly(α -methyl styrene sulfonate) (P α MSS); poly(diallyl-dimethyl ammonium) (PDADMA); hyaluronan (HA).

Second, we will report SAXS and SANS experiments performed on aqueous solutions of model interpolyelectrolyte complexes. The complexation between polycations and polyanions in the semidilute and concentrated regimes can then be described as a gelation process. This analogy is reliable for both couples PSS-PDADMA as well as HA-PDADMA and can be considered as universal. There is however a difference between these two complexes, which is associated with the primary self-assembling process. PSS and PDADMA interact through monomer units forming point junctions randomly dispersed in the semidilute or concentrated solution, while HA and PDADMA interact through long sequences of macroions. This results from the difference in the polyanion intrinsic stiffness.

SAXS/SANS and contrast matching: a unique key to highlight the structure-property relationships for petroleum industry related systems

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Knowing the refined structure of complex crude oils and the mechanisms of actions of these structures is of a central interest to understand and predict the behaviors of the petroleum fluids for many industrial applications: oil production, transportation and refining, enhanced oil recovery or gas sequestration. Crude oils are well known to be complex mixtures made of many different constituents. Among them, Asphaltenes are the enigmatic fraction of petroleum that can act as natural surfactants to stabilize water-in-oil emulsions, foams, to interact with flat surfaces or porous media and finally to drive the macroscopic properties of the fluids (viscosity, flow behavior, phase separation, affinity for interfaces etc...). Since twenty years, it has been demonstrated with pioneers works of Espinat [1] that small angle scattering techniques, namely SAXS and SANS, are very powerful to identify supramolecular structure of the Asphaltenes entities. Starting from that, we developed fifteen years ago a long term fruitful collaboration between IFPEN and LLB and ILL with Isabelle to address these critical questions by focusing on the use of specific neutron contrast variations on multi-components petroleum systems while associating SANS and SAXS. During the workshop, we will present three dedicated relevant examples of such unique approach (i) the characterization of the interfacial Asphaltenes layer in water-in-oil emulsions in line with the emulsion macroscopic stability [2] (ii) the first quantitative modeling of the Asphaltenes nano-aggregates [3] and (iii) a new methodology to probe in-situ the foam flow in porous media [4-5].

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Observing Assembly Processes in Colloidal Systems by Means of Stopped-Flow Experiments – Soft Matter in Motion

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Self-assembled systems composed of surfactants, copolymers, and/or polyelectrolytes exhibit a large variety of different structures in aqueous solution that depend in a subtle way on the molecular structure of the components, the composition of mixtures, concentration, and external parameters such as pH, ionic strength, temperature, etc.

The formation of such self-assembled structures is typically a highly dynamic process, but one where the typical time scales for structural changes can vary largely from nanoseconds to weeks and months. In many situations morphological changes in amphiphilic systems can be triggered by mixing with other surfactants, additives, or solubilisates. In our experiments, we concentrated on the time range of ms to many mins, a time range that can be studied well by means of the stopped-flow technique. Such experiments can be done in the lab by employing turbidity, conductivity, fluorescence, or DLS as detection methods. However, they can also be coupled to high-flux SANS/SAXS instruments, which allow to obtain detailed structural information in the size range of 1-1000 nm, with a time-resolution of 5-50 ms.

With this approach a variety of different morphological transitions was investigated, e.g. the formation of unilamellar vesicles or lamellar phases by mixing oppositely charged surfactant or adding a cosurfactant, as well as the solubilisation of hydrophobic compounds in micellar solutions, leading to micro- or nanoemulsions. Such processes like the formation of monodisperse unilamellar vesicles take place in a way purely governed by diffusion. In the particular case of vesicle formation, they proceed either via disk-like or rod-like intermediates. Their formation as well as further ageing processes can be described by means of the bending energy of the respective bilayers. The structural progression of such systems can be modelled by simple simulations which allow to understand the ageing processes in terms of simple coalescence processes. For the case of oil solubilisation clear correlations between the type of oil and surfactant can be observed. Finally, also the case of formation of interpolyelectrolyte complexes was studied, which depends largely on the type, but also Mw of the polyelectrolytes studied and can proceed via a number of different transformational steps.

In summary, the kinetics of self-assembly is typically much more complex and variable than their phase behaviour and can vary largely with respect to their time scales. It is very important for understanding the properties and can also be central to structure formation, if that is kinetically controlled.

