

## **French-Swiss Meeting : SANS for Soft Matter**

*Strasbourg (30-31 March 2022)*

**Booklet of abstracts**

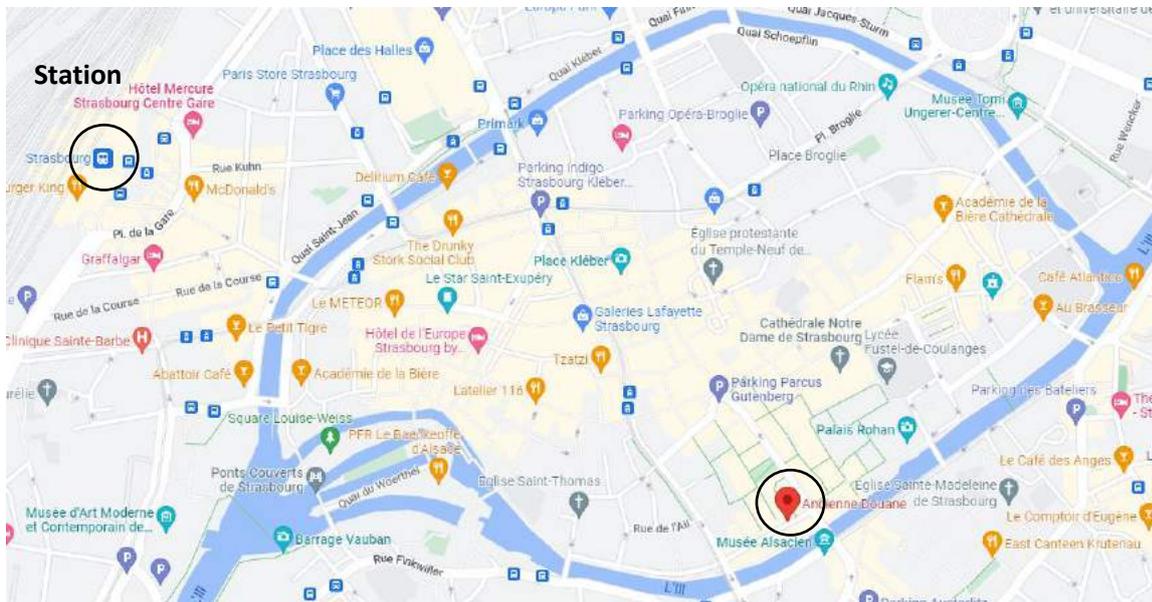
# Location of the conference



## L'ANCIENNE DOUANE

6 rue de la douane, 67 000 Strasbourg (+33 3 88 15 78 78)

[www.anciennedouane.fr](http://www.anciennedouane.fr)



## Program

### Wednesday 30 March afternoon

12:30 – 14:00      *welcome and buffet at L'Ancienne Douane*

#### **Introductory Session**

14:00 – 14:20      Michel Kenzelmann (PSI), Grégory Chaboussant (LLB), *Foreword*

14:20 – 14:40      Nicolas Martin (LLB) *Presentation of SANS outstations at LLB,*

14h40 – 15:00      Viviane-Lutz Bueno (PSI-LLB) *SANS-LLB at PSI: keeping up with the community needs*

#### **Session Polymers**

15:00 – 15:35      Julian Oberdisse, (LCC, Montpellier), *Polymer structure(s) seen by SANS: examples of single-chain nanoparticles, microgels, and interfacial segregation in nanocomposites*

*Coffee break*

16:15 – 16:50      Walter Richtering (RWTH, Aachen) *Are soft microgels tough?*

16:50 – 17:10      Boyang Zhou (PSI), *Direct measurements of the pNipam Microgel Counter-ion Cloud via Small -Angle Neutron Scattering*

17:10 – 17:30      Cécile Rerzki-Vérité (ECE Paris/LLB) , *Internally nanostructured Pn3m cubic droplets stabilized by clay nanoplatelets as physical cross-linkers for stretchable polyacrylamide-based hydrogels*

17:30 – 17:50      Alexis Chennevière (LLB), *Multiscale structure of poly(ionic liquid)s in melt and solutions by small angle neutron scattering*

18:00 – 19:30      *Aperitive and poster session*

20h00 *Dinner at L'Ancienne Douane*

## **Thursday 31 March morning**

### **Session Colloids and surfactants**

9:00 – 9:35                Véronique Receveur-Bréchet (IMM, Marseille), *Structural investigation of the intrinsically disordered protein CP12 in its cellular environment and in presence of its interacting partners using Small Angle Neutron Scattering by contrast variation*

9:35 – 10:05              Sylvain Prévost (ILL Grenoble), *Effect of ethanol on helical gels of glycyrrhizic acid investigated by SANS & SAXS,*

10:05 – 10:25            Martin In (LCC Montpellier), *Pre-micellar structuration of aqueous solutions of ionic liquid based surfactants*

10:25 – 10:45            Elise Guerinoni (ICSM Marcoule), *Understanding the effect of extractant and diluent alkyl chains on extraction, aggregation and third phase appearance in solvent extraction*

*Coffee break*

### **Session Biophysics and life science**

11:00 – 11:35            Frank Gabel (IBS Grenoble), *Time-resolved small angle neutron scattering provides unique insight into substrate processing by the PAN-proteasome complex in solution*

11:35 – 11:55            Olga Matsarskaia (ILL Grenoble), *Scattering techniques: powerful tools to elucidate the molecular mechanisms of Wilson's disease*

11:55 – 12:15            Julien Lamolinairie (ILL Grenoble), *(De)stabilization of non-ionic foam with ions*

12h15 – 12h35            Jérôme Combet (ICS Strasbourg): *Light stimuli-responsive wormlike micelles*

*Group photo/Lunch at L'Ancienne Douane*

## **Thursday 31 March afternoon**

### **Session Food Science and Pharmaceutics**

14:00 – 14:35            Peter Fischer (ETH, Zurich) *Structure and rheology of stimuli responsive nanocellulose interfacial layers*

14:35 – 14:55            Maja Napieraj (LLB), *Monitoring food structure in canola protein gels during digestion*

14:55 – 15:15            A. Murmiliuk (JCNS Jülich), *Structural design of polyelectrolyte-protein nanocarriers for targeted drug delivery*

15:15 – 15:35            Max Hohenschutz (RWTH Aachen University), *Solution structure and viscoelasticity of cellulose ethers in the presence of chaotropic nano-ions*

**15:35 Concluding remarks and End of conference. Poster prize**

## Posters :

- Laszlo Almasy (BNC, Budapest) *SANS facility at the Budapest Neutron Centre*
- I. Chazapi (ISCM Marcoule), *Solubilization of hydrophobic compounds by nano-ions*
- P. Denk (IPTC Regensburg) *A micellar shape restricted to spheroids: New nematic and hexagonal lyotropic liquid crystals evidenced by SAXS/SANS combination*
- F. Ferdeghini (ECE Paris), *Hybrid hydrogels with Pickering Emulsion as cross-linkers: a new smart system for drug delivery applications*
- M. Karpets (IEP SAS, Košice), *SANSPOL investigation of structural changes in transformer oil-based ferrofluids induced by electric and magnetic fields*
- Leonard Krupnik (Center for X-ray Analytics, St. Gallen), *Illuminating the structure of nanomedicines: small angle scattering of iron carbohydrates in complex biological environments*
- A. Mikhailovskaya (ICPME Thiais) *Reinforced hydrogels: polymer cross-linking by emulsion droplets,*
- W. Müller (ILL Grenoble), *SANS contrast variation for the localization of anionic dyes in DTAB-micelles*
- S. Prevost (ILL Grenoble), *D11+: renewal of the archetypal SANS*
- N. Shafqat (CSIC-UPV/EHU, San Sebastian), *Microscopic insight on thermally driven concentration fluctuations and component dynamics in polymeric mixtures of industrial interest*

**ORALS**

# Polymer structure(s) seen by SANS : examples of single-chain nanoparticles, microgels, and interfacial segregation in nanocomposites

*Julian Oberdisse*

*Laboratoire Charles Coulomb, University of Montpellier and CNRS, France*

Small-angle neutron scattering is the perfect tool to study the average conformation of macromolecules in about any environment, from solvents to other polymer molecules. The power of the method is intimately related to the length scale of observation, the virtual absence of artefacts due to the averaging, and most importantly, the possibilities to adjust contrasts and highlight chosen parts of the samples. In this talk, some recent applications will be reviewed.

During a stay with Arantxa Arbe and Juan Colmenero (San Sebastian), we have studied the structure of synthetic single-chain nanoparticles (SCNPs) in presence of linear polystyrene crowding molecules under contrast-matching of the crowdors [1]. A model describing the scattering of aggregating polydisperse SCNPs has been developed, resulting in the determination of the potentially squeezed size of the individual SCNPs within aggregates, their local chain statistics, and the average aggregation number, as a function of crowding. Secondly, in collaboration with Marian Cors and Thomas Hellweg (Bielefeld), we have investigated the internal structure of core-shell microgel particles in suspension. Using selective deuteration, core- and shell monomers could be measured independently, and the corresponding monomer profile described by a reverse Monte Carlo approach [2].

In the last part, an application to polymer nanocomposites will be discussed. Rubber-based nanocomposites show a large variety of spatial organization of the filler nanoparticles, which can be studied by small-angle scattering, and analyzed by large-scale reverse Monte Carlo simulation [3]. A key feature of rubber nanocomposites is linked to the influence of the filler surfaces on the polymer structure and dynamics, [4]. In particular, we have studied blends of short and long chains, where one chain type is deuterated, by small-angle neutron scattering. Different degrees of spatial segregation could be identified, including a peculiar, “fish-shaped” interfacial gradient.

[1] J. Oberdisse, M. González-Burgos, A. Mendia, A. Arbe, A. J. Moreno, J. A. Pomposo, A. Radulescu and J. Colmenero, *Macromolecules*, **2019**, 4295.

[2] M. Cors, O. Wrede, L. Wiehemeier, A. Feoktystov, F. Cousin, T. Hellweg, J. Oberdisse, *Scientific Reports* **2019**, 9, 13812.

[3] D. Musino, A.-C. Genix, T. Bizien, J. Oberdisse, *Nanoscale*, **2020**, **12**, 3907.

[4] A.C. Genix, V. Bocharova, B. Carroll, P. Dieudonné-George, M. Sztucki, R. Schweins, A. P. Sokolov, and J. Oberdisse, *ACS Applied Materials and Interfaces* **2021**, 13, 36262.

# Understanding the Behaviors of Adaptive Microgels with the Help of Neutrons

Walter Richtering

*Physical Chemistry, RWTH Aachen University, European Union*

Microgels are macromolecular networks swollen by the solvent they are dissolved in. They are unique systems that are distinctly different from common colloids, such as, e.g., rigid nanoparticles, flexible macromolecules, micelles or vesicles. When swollen, they are soft and have a fuzzy surface with dangling chains and the presence of cross-links provides structural integrity - in contrast to linear and (hyper-) branched polymers. Finally, microgels reveal interface activity without being amphiphilic. Due their properties, microgels can be used to tune the particle-to-macromolecule transition.