Self-association of clay platelets with or without other colloids as probed by SAXS and TXM imagery

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We had the privilege to collaborate time to time with Isabelle. We have been able to appreciate her exceptional scientific and human qualities. We had a common interest deciphering colloidal “portrait de phases” of mixed systems involving clay platelets and other partners such as magnetic spherical particles [1] or surfactant lamellar phases [2-3]. These works have paved the road to new researches in our group and I will present today one of them, related to self-association of clay platelets during flocculation by inorganics salts [4].

Combining SAXS patterns and Transmission X-ray Microscopy (TXM) projection images of unperturbed water suspensions, it was observed that small angle scattering evolves as $q^{-\alpha}$ on a large range of correlation lengths. Moreover, depending of the nature of the inorganic salt in water suspension, the exponent α can vary from 2 to 4. Meanwhile, as α increases, the pseudo 001 correlation peak is reinforced. An analytic model is proposed to explain such an evolution of SAXS patterns, showing that a cross-over from ($\alpha \geq 3$) to ($\alpha < 3$) appears without any geometrical transition but strongly depends on the lateral stacking disorder. Actual extension of this work to the case of concentrated associations of clay platelets and spherical particles is underway and will be outlined.

These different works reinforce our feeling that a bottom-up approach involving SAXS, SANS and 2D-3D imagery technics is highly needed for these types of multiscale complex systems.

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Polymer - Surfactant complexes

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Polyelectrolytes (PEs) are polymers with ionisable groups that dissociate in water. This water-solubility is a remarkable property commonly used in industrial formulations (thickener, gel...). The presence of electrical charges opens up additional possibilities through the formation of electrostatic complexes with oppositely charged species (colloids, surfactants, PEs, proteins...) leading to new potential applications (flocculent, drug delivery, chemosensors, coatings...).

The structure of these complexes results from a subtle balance between hydrophilic, hydrophobic and ionic interactions but also depends on the intrinsic stiffness of the polymers and the shape of the oppositely charged assemblies [1]. The organisation of the complexes is a fundamental point to control in order to improve applications. That concerns the average conformation and the dispersion state of the polyions, but also, the organization of the oppositely charged species. In this context, small angle neutron scattering (SANS) combined with isotopic substitution and contrast variation is the best technique since it allows to determine the partial structure functions of the different components and the form factor of the polyions in the dilute or semidilute regimes.

In this presentation, we focus on PEs / oppositely charged surfactant systems. The complexation can lead to different organisations according to the properties of the different constituents [2]. We considered mixtures of sodium sulfonated polystyrene (PSSNa, highly charged flexible PE) and oppositely charged dodecyltrimethylammonium bromide surfactants (DOTAB). Experiments were performed on D33 (ILL) in the semidilute regime for different surfactant concentrations. Solution of hydrogenated surfactants and hydrogenated or deuterated polyions in H₂O/D₂O were used to reveal the different structure functions.

The organisation of the PSSNa/DOTAB complexes will be presented and discussed in the light of the monomer and surfactant partial structure functions as well as the form factor of the polyions.

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The Concept of Melting Point Lowering due to Ethoxylation

Speaker: Werner Kunz¹

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Most of the commonly used Ionic Liquids (ILs) contain bulky organic cations with suitable anions. With our COMPLET (Concept of Melting Point Lowering due to Ethoxylation), we follow a different approach. We use simple, low-toxic, cheap, and commercially available anions of the type $C_x(EO)_yCH_2COO^-$ to liquefy presumably any simple metal ion, independently of its charge. In the simplest case, the cation can be sodium or lithium, but synthesis of Ionic Liquids is also possible with cations of higher valences such as transition or even rare earth metals.

Anions with longer alkyl chains are surface active and form surface active ionic liquids (SAILs), which combine properties of ionic and nonionic surfactants at room temperature. They show significant structuring even in their pure state, i.e., in the absence of water or any other added solvent.