We will discuss properties of stimuli-sensitive microgels of different architecture (as e.g. ultra-low crosslinked, hollow, multi-shell, anisotropic) in solution and at interfaces. The structure of microgels is investigated by means of scattering methods, especially exploiting the technique of contrast variation in small angle neutron scattering and reflectometry. We will discuss properties of individual microgels as well as the effect of crowding in dense packings and we compare experimental results to computer simulations.

Scotti, A. et al. *Phys. Rev. E* **2021**, *103*, 022612; **2020**, *102*, 052602

Nickel, A. C.; et al. *Nano Letters* **2019**, *19*, 8161.

Schmid, A. J.; et al. *Scientific Reports* **2016**, *6*, 22736.

Maccarrone, S. et al. *Macromolecules* **2014**, *47*, 5982.

# Direct measurements of the pNipam Microgel Counter-ion Cloud via Small-Angle Neutron Scattering

**Boyang Zhou**<sup>1</sup>, Urs Gasser<sup>1</sup> and Alberto Fernandez Nieves<sup>2,3,4</sup>

<sup>1</sup> *Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen, Switzerland*

<sup>2</sup> *Catalan Institution for Research and Advanced Studies (ICREA), Spain*

<sup>3</sup> *School of Physics, Georgia Institute of Technology, Atlanta, GA, USA*

<sup>4</sup> *Department of Condensed Matter Physics, University of Barcelona, 08028 Barcelona, Spain*

Microgels are formed by cross-linked polymer networks. Their responsiveness to external stimuli makes microgels interesting for applications and a good model system for soft colloids. However, unlike hard colloids, their behavior is not well understood, especially at high concentrations. pNipam microgels carry charged groups and counter-ions at the periphery due to the initiator used during synthesis, which does not influence the particle behavior when the suspension is dilute, Fig.1(A). However the counter-ion cloud plays a crucial role for the observed spontaneous deswelling behavior at high concentrations; microgels deswell below random close packing when the percolation of counter-ion clouds induces a suspension osmotic pressure that is greater than the particle bulk modulus [1,2], Fig.1(B). This deswelling mechanism can also resolve point defects that would otherwise hinder the crystallization in the case of a hard-incompressible particle suspension, Fig.1(C) [2,3,4]. In this study, we present the first direct measurements of the counter-ion cloud via small-angle neutron scattering (SANS). Note that the form factor can be decomposed as  $P(q) = F_p^2(q) + 2 F_p(q)F_c(q) + F_c^2(q)$ , where  $F_p(q)$  and  $F_c(q)$  are the scattering amplitudes of the pNIPAM polymer and the counter-ion cloud, respectively. We prepare one suspension with  $\text{Na}^+$  ions and the other with  $\text{NH}_4^+$  ions via dialysis to use the difference in the scattering-length densities of these ions to obtain an augmented scattering signal with structural information about the ion cloud and the arrangement of charged groups on a microgel, Fig.1 (D and E). Using this method, we show that the counter-ion cloud is indeed located at the particle periphery, as expected from particle synthesis. This result also corroborates our theory for microgel deswelling at high concentration. Importantly, our theory for microgel deswelling relates the particle softness and surface charges with the phase behavior [2,3]. The findings are crucial for developing a better understanding of soft and deformable colloids at high concentrations and for formulating a model for the phase behavior of microgels that takes spontaneous deswelling at high concentrations into account.

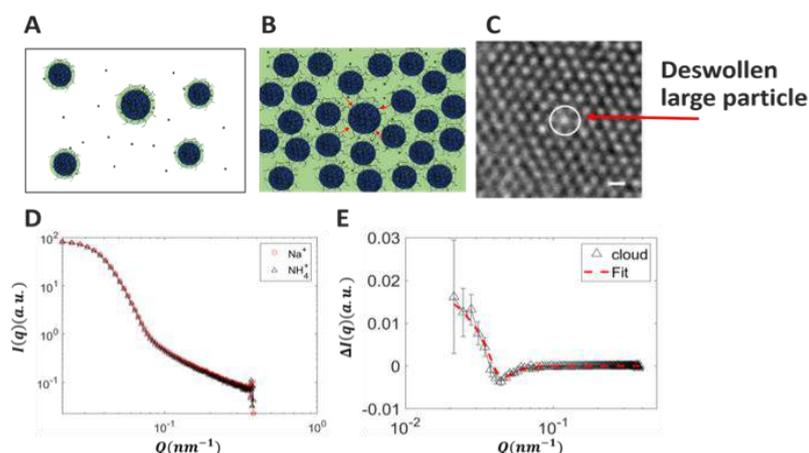


Fig.1 : (A) Microgels with counter-ion clouds in a dilute suspension (green ring at the periphery). (B) Deswelling of larger particles in a sea of small ones triggered by the percolation of the counter-ion clouds. (C) Microscopy image of a deswollen large pNIPAM microgel in a crystal of smaller pNIPAM microgels. (D)  $I_{\text{NH}_4^+}(q)$  is plotted with  $I_{\text{Na}^+}(q)$  at  $\zeta = 0.2$  and  $T = 20^\circ\text{C}$ . (E) Direct subtraction  $\Delta I(q) = I_{\text{NH}_4^+}(q) - I_{\text{Na}^+}(q)$  and the model fit giving the counter-ion cloud radius and width.

[1] U.Gasser, A. Scotti, and A. Fernandez-Nieves, *Physical Review E* 99, 042602 (2019).

[2] A. Scotti, U. Gasser, E.S. Herman, M. Peláez-Fernandez, J. Han, A. Menzel, L.A. Lyon and A.Fernandez-Nieves, *Proceedings of the National Academy of Sciences* 113, 5576 (2016).

[3] A. Scotti, U. Gasser, E.S. Herman, J. Han, A. Menzel, L.A. Lyon, and A. Fernandez-Nieves, *Phys. Rev. E* 96, 032609 (2017).

[4] A. S. J. Iyer and L. A. Lyon, *Angew. Chem.* 121, 4632 (2009).

# Internally nanostructured Pn3m cubic droplets stabilized by clay nanoplatelets as physical cross-linkers for stretchable Polyacrylamide-based hydrogels

C. Rerzki-Vérité<sup>1,2</sup>, F. Ferdeghini<sup>1,2</sup>, C. Le Cœur<sup>2,3</sup>, F. Cousin<sup>2</sup>, and F. Muller<sup>1,2</sup>

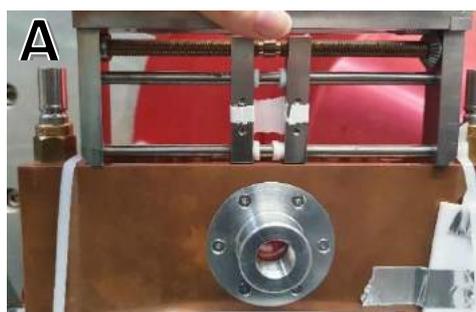
<sup>1</sup>Groupe Nanosciences et Nanotechnologie, ECE Paris-Lyon, Paris, France

<sup>2</sup>Laboratoire Léon Brillouin (CEA-CNRS)

<sup>3</sup>Institut de Chimie des Matériaux Paris-Est

Aqueous dispersions of lipid-based lyotropic liquid crystalline (LC) phases are viewed as potential nanocarriers for cosmetics or medical applications. Their stabilization in water by nanoparticles (NPs) has been reported during the last decade, as a function of the types of lipid and nanoparticles [1,2,3]. NPs can be used as physical cross-linkers in hydrogels, which are efficient candidates for biocompatible applications, and remarkably enhance their usually poor mechanical properties [4]. We extend this concept by using droplets of LC phases stabilized by NPs as physical cross-linkers, to create hybrid physical hydrogels. With these systems, we are aiming at developing external drug delivery-based applications under stretch, namely artificial skins and/or smart bandages. The goal would be to trap an active substance in the LC phase, and release it by stretching the hydrogel.

We first determined the quantity of Laponite clay nanoplatelets necessary to stabilize Phytantriol (PT)-based cubic phases in water, by varying the concentration of both compounds in the emulsions. Several techniques were used to pinpoint the threshold concentration of platelets necessary to stabilize a given amount of PT.



Pictures of a hydrogel made from a 1vol% PT, 1wt% Laponite emulsion at rest (A) and after a 1000% elongation (B), in the tensile setup used during SANS experiments at SANS1 (PSI).



SANS measurements have been performed on the emulsions using two different solvent contrasts that match either the PT scattering or the Laponite scattering to determine their structural organisation separately. We then studied Polyacrylamide-based hydrogels synthesized from the same emulsions using the droplets as physical cross-linkers, both at rest and under uniaxial stretching. We applied several stretching ratios using an in-house tensile setup allowing the *in situ* stretching of hydrogels within the neutron beam [5]. Impressively, these purely physical hydrogels could be stretched up to 1000% without breaking, but no anisotropy was observed on the SANS pattern for the contrasts probed. In these, the contribution from the polymeric chains is negligible for contrast reasons. The structure of the droplets, obtained when the Laponite is contrast-matched, was revealed to be similar in emulsions and hydrogels, displaying the robustness of such droplets that do not undergo deformation along the hydrogel stretching direction. It is then likely that only the polymer chains between these droplets cross-linkers are deformed under stretching. Although such a study demonstrates that drug delivery from the droplets cannot be induced by stretching in such hydrogels, their very high stretchability before breaking makes them very promising for bandage applications. Once the gel is applied onto the targeted zone, the internal structure of the LC may be modified by a moderate increase of temperature, as the PT display a rich phase behaviour in the 20°C- 50°C range.

[1] Salonen et al., *Langmuir*, 24 (2008) 5306-5314.

[2] Salonen et al., *JCIS*, 342 (2010) 392-398.

[3] Muller et al., *Soft Matter*, 8 (2012) 10502-10510.

[4] Haraguchi et al., *Macromolecules*, 35 (2002) 10162-10171.

[5] Ducrot et al., *Macromolecules*, 48 (2015) 7945-7952.

# Multiscale structure of poly(ionic liquid)s in melt and solutions by small angle neutron scattering

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**T. Outerele Corvo**<sup>1,3</sup>, A. Jourdain<sup>2</sup>, S. O'Brien<sup>2</sup>, F. Restagno<sup>3</sup>, E. Drockenmuller<sup>2</sup> and A. Chenneviere<sup>1</sup>

<sup>1</sup> Université Paris Saclay, Laboratoire Léon Brillouin, UMR 12 CNRS-CEA, CEA-Saclay, 91191, Gif-sur-Yvette, France

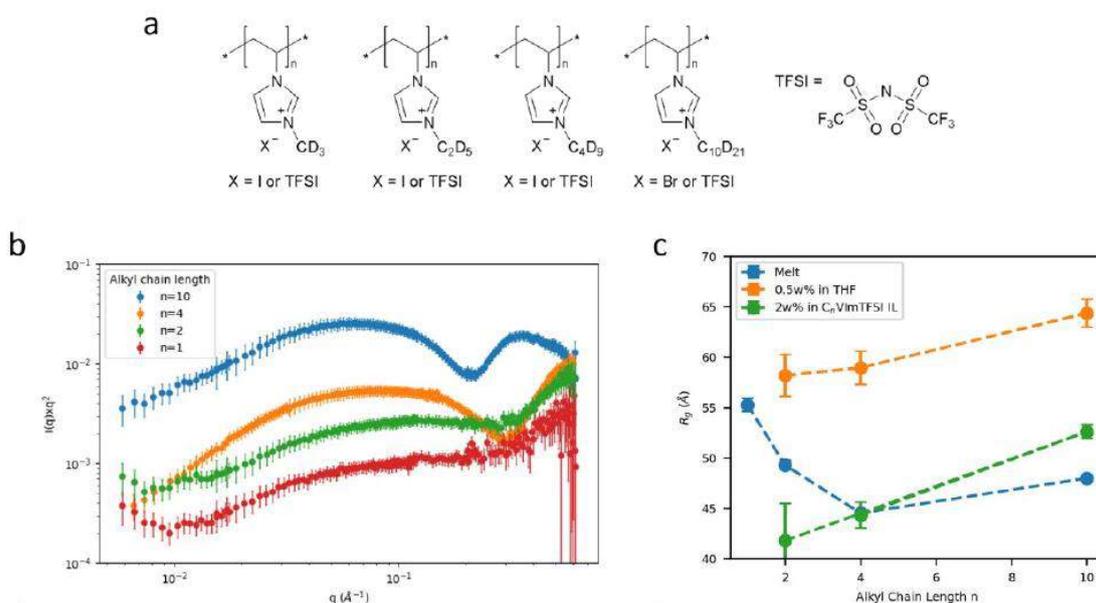
<sup>2</sup> Univ Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223, F-69003 Lyon, France

<sup>3</sup> Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France

¶

Poly(Ionic Liquid) (PIL) refer to a special type of polyelectrolyte in which each monomer unit is composed of an ionic liquid (IL). They have recently drawn significant attention since they present a unique combination of the properties of ILs (e.g. high thermal, chemical, electrochemical stabilities, interfacial adsorption and enhanced ionic conductivity. . . ) with those of polymer materials (e.g. processability, viscoelasticity, adhesion, film-forming properties, and broad macromolecular design...). ILs show a local phase separation which confers the bulk with either a globular or a sponge-like structure in which the ionic domain organizes in channels across the bulk [1].

On a polymer physicist point of view, the main difference between an ideal polymer melt and PILs stems from the presence of counter-ions and local interactions between IL monomer units due to their amphiphilic nature. The structure of bulk Poly(*n*-alkyl)vinylimidazolium PIL with varying side chain length *n* and counter-ion was determined by small angle neutron scattering (SANS). The considerable differences in behavior between melts and solutions originates from modulated electrostatic repulsions, either dominant for short side chains or screened by the counter-ions and long side chains. These interactions shape the conformation of the PIL chains but also the overall bulk structure. These considerations are precious insights for future applications of these polymers, particularly by exploiting their viscoelastic properties which deviate from those of ideal polymer chains.



**Figure 1:** (a) Structure of Poly(*n*-alkyl)vinylimidazolium Poly(Ionic Liquid). (b) Kratky representation ( $I(q)q^2$ ) of SANS data for melt  $\text{PC}_n\text{VImTFSI}$ . (c) Radius of gyration of  $\text{PC}_n\text{VImTFSI}$  determined by SANS as a function of the side chain length *n*.

¶

[1] R. Hayes G.G. Warr and R. Atkin. Structure and nanostructure in ionic liquids. Chemical reviews, 115(13):6357–6426, 2015.

## Structural investigation of the intrinsically disordered protein CP12 in its cellular environment and in presence of its interacting partners using Small Angle Neutron Scattering by contrast variation

Véronique Receveur-Bréchet<sup>1</sup>, Frank Gabel<sup>2</sup>, Hélène Launay<sup>1</sup>, Trevor Forsyth<sup>3</sup>, Martine Moulin<sup>3</sup>,  
Michael Haertlein<sup>3</sup>, Brigitte Gontero<sup>1</sup>

<sup>1</sup> Bioénergétique et Ingénierie des Protéines (BIP – AMU CNRS UMR 7281), Marseille

<sup>2</sup> Institut de Biologie Structurale (IBS), Grenoble

<sup>3</sup> Deuteration Laboratory (D-Lab), Institut Laue Langevin, Grenoble

Microalgae are prominent actors of CO<sub>2</sub> assimilation on Earth. CO<sub>2</sub> assimilation occurs during the Calvin cycle, which is the primary metabolic pathway of photosynthetic organisms including microalgae. The Calvin cycle is regulated by the small chloroplast protein CP12 upon the light-dark transitions and redox conditions. In the dark, that is in oxidizing conditions, CP12 binds and sequesters two key enzymes of the Calvin cycle, GAPDH and PRK, thus inhibiting the Calvin cycle. In the day, that is in reducing conditions, CP12 is inactive and releases GAPDH and PRK, and the Calvin cycle can operate. We showed *in vitro* using NMR and SAXS that reduced CP12 from the model green microalga *Chlamydomonas reinhardtii* is fully disordered, while oxidized CP12 oscillates between a disordered and a partly ordered state. Intrinsically disordered proteins are known to sometimes undergo disorder-to-order transitions depending on the physico-chemical environment, or upon binding to their partners. The structural properties and equilibrium of CP12 are therefore likely to be modified in physiological environment, and in presence of GAPDH and PRK. We have therefore investigated, using a combination of SANS with contrast variation, SAXS and NMR, the structural conformations of CP12 in presence of cell lysate to mimick the cellular environment, and within the complex with its binding partners.

## Effect of ethanol on helical gels of glycyrrhizic acid investigated by SANS & SAXS

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S. Prévost<sup>1</sup>, P. Denk<sup>2</sup>, L. Matthews<sup>3</sup>, Th. Zemb<sup>4</sup> and W. Kunz<sup>2</sup>

<sup>1</sup> Institut Laue-Langevin, 71 avenue des Martyrs, CS 20156, 38042 GRENOBLE Cedex 9, France

<sup>2</sup> Institute of Physical and Theoretical Chemistry, University of Regensburg, 93053 Regensburg, Germany

<sup>3</sup> European Synchrotron Radiation Facility, 71, avenue des Martyrs, CS 40220, 38043 Grenoble Cedex 9, France

<sup>4</sup> Institut de Chimie Séparative de Marcoule, BP 17171, F-30207 Bagnols sur Cèze Cedex, France

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Glycyrrhizic acid ("AGA", aka glycyrrhizin) is a component of liquorice and present in i.a. Pastis. This saponin, unlike most, has a sweet taste (about 40 times as sweet as sucrose) and is thus used as sweetener in the food industry (E956).

The ammonium salt of glycyrrhizic acid (AGA) makes birefringent hydrogels at low concentration that are built from helices of 2.3 nm diameter.[1] At concentration lower than 1 %, these rigid beams fill up the space. Upon concentration increase, as there is no space to grow "infinite" beams anymore, the added AGA forms pieces of the beams as "micelles" that are short helices coexisting with long fibres; however this "micelle" formation concentration is not a classical cmc.

Alcohol addition induces initially partial dissolution of the small "micelles" – helices with unfavorable end-caps. Alcohol changes the permittivity of the solvent, therefore acts on the condensation equilibrium of the counterion ammonium on the fiber. Only when all the "micelles" are finally dissolved does the alcohol start attacking the gel-forming rods, which are much more favorable due to the lack of end-caps.

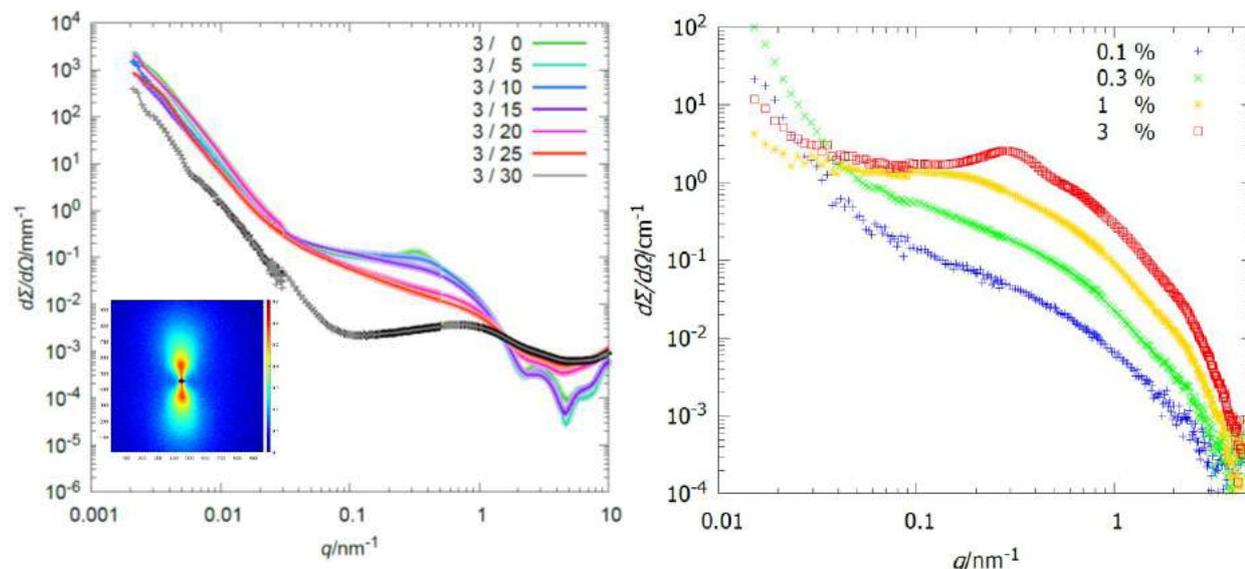


Figure: [left] SAXS profiles (ID02@ESRF) from solutions of ammonium glycyrrhizate at 3 % upon addition of ethanol (0 to 30 % by volume as indicated by the second digit in the legend); [insert] 2D SAXS data at 5 m showing the alignment induced by shear when filling the capillary. [right] SANS profiles (D33@ILL) from solutions of AGA at 0.1 to 3 % in  $\text{D}_2\text{O}$ .

Combined SANS and SAXS experiments allow to identify the equilibrium between long fibers, short "micelles" as well as ethanol adsorbed on the fibers in each region of the phase diagram with the corresponding structure; the sol-gel transition is attributed to the lack of long fibers, that need to space with local nematic order.

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[1] A. Saha, J. Adamcik, S. Bolisetty, S. Handschin, R Mezzenga, *Angew. Chem. Int. Ed.*, 54 (2015) 5408-5412.

# Pre-micellar structuration of aqueous solutions of ionic liquid based surfactants

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Lydie Viau<sup>1</sup>, Corine Tourné-Péteilh<sup>2</sup>, Benoit Coasne<sup>3</sup>, and **Martin In**<sup>4</sup>

<sup>1</sup> Institut UTINAM UMR 6213, Besançon, France

<sup>2</sup> Institut Charles Gerhardt Montpellier, UMR 5253, CNRS-UM-ENSCM, Montpellier, France

<sup>3</sup> LiPhy, UMR 5588, CNRS-U Grenoble Alpes, Grenoble, France

<sup>4</sup> Laboratoire Charles Coulomb, UMR 5221, CNRS-UM, Montpellier, France

Aqueous solutions of three cationic compounds based on alkyl imidazolium cations (C<sub>n</sub>MIm, n=4, 6 and 8) and ibuprofenate anion (Ibu) have been studied by small angle neutron scattering (SANS) on either side of the critical concentration. For comparison sodium ibuprofenate has also been considered. The critical concentration decreases exponentially from 0.1M to 0.004M when the alkyl chain length n increases from 4 to 8 [1] and beyond the systems either micellize (n=4 and 6) or phase separate (n=8) [2]. The micelles are either spherical (n=4) or elongated (n=6). Despite this diverse behaviour beyond the transition, the aqueous solutions of all these compounds show the same type of structuration in the pre-transitional range of concentration. Analysis of the structure factor shows that micellization as well as demixing of the cationic ionic liquids do not proceed through nucleation of dense pre-micellar aggregates containing few molecules, as usually admitted for the pre-micellar state, but rather occur within spatially extended concentration fluctuations of small amplitude. This was also recently observed in the course of the self-assembling of block copolymers by liquid phase transmission electron microscopy [3].