In particular, we studied the octyl ether octaethyleneoxide carboxylic acid ($[H^+][C8E8c^-]$, AkypoTM LF2), with partial replacement of H^+ by Na^+ and Ca^{2+} in its pure state and in mixtures with water as well as with dodecane. The resulting phase diagrams are remarkable. The surfactants always form spheroidal or only slightly prolate direct micelles, from the dilute aqueous solution via interdigitated micelles in the pure IL state and even when oil is added to the pure IL without water. Further, this type of surfactants (CiEi-carboxylates) shows a completely different type of lower critical separation behaviour: the dynamic equilibrium is between highly cross-linked and classical core-shell globular micelles since micellar shape-transitions are sterically forbidden.

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The limits of mixing of clay- and bilayer -based lamellar phases

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Isabelle's Grillo PhD goal in 1998 was to explore the conditions and therefore the limits of mixing synthetic anionic clays and all known types of surfactant-based lamellar phases: anionic, nonionic and cationic.

Only a fraction of the conditions of mixing, including osmotic pressure compatibility, adsorption and depletion effects were understood at that time. Isabelle Grillo published core knowledge in 2001, 2004, 2008 and 2011.

In this talk, we will summarize the seminal inputs of Isabelle Grillo in the characterization and therefore understanding of mixing “flat” colloids in known phase diagrams. We will illustrate further steps based on Isabelle's findings by the papers published since then.

Posters

Bulk properties of aqueous graphene oxide and reduced graphene oxide with surfactants and polymers: adsorption and stability

Presenter: Thomas McCoy¹

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A diverse range of molecular surfactants and polymers have been incorporated into aqueous graphene oxide (GO) and reduced graphene oxide (rGO) dispersions in order to understand the complex relationship between surface chemistry, surface forces and interfacial thermodynamics of these materials with typical amphiphiles. Surfactant additives were systematically varied in terms of their charge and hydrophobicity to reveal important structure–function relationships affecting adsorption and interaction with GO and rGO surfaces. Small-angle (and ultra small-angle) neutron scattering was employed to examine and monitor the interactions and self-assembly in each system. Modelling the neutron data revealed in many cases a q^{-2} slope in the low q and ultra low q regions, indicating that scattering was occurring from large, flat surfaces (lamellae or bilayers), suggesting an effective flattening of the sheets in dispersion. The results presented thus help to form a roadmap for the behaviour of GO and rGO with surfactants and polymers, relevant to adsorption, stabilisation, formulation and coating in aqueous environments as adsorbent and functional materials.

Characterization of ionic liquid films in mesoporous SBA-15 by small-angle X-ray scattering

Presenter: Nadine Schnabel¹

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The immobilization of molecular catalysts in confined geometries of mesoporous support materials has been shown to selectively control the catalytic performance. An additional increase in yield and selectivity of catalytic reactions are expected by combining the spatial confinement of the pores with that of a thin ionic liquid film at the pore surface. Small angle X-ray scattering (SAXS) can provide an important contribution to the structural characterization of such materials. To prove the efficiency of this method, mesoporous silica materials with cylindrical mesopores ordered in a two-dimensional hexagonal lattice and a defined pore radius of 3.1 nm were filled with imidazolium based ionic liquids and investigated with SAXS. Using comprehensive multi-scale scattering models [1], we found that the scattering data can be quantitatively analysed considering the scattering contributions from the silica grain surfaces [2], as well as meso- and micropores by combining appropriate form [3] and structure factor [4] models. This enabled us to determine the key structural parameters of the mesoporous silica materials, such as the lattice parameter, the pore radius as well as the thickness and correlation length of the microporous corona. Finally, the growth of the ionic liquid film, induced as the porous materials became increasingly loaded with ionic liquids, could be monitored on the Angström scale by systematic SAXS measurements.

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Efficiency Boosting of Surfactants in Microemulsions with Novel Amphiphilic Poly(ethylene oxide)-poly(alkyl glycidyl ether) Polymers