The structure factor in the pre-transitional state can be accounted for by a modified Ornstein–Zernike equation that includes some ordering within the higher concentration domains. Moreover, the ratio  $\chi_T/\xi^2$  of the compressibility over the square of the correlation length scales as  $C^{-1.4}$ , where C is the concentration, for all systems, whatever the final morphology of the micelles. This is in contrast to what was reported for the formation of copolymer vesicles [3], where the structure of the pre-transitional state determines the structure of the final vesicles. Our results as well as those presented in [3], suggest to generalize to self-assembling the scenario of crystallization [4] recently proposed as an alternative to nucleation and growth.

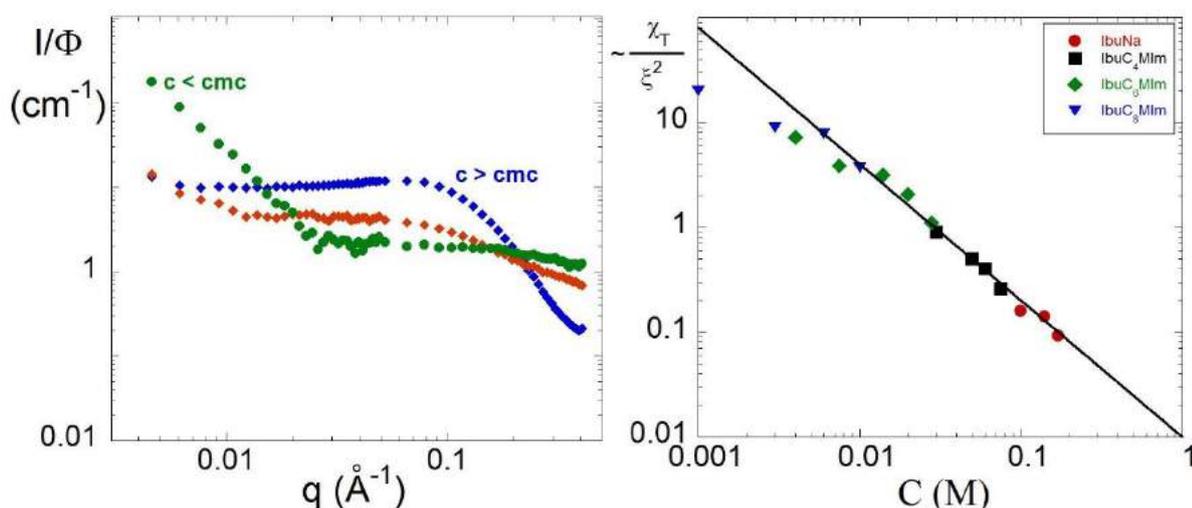


Figure 1 Left: Scattering patterns of IbuC6MIm on either side of its cmc. Right: Master curve characterizing a universal feature of the pre-transitional state of compounds about to micellize or to demix.

[1] Tourné-Péteilh, C.; Devoisselle, J. M.; Vioux, A.; Judenstein, P.; In, M.; Viau, L. *Phys. Chem. Chem. Phys.* 2011, 13, 15523–15529.

[2] Tourné-Péteilh, C.; Coasne, B.; In, M.; Brevet, D.; Devoisselle, J.-M.; Vioux, A.; Viau, L. *Langmuir* 2014, 30, 1229-1238

[3] A. Ianaro et al. *Nat. Chem.* 11 (2019) 320-328.

[4] J. F. Lutsko *J. Chem. Phys.* 136 (2012) 134502

# Understanding the effect of extractant and diluent alkyl chains on extraction, aggregation and third phase appearance in solvent extraction

E. GUERINONI, S. DOURDAIN and S. PELLET-ROSTAING

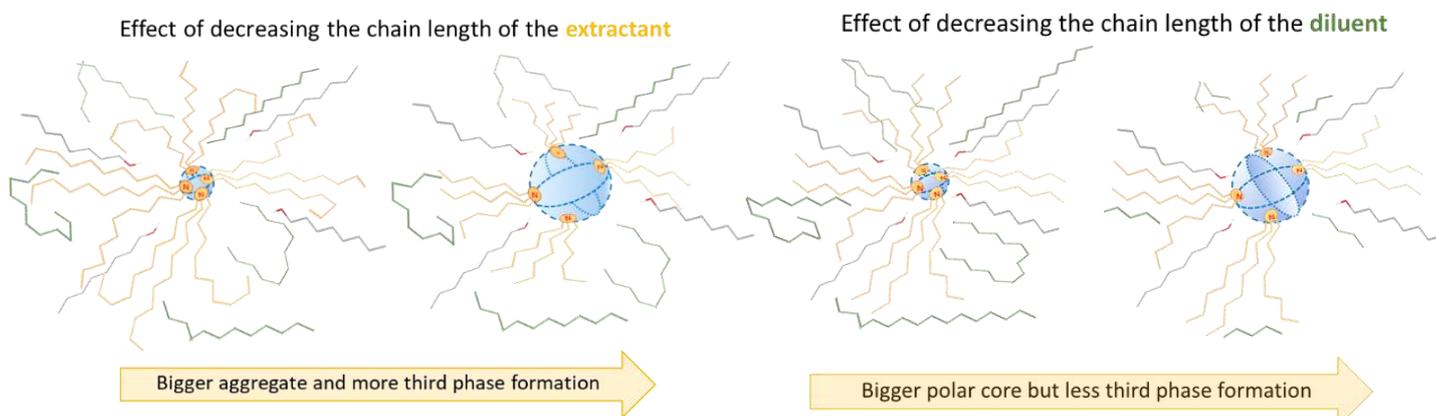
Institut de Chimie Séparative de Marcoule, CEA, Bagnols sur Ceze, 30207, FRANCE

## ABSTRACT:

Solvent extraction is a crucial method used for many industrial applications to recover elements of interest as precious metals or organic molecules. Among the processes implemented in nuclear fuel cycle, AMEX process uses mixtures of amines to selectively extract uranium from the front-end sulfuric leaching liquors. Despite its extensive application, this economically efficient process presents drawback as the formation of a third phase.

We target therefore new formulation of optimized extraction systems by playing on the diluent and extractant alkyl chains length. SANS measurements showed here that tertiary amines with longer or slightly branched alkyl chains demonstrate better phase stability and maintain efficient extraction. However too much branching of the alkyl chains hinders the formation of a highly curved interfacial film and preventing efficient extraction.<sup>1</sup> A complete fit of SANS data confirms quantitatively that the third phase quenching is related to smaller reverse micelle-like aggregates and to reduced attractive interactions for longer or branched alkyl chains. This results was also rationalized with a thermodynamic approach.<sup>2</sup>

However, whereas the extractant chains prevent the third phase formation by limiting the extractant aggregation, we also observed that shorter diluent chain lengths prevent 3<sup>rd</sup> phase formation with a better extractant aggregation. This unexpected and unprecedented result suggests that the known mechanisms at the origin of the 3<sup>rd</sup> phase are incomplete and need to be further investigated with SANS.



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- (2) Lu, Z.; Dourdain, S.; Dufrêche, J.-F.; Demé, B.; Zemb, T.; Pellet-Rostaing, S. Effect of Alkyl Chains Configurations of Tertiary Amines on Uranium Extraction and Phase Stability - Part II: Curvature Free Energy Controlling the Ion Transfer. *Journal of Molecular Liquids* **2021**.

## Time-resolved small angle neutron scattering provides unique insight into substrate processing by the PAN-proteasome complex in solution

Frank Gabel<sup>1</sup>

<sup>1</sup>Institut de Biologie Structurale, 71 avenue des Martyrs, 38044 Grenoble, France

A multitude of structural biology techniques, including crystallography, NMR and cryo-EM, as well as single molecule experiments, have recently provided new and exciting mechanistic insight into protein substrate degradation by AAA+ ATPases and the proteasome. However, direct structural information on the conformational changes of the working complex and on the respective substrate state(s) and populations, during the active unfolding and degradation process in solution, remains scarce.

We use time-resolved small angle neutron scattering (TR-SANS), in combination with selective macromolecular deuteration and solvent contrast variation (H<sub>2</sub>O:D<sub>2</sub>O exchange), to obtain structural information on the respective components during the active degradation process in solution. SANS, in contrast to its sister technique SAXS (small-angle X-ray scattering), allows to distinguish between individual proteins in solution if they are differentially labeled (deuterated vs hydrogenated).

By using the PAN-proteasome complex from the hyperthermophilic archaeon *Methanocaldococcus jannaschii*, it is possible to temperature-activate and fine-tune the unfolding and hydrolysis process at 55 °C. Combined with online fluorescence and specific deuteration, we were able to obtain separate structural information on the conformational state of PAN and on the GFPssrA substrate during the active reaction in solution [1]. We find that PAN undergoes a reversible conformational contraction during the substrate unfolding process. GFP aggregates rapidly in the presence of PAN alone but is being hydrolyzed very efficiently once the proteasome is present during the reaction [2].

Our SANS data allow to quantify the time evolution of natively folded GFP substrates and oligopeptide products at a sub-minute time resolution and to propose a working mechanism for substrate processing in solution. In particular, they suggest a tethering of the PAN-proteasome complex by the substrate in a conveyor belt-like, coupled unfolding and hydrolysis process, and the necessity of a tight regulation of the degradation process *in vivo*. Furthermore, we find a strong direct correlation between the time-rates of the disappearance of native GFP structures with those of ATP-hydrolysis and fluorescence decay [2].

In conclusion, TR-SANS is a very promising technique that can provide structural kinetics data on solution ensembles, complementary to results obtained by crystallography, cryo-EM, NMR and single molecule experiments [3]. AAA+ ATPases and the proteasome, as well as related biological systems, are ideally suited for these kind of studies.

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## Scattering techniques: powerful tools to elucidate the molecular mechanisms of Wilson's disease

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**O. Matsarskaia**<sup>1</sup>, M. Sandroni<sup>1</sup>, L. Matthews<sup>2</sup>, and R. Schweins<sup>1</sup>

<sup>1</sup> *Institut Laue-Langevin, 71 Avenue des Martyrs, 38042 Grenoble, France*

<sup>2</sup> *European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38042 Grenoble, France*

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Copper (Cu) is an essential element for mammals and its metabolism is tightly regulated [1]. In the case of Wilson's disease, however, Cu metabolism is impaired, resulting in pathologically high Cu levels in the body [2]. Severe, often lethal, consequences ensue, such as liver and neurological damage [3,4] as well as the destruction of hemoglobin (Hb) and red blood cells (RBCs) [5]. The latter two symptoms are believed to be due to Cu-induced aggregation of Hb [6,7]. Generally, however, the current understanding of Wilson's disease is predominantly phenomenological. To obtain quantitative information on this condition, this project applies an interdisciplinary array of techniques including SANS and SAXS. Scattering data demonstrating real-time effects of Cu addition on Hb and RBC will be presented. The results obtained will be discussed in the broader context of medical research with the goal of inspiring an interdisciplinary dialogue between fundamental science and clinical applications.

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## (De)stabilization of non-ionic foam with ions

**J. Lamolinarie**<sup>1</sup>, L. Chiappisi<sup>1</sup>, O. Diat<sup>2</sup>, G. Fragneto<sup>1</sup>, L. Girard<sup>2</sup>, C. Pasquier<sup>2</sup>, P. Bauduin<sup>2</sup>, P. Lechevalier<sup>3</sup>, and J-L. Bridot<sup>3</sup>

<sup>1</sup> Institut Max von Laue-Paul Langevin, 71 avenue des Martyrs, 38042 Grenoble Cedex 9, France

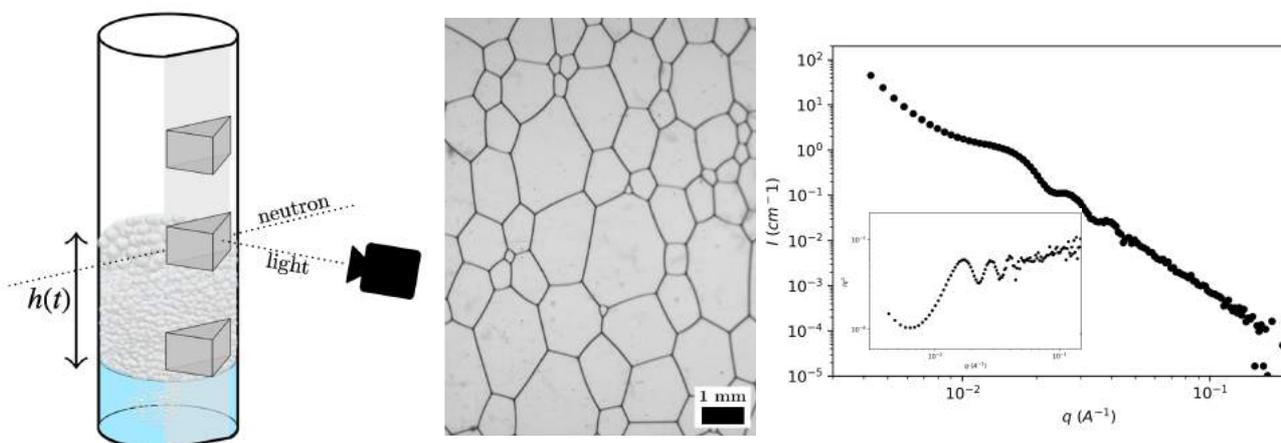
<sup>2</sup> Institut de Chimie Séparative de Marcoule, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Marcoule, France

<sup>3</sup> Teclis Scientific, 22 Chemin des Prés Secs, 69380 Civrieux-d'Azergues, France

Very recently, it was shown that non-ionic foam aging could be strongly impacted by adding nanometer-sized anions (also called nano-ion).[1] Indeed, when the charge density of a nano-ion is lower than  $12 e/nm^3$  these nano-ions have a superchaotropic behavior, i.e. that they can adsorb onto a polar and hydrated surface.[2,3] So, when superchaotropic nano-ions are solubilized within a foam made with a non ionic surfactant such as a polyethoxylated amphiphiles, the nano-ions adsorb onto the surface and charge the interface that become repulsive. This repulsive interaction has been already observed and analyzed for micelles but not in real foam. [3]

In this work, the first objective was to build a new cell in order to make a foam that can be studied simultaneously via small angle neutron scattering and macroscopic imaging (see Fig. 1). Both measurements allow to correlate bubble size distribution and evolution with the bubble film thickness during the drainage and as a function of the height of the foam. The studied system was composed of BrijO10 in D2O and the silicatingtungstic acid polyoxometallate as the nano-ion at different molar ratio. Comparisons were carried out using sodium dodecyl sulfate surfactant for which numerous studies were already published. [4, 5]

Fig. 2 correspond to a picture of the foam structure at the same time. Fig. 3 presents a typical scattering curve from a foam during the first step of the drainage. A  $Iq^4$  vs  $q$  plotted in the inset emphasize the oscillation coming from the reflected beam on the bubble interfaces. From these mesoscopic and macroscopic information we expect to get deeper knowledge of all the mechanisms that are destabilizing the foam (foam drainage, bubble coarsening and coalescence).



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## Light stimuli-responsive wormlike micelles

Y. Liu<sup>1</sup>, G. Fleith<sup>1</sup>, A. Chenevière<sup>2</sup>, A. Helary<sup>2</sup>, J.P. Lamps<sup>1</sup>, M. Schmutz<sup>1</sup>, M. Er Rafik<sup>3</sup>, P. Mésini<sup>1</sup>, **J. Combet**<sup>1</sup>

<sup>1</sup> Université de Strasbourg, Institut Charles Sadron, Strasbourg

<sup>2</sup> Laboratoire Léon Brillouin, Gif sur Yvette

<sup>3</sup> Tech Univ Denmark, DTU Nanolab, Lyngby, Denmark

“Smart” materials have the ability to change their structure and functionality in response to an external stimulus. The triggers can be diverse such as mechanical stress, electric or magnetic field, light, temperature, pH etc. In this work, we are interested in smart light-responsive wormlike micelles (WLM) [1] able to change their rheological response upon UV irradiation.

The light-responsiveness of these systems originates from the incorporation of a photochromic group (azobenzene, Azo, figure 1a) in the chemical structure of the surfactant. UV irradiation provokes a reversible isomerisation from a *trans* stable apolar state to a *cis* metastable polar isomer that changes the polarity and the hydrophobicity of the molecule (figure 1b) leading to a structural reorganization that can change the rheological properties at the macroscopic scale.

We focus here on a simple two component systems made of Azo-surfactants (figure 1b) and sodium benzenesulfonate as cosurfactant (figure 1c). This mixture forms a gel-like state in absence of irradiation (dark) that can be switched ‘off’ or ‘on’ upon UV or blue light irradiation (figure 1d). The aim of the study is to give a precise picture of the structural modification that causes such a reversible sol-gel transition.

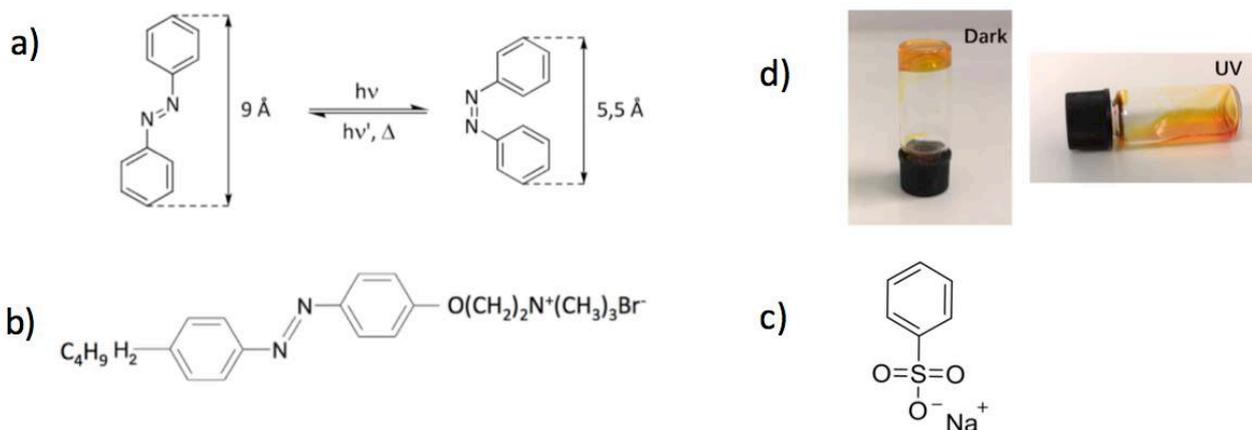


Figure 1. a) Azobenzene and photo-isomerisation between *trans* (stable apolar) and *cis* (metastable polar) isomers.. b) Azo-surfactant. c) sodium benzenesulfonate d) gel-like behaviour

In this talk, we will present Small Angle Neutron Scattering experiments recently performed on PAXY at the LLB in dark and upon UV using a particular irradiation setup. These measurements will be completed by SAXS and cryo-TEM experiments.

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# Structure and rheology of stimuli responsive nanocellulose interfacial layers

Peter Fischer

Institute of Food, Nutrition and Health, ETH Zurich, 8092 Zurich, Switzerland

The use of particles such as nanocelluloses, i.e. cellulose nanocrystals (CNC) and nanofibrils (CNF) received increasing attention for the Pickering stabilization of fluid interfaces [1]. The adsorption of nanocellulose and nanocellulose-protein composites at oil-water or air-water interfaces facilitates the formation of stable and biocompatible emulsions and foams but depends heavily on the particles' surface properties. In this contribution, we review the structure of differently designed adsorption layers by neutron reflectivity and interfacial rheology measurements as a function of physico-chemical boundaries conditions (pH, salts, enzymes) [2, 3], surface properties of the cellulose crystals (natural, methylation, esterification) [4, 5], and protein or polysaccharide addition [6]. Native unmodified CNC (hydrophilic, negatively charged, and anisotropic nanoparticles) showed negligible viscoelasticity that could be increased by charge screening due to a shift from repulsive to attractive CNC interactions. Methylated CNCs formed dense monolayers with higher dynamic moduli compared to native CNCs and could be thermo-gelled into multilayers. The esterified CNCs formed aggregated clusters at the interface, resulting in a Maxwellian frequency behavior with distinctive relaxation times, a rarely observed phenomenon for interfacial layers. Scattering length density profiles obtained from neutron reflectivity measurements are used to elucidate the thickness and roughness of the adsorption layer, and in case of nanocellulose-protein composites, their spatial composition. Supported by in vivo digestion experiments in humans we rationalize the design principles of nanocellulose-stabilized emulsions and foams for food and drug delivery vehicles [7].

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# Abstract title: "Monitoring food structure in canola protein gels during digestion"

**M. Napieraj**<sup>1</sup>, A. Brûlet<sup>1</sup>, E. Lutton<sup>2</sup>, A. Boire<sup>3</sup> and F. Boué<sup>1</sup>

<sup>1</sup> CNRS, Lab. Léon Brillouin, UMR12, CNRS-CEA, Univ Paris- Saclay, Gif-sur-Yvette

<sup>2</sup> INRAE, UMR MIA 518, INRAE-AgroParisTech, Paris

<sup>3</sup> INRAE, Biopolymères, Interactions, Assemblages, Nantes

Nutritional value of proteins in human diet depends not only on their amino acid composition but also on the ingested food digestibility, which can be largely influenced by the specific food microstructure. In our work, we study different types of such microstructures in our model solid-like foods – canola protein gels (containing napin and cruciferin), obtained by a heat-treatment of the corresponding protein solutions at different pH values. We focus on monitoring of the protein structures evolutions of such gels during the simulated gastric and intestinal digestion experiments.