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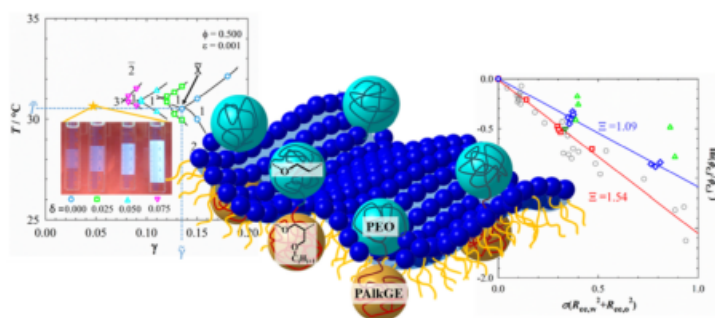
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By adding small amounts of amphiphilic diblock copolymers like poly(ethylene oxide)-co-poly(ethylene propylene) (PEO-PEP) to water – oil – non-ionic surfactant systems, Jakobs et al. showed that the efficiency of medium-chain surfactants to solubilize equal amounts of water and oil can be strongly increased (so-called efficiency boosting) [1]. In order to obtain a similar boosting while circumventing the drawback of a difficult large-scale synthesis, two new types of amphiphilic polymers were used in this work, namely poly(ethylene oxide)-poly(alkyl glycidyl ether)s (PEO-PAlkGE) and their carbonated poly(ethylene oxide)-poly(carbonate alkyl glycidyl ether) derivatives (PEO-PCO₂AlkGE) [2]. By studying their influence on the phase behavior of ternary non-ionic microemulsions containing different oils, ranging from the medium-chain *n*-decane (C₁₀H₂₂) to the long-chain *n*-octacosane (C₂₈H₅₈) to the technical-grade Sasolwax 5805 (equivalent alkane carbon number of 30.8), a significant increase in efficiency was found for both types of amphiphilic polymers [3]. This strong boosting effect was further observed for systems with technical-grade surfactants, which could be of interest for industrial applications where a reduction in surfactant needs is of substantial economic as well as ecological advantage. Endo et al. attributed this strong increase in efficiency to the adsorption of the amphiphilic copolymer molecules into the surfactant membrane, whereby the boosting was found to scale with the number density of copolymers in the membrane and the end-to-end distances of the hydrophilic and hydrophobic polymer blocks [4]. In this work, end-to-end distances of PEO and PAlkGE blocks were determined by small-angle neutron scattering or calculated from literature. For *n*-decane microemulsions, the boosting effect of the new PEO-PAlkGE's and the extensively investigated PEO-PEP's could be scaled on top of each other. A different scaling was found for *n*-octacosane microemulsions, which was attributed to the polymers behaving more like ideal chains at elevated temperatures.



Efficiency Boosting with PEO-PAlkGE Block Copolymers

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How a hydroxyl group on hydrophobic chain can change surfactant self-assembly?

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With global warming, green chemistry has experienced a great development. In this context, fatty acids are surfactants of particular interest since they can be extracted from agricultural resources. The use of an organic counter-ion enables their solubilization in aqueous solution at room temperature where they self-assemble into different supramolecular structures.

Stearic Acid (SA), one of the most common fatty acids in nature, self-assembles in lamellar phases in water[1]. In the other hand, the 12-Hydroxy-Stearic-Acid(12-HSA) fatty acid, self-assembles (using the same counter ion) in micrometric long multilamellar tubes[2]. Their packing parameter is very similar, and both structures are thermo-sensitive with a transition towards spherical micelles above a threshold temperature, which is however very different from SA to HSA.

In this sense, we have studied the behaviour of SA/12-HSA mixtures in order to find out how this OH group in 12-HSA's main chain influences thermally, structurally and mechanically the self-assemblies. To determine the structure and thermal properties of the SA/12-HSA self-assemblies, we used different techniques such as DSC, transmittance measurements and SANS experiments. We demonstrated that a doping of SA by a few amount 12-HSA molecules induces strong structural rearrangements whereas the reverse, i.e. doping 12-HSA by SA, almost does not change the structure. By rheology we have found three different modules (G' and G'') states according to the SA/12-HSA ratio.

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Limoncello and the art of mixing water and oil

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Whoever tried to prepare homemade mayonnaise, knows how much energy input the formation of water/oil emulsions require. In addition to that, in order to provide stability to the emulsion, the presence of components which stabilize the system are required. This role is played by some of proteins and the lecithin contained in the egg yolk, for the case of mayonnaise. In most of other emulsions, surfactants and polymers are used to provide stability to the emulsion.

In a different approach, meta-stable emulsions can be prepared when three liquids, two partly miscible liquids (water and oil) and a common solvent, such as ethanol, are mixed. Close to the phase-separation boundary, strong composition fluctuations take place. In this portion of the phase diagram, called ‘Ouzo region’, the formation of 100-1000 nm sized oil rich domains are found. The name ‘Ouzo’ derives from the famous Greek liquor, which exhibits a typical opalescence when diluted with water, due to the formation of anethole (the oil) rich droplets.