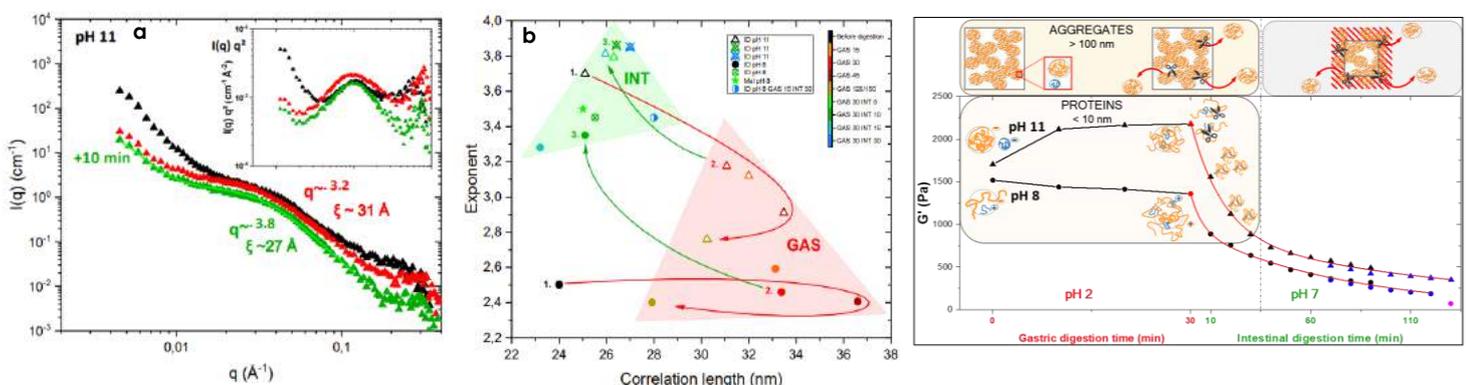
We used different techniques to study the digestion on different structural scales, i.e. Small-Angle Neutron Scattering for the nanometric characterization and rheometry for the general flow/deformation properties. The choice of those two techniques permitted us using the gel samples with dimensions close to the real-size food particle - gels with diameters of ~10 mm. The samples were initially infused with the inactive digestive enzymes to achieve their homogeneous distribution in the samples prior to the digestion and then measured after a given digestion time (SANS) or during the digestion (rheometry).

SANS measurements showed a dynamic process of gastric digestion of proteins, comprising local rearrangements (i.e., protein unfolding, compaction or aggregation, dependent on the initial state of proteins in networks). For longer digestion times (120-150 min), significant decays of the correlation length values, related here to the enzymatic scissions in proteins were visible, together with stronger destruction of protein aggregates (low  $q$  SANS signal). During intestinal steps, protein compactions were observed for both types of gels, already after 10 min.

The rheological observations gave us the information about the change of the gel strength in the course of digestion. During 2 h of the intestinal step, the viscoelastic moduli were gradually decreasing with double-exponential rates, dependent on the sample's structure; during gastric digestion however, an increase in elasticity was surprisingly observed for one of the samples. SANS results enabled us to explain this behavior by linking the protein unfolding with increasing interactions in the sample and thus its higher modulus; masking of the effect of the enzymatic scission by the increased elasticity was indeed visible for the gel consisting of compact proteins, in which the unfolding process was taking longer time.

In both experiments, the effect of digestion and its kinetics depended significantly on the initial gel structures (protein conformations and levels of aggregation), induced by the pH of protein solution during gelation.

Fig. 1. a - SANS profiles of canola gels at pH 11 after 30 min gastric (red), followed by 10 min intestinal (green) digestion. The curves are fitted with a double Lorentzian function, giving the parameters of correlation length and exponents, shown on the graph b; c – elastic and viscous moduli in the function of gastric digestion time.



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# Structural design of polyelectrolyte-protein nanocarriers for targeted drug delivery

A. Murmiliuk<sup>1</sup>, M.-S. Appavou<sup>1</sup>, S. Vagin<sup>2</sup>, H. Frielinghaus<sup>1</sup>, A. Radulescu<sup>1</sup>

<sup>1</sup> Jülich Centre for Neutron Science, Forschungszentrum Jülich, D-857478 Garching, Germany

<sup>2</sup> Technical University of Munich, Lichtenbergstr. 4, 85748 Garching,

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Co-assembly of oppositely charged polyelectrolytes with proteins is a well-studied approach for designing stimuli-responsive nanocarriers for targeted drug delivery. [1,2] However, the complexity of protein structure limits the ability to predict and tune properties of the formed nanoparticles. The ultimate goal of our research is to reveal the main triggers for the morphological transition of protein/polyelectrolyte complexes, their encapsulation efficacy and particles stability by systematic study of complexes formed by block copolymers with proteins and encapsulated ionic drug. Using scattering and microscopy techniques, we showed that block copolymers consisting of a weak polyelectrolyte block and a neutral hydrophilic block co-assemble with proteins at pH close to protein isoelectric point and the morphology of the formed particles can be tuned by varying pH and nature of proteins. Moreover, we observed that formed protein/polyelectrolyte complexes with an excess of a charge can be used for encapsulation of an oppositely charged drug thus allowing us to use one carrier for both protein and drug delivery, and to design nanocapsules with such tunable properties as charge, stability and size.

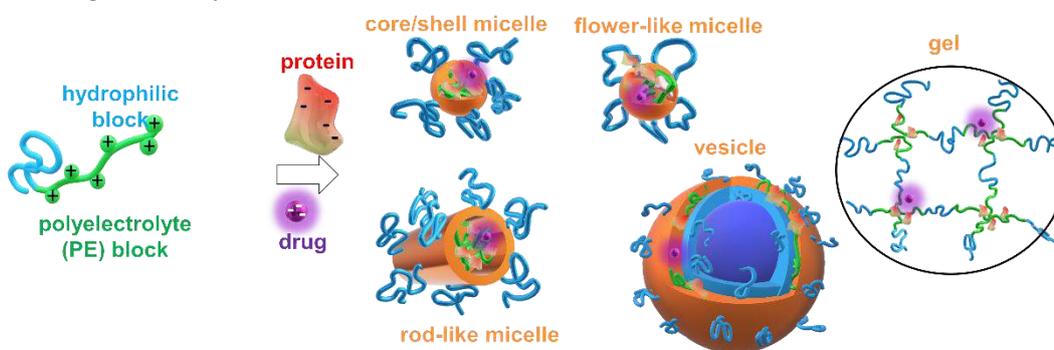


Fig. 1. Co-assembly of a block copolymer with a protein and a drug.

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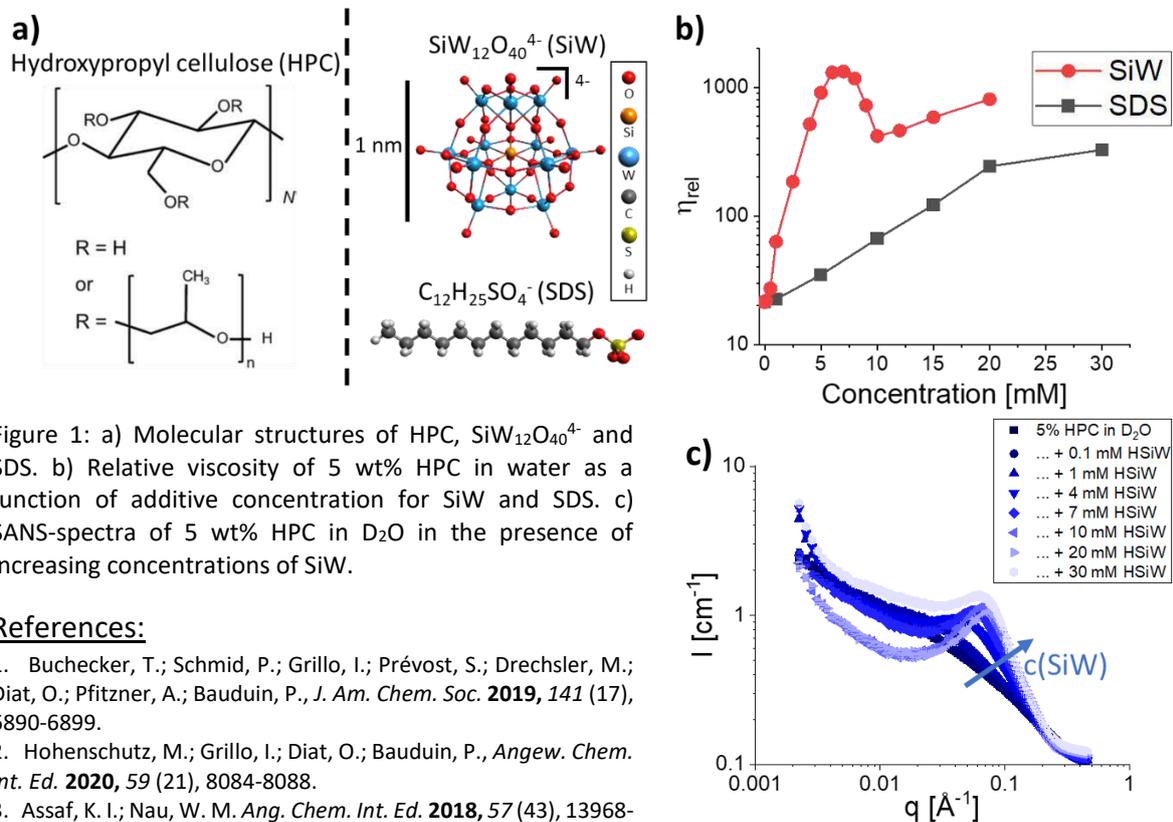
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# Solution structure and viscoelasticity of cellulose ethers in the presence of chaotropic nano-ions

**Max Hohenschutz<sup>1</sup>**, Carlos G. Lopez<sup>1</sup>, Walter Richtering<sup>1</sup>

<sup>1</sup> Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, Aachen 52056, Germany

Cellulose derivatives, such as non-ionic cellulose ethers find ample application as rheology modifiers in cosmetics, foods and drilling fluids in particular due to their molecular stiffness, expressed by large Kuhn lengths of 10-20 nm, and their intrinsic tendency to aggregate in solution. Often cellulose ethers are used in the presence of additives, such as salts and surfactants, to fulfil the needs of the given application and to tailor the polymers rheological behavior. Here, we investigate the effects of nanometer-sized ions (nano-ions) on the aqueous solution rheology and structure of hydroxypropylcellulose (HPC, see Fig.1a). Nano-ions, such as the polyoxometalate  $\text{SiW}_{12}\text{O}_{40}^{4-}$  (SiW, structure in Fig.1a), were shown to interact strongly with non-ionic soft matter, such as polymers<sup>1</sup> and non-ionic surfactants<sup>2</sup>, due to a water-mediated driving force, called the chaotropic effect.<sup>3</sup> We thus find that millimolar SiW-concentrations increase drastically (by a factor of 100) the viscosity of aqueous HPC-solutions, see Fig.1b, leading to gelation at higher SiW-concentrations ( $\approx 50$  mM). These rheological effects are unprecedented in comparison to classical additives such as salts, or ionic surfactants as exemplified for SDS, see Fig.1b and appear presumably due to physical nano-ion crosslinking between polymer chains. Small Angle Neutron Scattering further revealed the emergence of a correlation peak (Fig.1c) at low SiW-concentrations that disappears in the presence of an electrolyte like NaCl (not shown) or at higher SiW-concentrations (Fig.1c). This intermittent polyelectrolyte-like behavior relates to the observed rheology trends. Chaotropic nano-ions thus emerge as novel rheology modifiers and nano-ion/polymer complexes might serve as smart soft materials due to their UV and heat sensitivity.



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# POSTERS

# Solubilization of hydrophobic compounds by nano-ions.

*I. Chazapi*<sup>1</sup>, O. Diat<sup>1</sup> and P. Bauduin<sup>1</sup>

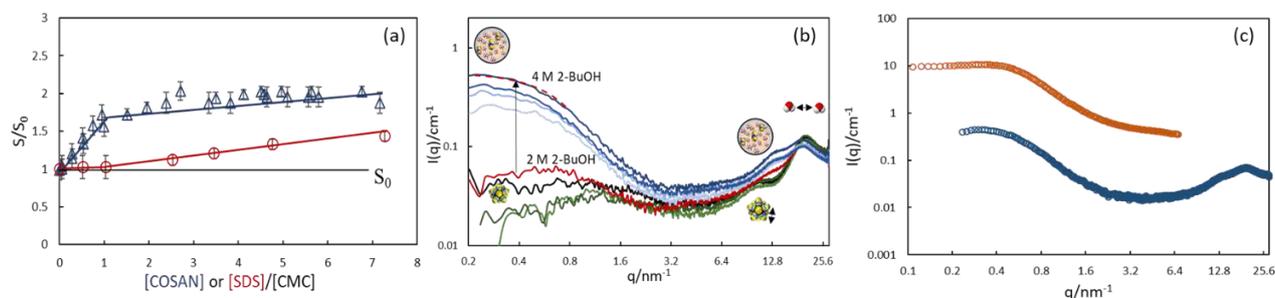
<sup>1</sup>ICSM, CEA, CNRS, ENCSM, Univ Montpellier, Marcoule, France

Solubilization of hydrophobic compounds in water is essential in many applications, such as in pharmacy, fragrancancy, detergency, and crop science. The solubilization of hydrophobic compounds by surfactants in water has been extensively studied. [1] In this present work, we studied a new approach of solubilization partially hydrophobic compounds by nano-metric sized inorganic ions, such as cobalta-bis-dicarbollides (COSAN), which do not have the classical hydrophilic-hydrophobic structure of surfactants.

COSAN and its derivatives are inorganic and ionic clusters composed of a central cobalt ion, sandwiched between two dicarbollide cages formed by boron and carbon atoms (and halogens for derivatives) with two negative charges. Despite lacking a classical amphiphilic structure, COSAN is distinguished by its surfactant properties such as self-assembly in water, [2] surface activity, [3, 4] foaming [5] and formation of lyotropic phases. [6]

We have found that COSAN anion effectively solubilizes organic and partially hydrophobic compounds in water and we studied 2-butanol in particular. On the contrary, with classical surfactants, such as SDS, where there is no solubilization below the critical micelle concentration, COSAN anion is an efficient solubilizer as soon as some COSAN molecules are added. Moreover, as COSAN concentration increases, the amount of solubilized hydrophobic compound increases, which is not the case with classical surfactants (Fig. 1a).

Spectroscopic and scattering techniques were used in order to decipher this unconventional solubilization mechanism at the molecular and supramolecular levels. As revealed by SWAXS (Fig. 1b) and preliminary SANS (Fig. 1c), the alcohol solubilization by COSANs is made by the formation of thermodynamically stable (COSAN/hydrophobic compounds) nano-droplets (2 to 10 nm in size) that we will develop in this presentation. A new concept of solubilization using COSANs creates a new opportunity for the solubilization of other hydrophobic compounds in many applied fields.



**Figure 1:** (a) Normalized solubility of 2-butanol in water as a function of COSAN (blue triangles) or SDS (red circles) normalized concentration. (b) SWAXS spectrum of 0.09 M COSAN (dark), in the presence of different 2-butanol concentrations. (c) SANS (orange) and SAXS (blue) spectrum of 0.04 M COSAN in the presence of 4 M 2-butanol.

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# A micellar shape restricted to spheroids: New nematic and hexagonal lyotropic liquid crystals evidenced by SAXS/SANS combination

**P. Denk**<sup>1</sup>, A. El Maangar<sup>2</sup>, S. Prévost<sup>3</sup>, T. Zemb<sup>2</sup>, and W. Kunz<sup>1</sup>

<sup>1</sup> *University of Regensburg, Institute of Physical und Theoretical Chemistry, Universitätsstr. 31, Regensburg D-93053, Germany*

<sup>2</sup> *ICSM, Univ. Montpellier, CEA, CNRS, ENSCM, Marcoule, France*

<sup>3</sup> *Institut Laue-Langevin (ILL), 71 avenue des Martyrs CS 20156, 38042 Grenoble Cedex 9, France*

SAXS and SANS are used to determine the molecular mechanisms involved in binary solutions of octyl ether octaethylene oxide carboxylic acid ( $[H^+][C_8E_8C^-]$ , Akypo™ LF2) in acidic, sodium and calcium forms. Independently of temperature and concentration, only spherical or slightly prolate micelles are formed due to the surfactant's strong packing constraint. In the presence of sodium or calcium ions, the micelles cannot only be negatively charged, but also intermicellar cross-linking is made feasible by divalent calcium ions or by two monovalent sodium ions. Even in the presence of multivalent ions, the micelles are stable only in two morphologies: the classical core-shell state ( $L_1$ ) and the water-poor state with partially interdigitated head-groups ( $L_1'$ ). At the borderline of these two regimes, the 'flocculated' micellar regime ( $L_1/L_1'$ ), a new wormlike hexagonal (WH) phase made from linear chains of charged prolate micelles is found. The peak shift in SAXS/SANS allows a direct proof that the WH phase is an unusual lyotropic liquid crystalline phase because the hydrocarbon cores have the same shape as in the micelles. The WH phase of  $[H^+][C_8E_8C^-]$  shares some characteristics with a proposed transition from a classical hexagonal phase of infinite cylinders ( $H_1$ ) to a cubic  $Im3m$  phase by Sakya et al. [1] in binary mixtures of  $C_{12}E_{12}OH$  and water. Sakya et al. proposed that undulations form in the hexagonally packed cylinders with the cylinders subsequently being 'pinched' at regular intervals to form the isotropic cubic phase made of spherical micelles. In the case of  $[H^+][C_8E_8C^-]$ , however, neither a  $H_1$  nor a cubic phase are observed. Instead of a cubic phase made of spherical micelles, a hexagonal phase made of prolate micelles is found. An increase in temperature leads to a decrease of the average number of micelles per chain, 'melting' the hexagonal phase into a nematic phase (N) and eventually into an isotropic micellar phase. While there are some examples of nematic phases made of prolate or oblate micelles made of charged surfactants and a co-surfactant in literature [2,3], they always involve a micellar shape transition through the right ratio between surfactant and co-surfactant. Thus, they are intermediate states between lamellar or  $H_1$  phases and do not form a hexagonal phase made of the same prolate or oblate micelles but have a shape transition to cylinders. In the present case, there is no shape transition involved and all phases are made of the same prolate micelles. The presence or absence of a lower critical solution temperature (LCST) located on the clouding line is related to intermicellar interactions between small spherical or prolate micelles. Clouding is driven by intermicellar attraction and impeded by electrostatic repulsion. If electrostatics are screened, ion bridging can enhance intermicellar attraction especially well at higher concentrations (in the  $L_1/L_1'$  phase), thus lowering the LCST and shifting it to higher concentrations. Auto-coacervation triggered by polar head-group heterogeneity occurs as equilibrium between a sub-critical micelle concentration bulk phase and small quantities of a coacervate that is made of macroscopically observable droplets formed by flocculated, partially head-group interdigitated micelles well inside the single-phase domain at the borderline between core-shell micelles and head-group interdigitated micelles ( $L_1/L_1'$ ).

[1] P. Sakya, J.M. Seddon, R.H. Templer, R.J. Mirkin, G.J.T. Tiddy, *Langmuir*, 13 (1997) 3706-3714.

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# Hybrid hydrogels with Pickering Emulsion as cross-linkers: a new smart system for drug delivery applications

**F. Ferdeghini**<sup>1,2</sup>, **C. Rerzki-Vérité**<sup>1,2</sup>, **Z. Guennouni**<sup>1,2</sup>, **C. Le Cœur**<sup>2,3</sup>, **F. Cousin**<sup>2</sup>, and **F. Muller**<sup>1,2</sup>

<sup>1</sup>Groupe Nanosciences et Nanotechnologie, ECE Paris-Lyon, Paris, France,

<sup>2</sup>Laboratoire Léon Brillouin (CEA-CNRS)

<sup>3</sup>Institut de Chimie des Matériaux Paris-Est

Due to their high water content, lipid liquid crystalline (LC) phases are prime candidates for biocompatible applications [1]. These systems can be stabilized in water by adding inorganic colloids and thus forming stable (water-in-oil)-in-water micro-Emulsions as Pickering emulsions (PEs) with an additional inner nanostructure [2,3]. Such submicronic particles as illustrated in Figure 1 in the case of Phytantriol droplets, that display a Pn3m symmetry, are stabilized by clay nanoplatelets of Laponite.

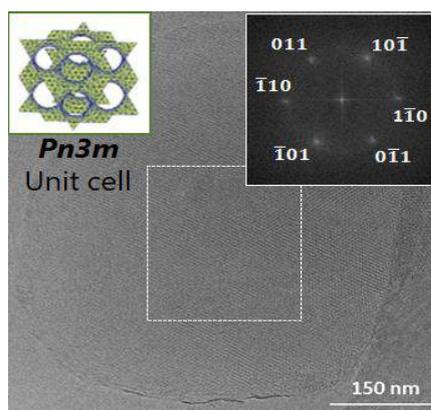


Figure 1 Cryo-TEM image of Phytantriol PE drop stabilized by Laponite nanoplatelets.

We apply such an approach for the formulation of physical hydrogels, where the PE drops act as cross-linkers. We chose a synthesis route for which a part of polymer chains penetrates the emulsion drops, in order to ensure the cross-linking of hydrogels. The use of PEs has two main advantages : i) the drops act like a physical cross-linker, which guarantees very good mechanical properties and ii) the core of the cross-linkers is liquid, so it can be loaded with other molecules. These systems are then very interesting for drug delivery-based applications since both hydrophobic and hydrophilic molecules can be loaded into the LC phases.

The goal of this work is to investigate the correlation between the mechanical and structural properties of Polyacrylamide-based hydrogels cross-linked by the LC stabilized emulsions.

We performed small angle neutron scattering measurements in order to characterize the structure of these systems at the nanoscale.

Firstly, we studied the impact of the in situ polymerization on the organisation of the LC phase. We demonstrated that the addition of the monomers and the consequent polymerization have a strong influence on the crystalline phase, which evolves during the hydrogel formation.

Secondly, we studied the structural organization of the hydrogels when a mechanical stress is applied. We observed a remarkable effect on the drop shape at severe deformations only. At medium deformation range, an isotropic pattern is observed, suggesting that no shape modification occurred. On the reverse, at large deformation (elongation higher than 100%), a spectacular effect is observed at low Q as the 2-D pattern becomes anisotropic in the stretching direction, revealing that the drops were deformed. Furthermore, in these conditions, the mechanical stress also induces a slight deformation of the inner structure of the lipid LC phase.