In this contribution, we focus on Limoncello, the famous Italian liquor based on lemon essential oils. In contrast to similar, ‘Ouzo-like’ systems, Limoncello shows an exceptional stability. Small-angle neutron scattering was used to probe the microscopic structure of Limoncello, revealing the presence of self-emulsified submicrometer small droplets, whose size shows only little variation in a large range of composition and temperature. These findings open two fundamental questions to be addressed in forthcoming studies: what are the physical forces leading to the formation of oil domains with such an exceptional size and what is the mechanism guaranteeing a long term stability to Limoncello systems.

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

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

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Microflow-induced Structural Changes of Bicontinuous Microemulsions Studied by SANS

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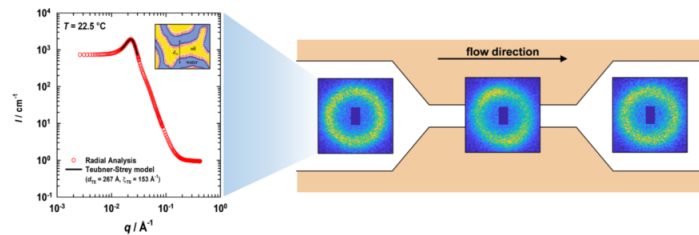
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Understanding and engineering the flow-response of complex fluids made by surfactant membranes is a key challenge for their practical utilization. Nevertheless, the predicted sponge-to-lamellar transition of self-assembled surfactant membranes upon shear flow [1] has, to our knowledge, only been shown for surfactant bilayers [2,3]. The lack of experimental reports of such a transition for the monolayer analogue, namely a bicontinuous microemulsion, can be justified by the extraordinarily high shear rates required for the transition, which exceed the limitations of most rheological setups. For the first time and via the combination of small-angle neutron scattering (SANS) and microfluidics [4], we are able to show a gradual deformation of a monolayer sponge to a lamellar-like structure with applied flow. In order to achieve this deformation, we expose different bicontinuous microemulsions stabilized by a nonionic surfactant (Fig. below, right) to microflows of up to 40 mL min^{-1} , resulting in shear rates above 10^5 s^{-1} . The orientation-dependent analysis of the SANS patterns reveals the increasing formation of lamellar layers which, however, seem to be connected via passages even at these high shear rates. The exceptionally high spatial resolution of this method allows us to link structural properties like anisotropy (Fig. below, left) and domain size along with the surfactant membrane rigidity to the variation of the flow field while we probe sample volumes of down to 10 nL. As it turns out, the structure does not only vary with the flow applied but also within the flow field itself. Furthermore, one is able to amplify this response by modifying the surfactant membrane elasticity through decoration with amphiphilic diblock copolymers, known also for their efficiency boosting effects [5].



(Left) SANS curve of a bicontinuously structured microemulsion, fitted with the Teubner-Strey model [6] (Right) 2D-scattering patterns of the same system under flow before, inside, and after the constriction of a Microfluidic SANS chip.

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Monitoring food enzymatic digestion by small angle scattering

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Proteins – here dairy and plant proteins (the latter being environmentally advantageous), are crucial macronutrients, but they also structure food. They form structures at multiple spatial scales, in particular in gels. Those are prepared from milk at low pH or enzymatically, or from an isolate of cruciferin and napin from canola seeds by heating.

To obtain structural information on digestion mechanisms, a multilength and multi-time scale monitoring was developed in vitro (gastric and intestinal steps – cf. Infogest protocols). Results: Neutron imaging (ICON, PSI) gives information at micron scale: on milk gels - casein network and fat globules, and on canola gels (aggregates), monitored under digestion. At nanometric scale, as seen accurately by Small-Angle Neutron (completed by X Rays) Scattering, reorganization under digestion makes vanish the largest objects at the profit of mini-micelles in sponge-like casein, or of mini-clusters of canola proteins after progressive unfolding. In parallel, rheology shows a loss of the network connectivity until complete deconstruction, while UV microscopy shows progressive diffusion-reaction inside a 50-200 μm gel piece with apparent external erosion of the gel.

Interestingly, coupling these methods enables to tackle the problem of the intrinsic heterogeneity of samples during digestion. It is (i) prevented by cold digestive juice imbibition for big samples for SANS, neutron imaging, and rheology (ii) observed directly by microscopy, or by spatially scans with Synchrotron X rays. Using different preparations (acid versus rennet dairy gel, or variable pH for canola) leads to clear differences in initial structures, and in their evolutions before complete deconstruction. Conclusions: The feasibility of finely linking the behaviors at the lowest scales with the larger ones, can be extended to different proteins, and other foods. In particular neutron contrast matching possibilities enables to study multi-ingredients food.

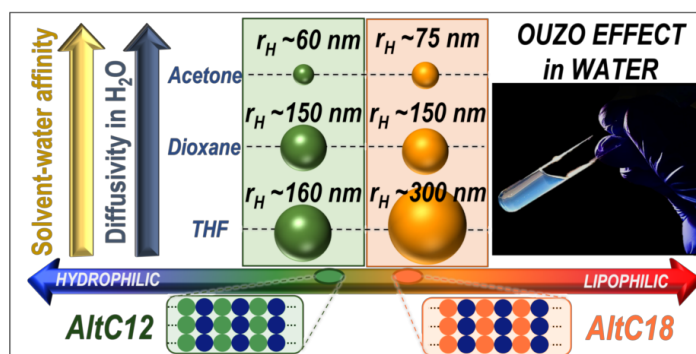
Ouzo phase occurrence with sequence control copolymers: influence of the lateral amphipathic units on the size and structure of nanoparticles

Presenter: Henrique Trevisan¹

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Sequence regulation can be assured by the selection of monomer couples with reactivity ratios close to zero, which allows spontaneous cross-propagation copolymerization. The specific control of the polymer backbone strongly impacts the physicochemical properties of polymer materials. For instance, monomer design and customization of the solvent–monomer interactions open the way to functional copolymers showing molecular self-assembly relevant to their regular amphipathic structure. In this work, we show that the design of comonomers with adequate reactivities and interactions can be used to direct copolymer self-assembly on a mesoscopic scale. We investigate spontaneous formation of nanoparticles through solvent/non-solvent interactions using the so-called “Ouzo effect”. In this way, an ouzo diagram was built to determine the operation window for the self-assembly, in aqueous suspensions, of alternating copolymers consisting of vinyl phenol and maleimide units carrying long alkyl-pendant groups (C₁₂H₂₅ or C₁₈H₃₇). Also, investigations were pursued to account for the influence of the lateral lipophilic pendant units on the size and structure of the nanoaggregates formed during one-shot water addition. Structure characterization by light scattering techniques (DLS and SLS), small-angle neutron scattering (SANS) and transmission electron microscopy (cryo-TEM and TEM) confirmed the self-assembly of copolymer chains into nanoparticles (size range: 60-300 nm), the size of which is affected by the lipophilicity of the alternating copolymers, solvent–water affinity and the solvent diffusion in water. Altogether, we present here the spontaneous ouzo effect as a simple method to produce stable alternating copolymer nanoparticles in water without the addition of stabilizing agents.



AB-alternating copolymers based on vinyl phenol and n-alkyl (C12 or C18) maleimide self-assemble into nanoparticles via ouzo effect. Size and structure are determined by copolymer lipo/hydrophilicity, solvent/water affinity and solvent diffusivity.

Protomembranes at the origin of life

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Planet Earth is about 4.5 billion years old. In this study, we focused on the membranes of the first forms of living entities that assembled from a set of simple molecules available on the prebiotic Earth. The lipid membrane is a structure formed by hydrophobic or amphiphilic biomolecules called lipids, which are used in living organisms for many purposes, as a barrier between the interior of the cell and their environment, for energy storage, or signalling. The amphiphilic character of lipids allows the self-assembly in solution into a variety of supramolecular structures. The main structures are micelles, vesicles and droplets. In particular, membranes are the structures that form vesicles and can be used to mimic the walls of living cells. As the prebiotic synthesis of amphiphilic molecules favours the shorter chains, this work has focused on fatty acids, fatty alcohols and phospholipids including saturated chains of 10 carbon atoms, which are among the shortest capable of self-assembling into bilayers. Different models, all closely related to each other, have been used and studied here as proto-membrane models.

Various neutron scattering techniques, among them SANS, diffraction, EINS and NSE, have been employed to characterize physico-chemically these systems [1 - 3] and to conclude about their ability to form proto-membranes.

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Regioselective chemical modification of cellulose nanocrystals: tuning of the colloidal interactions and new properties

Presenter: Bruno Jean¹

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Native cellulose nanocrystals (CNC-I) and nanocrystals of the allomorph II of cellulose (CNC-II) are biosourced colloidal rods that are very interesting building blocks for the design of innovative materials thanks to their inherent properties (renewable origin, biocompatibility, self-organization and mechanical properties, etc.). In sharp contrast with CNC-I, CNC II have only been discussed in a limited number of paper and their surface derivatization has received very little attention. Additionally, both types of particles exhibit an interesting feature that has only scarcely been exploited yet: aldehyde groups are regioselectively present at one end of the CNC-I and at the two ends of the CNC-II, allowing for a localized chemical modification. In this framework, we investigated strategies to efficiently modify CNC-I and CNC-II with gold nanoparticles or thermosensitive polymers in a regioselective manner in order to generate innovative assemblies (star-like or flower-like complexes, bundles, networks) exhibiting various functional, e.g. rheological, properties. Since the undertaken modifications concern a reduced fraction of the available anhydroglucose units, a quantitative direct characterization of the regioselective derivatization of CNCs remains challenging, even if the use of advanced techniques such as scattering methods gives fruitful information.

Translational and rotational diffusion coefficients of chitin nanocrystals determined by depolarized dynamic light scattering

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Chitin, which is mainly found in arthropods such as insects and crustaceans, is the second most abundant biopolymer besides cellulose.[1] Although about 1000 billion tons of chitin are produced in the biosphere every year, it is barely used to produce high-value products due to its difficult processability.[2] One promising approach to obtain such high-value products is the use of chitin nanocrystals produced by hydrolysis. By imaging the prepared chitin nanocrystals with transmission electron microscopy (TEM) we were able to show that they exhibit a cylindrical shape. Complementary, the rotational and translational diffusion coefficients as well as diameter and length of the cylindrical chitin nanocrystals were determined by analyzing angle-dependent depolarized dynamic light scattering data.[3,4] We found, that the length and radius of the chitin nanocrystals decreases with increasing hydrolysis time. It was found that the values obtained from light scattering were systematically larger than those determined in the TEM. The hydrate shell and the possibility that the nanocrystals experienced already some agglomeration at the time of the light scattering experiments are potential reasons for the observed differences.

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Tuning hydrogel properties by the addition of clay nanoplatelets and counterion specific effects

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Hydrogels are at the forefront of scientific attention especially in the biological and biomedical fields where they provide the basis for stimuli-responsive artificial tissues, vehicles for drug delivery or biosensors. We study physically crosslinked hydrogels based on ionenes, positively charged polyelectrolytes, for which strong counterion-specific effects have been observed previously [1]. The nature of the ionene counterion modifies the rheological properties of the hydrogels, including significant shifts in the critical gelation concentration (cgc). Small angle scattering data (SAXS, SANS) reveal different mesh sizes for the cross-linking polymer networks and help to rationalized the observed elastic moduli and their concentration dependence [2]. Further, we were able to introduce anisotropic (platelike) clay nanoparticles into the ionene-based hydrogels [3]. Clay nanoplatelets organise in a regular face-to-face stacking manner, with a large repeat distance, following rather closely the hydrogel mesh-size (20-30nm). The presence of the nanoplatelets does not modify the hydrogel mesh size. The degree of nanoplatelet ordering in the hydrogel is very sensitive to the negative charge location on the clay platelet (different for each clay type). Increased nanoplatelet ordering leads to an improvement of the elastic properties of the hydrogel, especially for concentrations close to the cgc. On the contrary, the presence of dense clay aggregates (tactoids), induced by multi-valent clay counterions, destroys the hydrogel network as seen by the reduction of the elastic modulus of the hydrogel.

We are currently exploring the possibility of nanoplatelet orientation inside the hydrogel, in order to yield a versatile system with potentially anisotropic permeability properties.

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Wan Meenen, Isabelle	Institut Laue-Langevin, France	organizer
Wiedenmann, Albrecht	Retired from Institut Laue-Langevin, France	in person
Zemb, Thomas	Institut de Chimie Séparative de Marcoule, France	talk