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[2] A. Salonen et. al., *Langmuir*, 24 (2008) 5306-5314

[3] F. Muller et. al., *Soft Matter*, 8 (2012) 10502-10510

# SANSPOL investigation of structural changes in transformer oil-based ferrofluids induced by electric and magnetic fields

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**M. Karpets**<sup>1,2</sup>, M. Rajnak<sup>1,2</sup>, D. Honecker<sup>3,4</sup>, V. Petrenko<sup>5,6</sup>, A. Feoktystov<sup>7</sup>, M. Avdeev<sup>8</sup>, M. Timko<sup>1</sup> and P. Kopčanský<sup>1</sup>

<sup>1</sup> IEP SAS, Košice, Slovak Republic

<sup>2</sup> FEI TUKE, Košice, Slovak Republic

<sup>3</sup> University of Luxembourg, Luxembourg

<sup>4</sup> Institut Laue-Langevin, Grenoble, France

<sup>5</sup> BCMaterials, Leioa, Spain

<sup>6</sup> IKERBASQUE, Bilbao, Spain

<sup>7</sup> Jülich Centre for Neutron Science, Garching, Germany

<sup>8</sup> FLNP JINR, Dubna, Russia

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Dispersion of superparamagnetic nanoparticles (SPN) in transformer oils constitute an extraordinary cooling and electrical insulating medium (ferrofluid). The peculiar dielectric behaviour and breakdown mechanism is still not clear. Recently, SPN aggregation in electric fields was deduced from dielectric measurements and formation of anisotropic structures was proved by SANS (Fig. 1) [1]. We also have demonstrated the influence of the concentration of nanoparticles, carrier liquid and experimental setup on SANS measurements of the classical magnetic fluids (magnetite coated with oleic acid in transformer oil) [2]. The aim of the presented experiment was to investigate the relation of the electric field induced structural changes in a ferrofluid regarding their magnetic properties. SANSPOL intensities  $I+(q)$ ,  $I-(q)$  were measured depending on the magnetic field acting both, alone and simultaneously with the external electric field. The experiment was conducted at D33 instrument (ILL). It was found that the electric voltage acting on the ferrofluid causes a remarkable increase in scattering intensity at small  $q$  range. This increase is proportional to the strength of the field. The increase in the intensity originates from the presence of larger aggregates in the sample which were induced by the applied electric field. However, there is no remarkable difference between the scattering intensity of up and down neutron spins, so pointing out the absence of any magnetic structure in the created aggregates. The identical SANSPOL curves are observed for both cases, in the absence and presence of the electric field. A noticeable difference in the SANSPOL curves has been detected in the case, when the sample is simultaneously exposed to both, electric and magnetic field. In magnetic field only, the SANSPOL curves indicate the well-known chain like anisotropy in the magnetic field induced aggregates. The most pronounced difference in the SANSPOL curves is seen in the case when both, magnetic and electric fields act on the ferrofluid sample. As the magnetic field was applied firstly on the sample and subsequently the electric voltage was switched on, one can assume that the electric field enhanced the magnetic anisotropy in the formed aggregates.

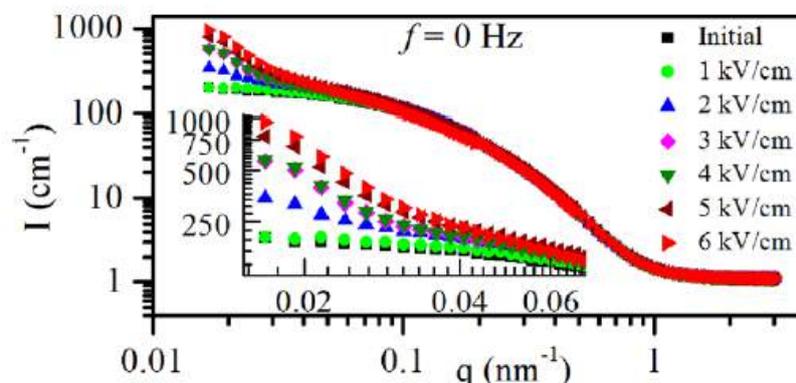


Fig. 1. SANS curves for the ferrofluid exposed to the dc electric field strengths from 0 kV/cm (initial) to 6 kV/cm [1].

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[1] M. Rajnak et al., Appl. Phys. Lett., 107, 7 (2015) 073108.

[2] M. Karpets et al., Ukr. J. Phys. 65 (2020) 729.

# Illuminating the structure of nanomedicines: small angle scattering of iron carbohydrates in complex biological environments

Leonard Krupnik<sup>1,2,3</sup>, Neda I. Anaraki<sup>1,2,3</sup>, Marianne Liebi<sup>4</sup>, Joachim Kohlbrecher<sup>5</sup>, Clement Blanchet<sup>6</sup>, Peter Wick<sup>2</sup>, Antonia Neels<sup>1,3</sup>

(1) Center for X-ray Analytics, Empa, Swiss Federal Laboratories for Materials Science and Technology, St. Gallen, Switzerland

(2) Laboratory of Particles-Biology Interactions, Empa, Swiss Federal Laboratories for Materials Science and Technology, St. Gallen, Switzerland

(3) Department of Chemistry, University of Fribourg, Fribourg, Switzerland

(4) Laboratory for Condensed Matter, PSI Paul Scherrer Institute, Villigen, Switzerland

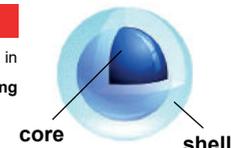
(5) Laboratory for Neutron Scattering, PSI Paul Scherrer Institute, Villigen, Switzerland

(6) European Molecular Biology Laboratory (EMBL), Hamburg Outstation c/o DESY, Hamburg, Germany



## Introduction

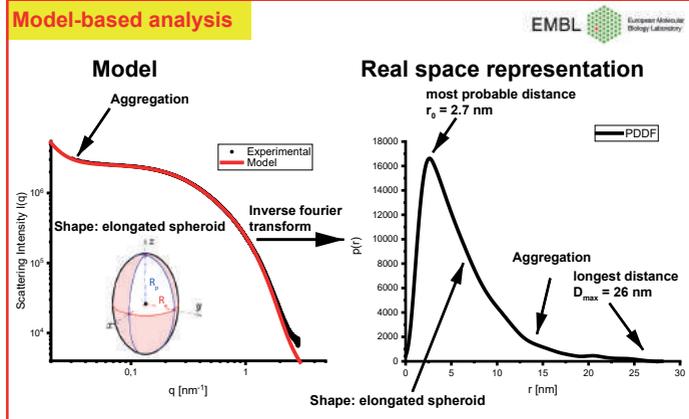
**Intravenous iron carbohydrates** are promising and dominant **nanomedicines** for treatment of iron deficiency anemia<sup>1,2</sup> which is linked to illnesses including chronic kidney disease and chronic inflammatory arthritis. These products aim to treat anemia in the same way, however biological studies show differences in efficacy<sup>3</sup>. These changes are caused by structural differences, which could be related to a hypothetical **carbohydrate shell** forming around the **iron core**<sup>4</sup>. Using **small angle x-ray scattering (SAXS)** and **small angle neutron scattering (SANS)** we aim to characterize the physicochemical properties of the iron core and the carbohydrate shell in their original environment and in biological environments.



Assumed structure of iron carbohydrates

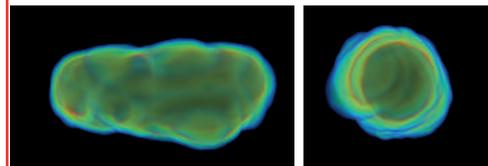
## 1 SAXS resolves iron core

SAXS resolves **particle size, shape** and **aggregation behavior** of the iron core of iron sucrose.



## Model-independent analysis (DENSS)

Electron density reconstructions from experimental SAXS data



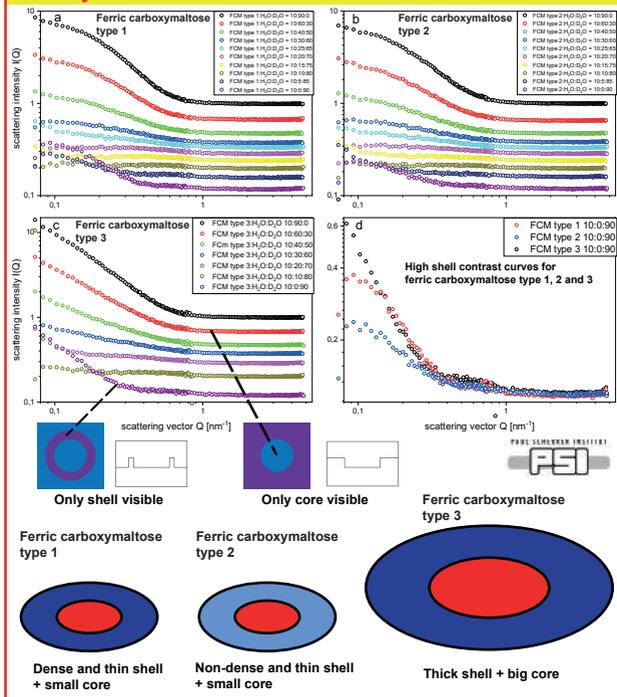
Model-independent approach suggests elongated particles!

Grant, T. Ab initio electron density determination directly from solution scattering data. *Nat Methods* 15, 191–193 (2018).

## 2 SANS resolves carbohydrate shell

SANS resolves the carbohydrate shell of different types of ferric carboxymaltose (FCM) by **variation of the contrast** of the solvent through addition of D<sub>2</sub>O and H<sub>2</sub>O.

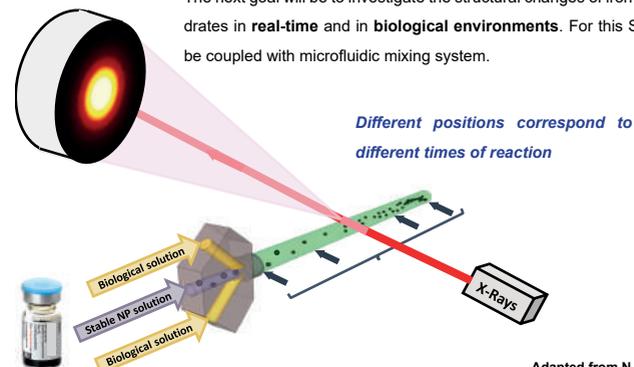
### Differences in shell thickness and density between iron carbohydrates



## Outlook: In-situ SAXS investigations

### Characterization in dynamic conditions

The next goal will be to investigate the structural changes of iron carbohydrates in **real-time** and in **biological environments**. For this SAXS will be coupled with microfluidic mixing system.



Adapted from N. Anaraki<sup>5</sup>

## Conclusion

We were able to resolve the iron core of various iron carbohydrates and characterize its physicochemical properties via SAXS. In addition, we resolved the carbohydrate shell by contrast variation via SANS and determined differences in shell thickness between iron carbohydrates.

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## Reinforced hydrogels: polymer cross-linking by emulsion droplets

**A. Mikhailovskaya**<sup>1</sup>, C. Le Cœur<sup>1</sup>, F. Cousin<sup>2</sup>, C. Amiel<sup>1</sup>, J. Goyon<sup>3</sup>, F. Rouyer<sup>3</sup>, F. Ferdeghini<sup>4</sup>, F. Muller<sup>4</sup>

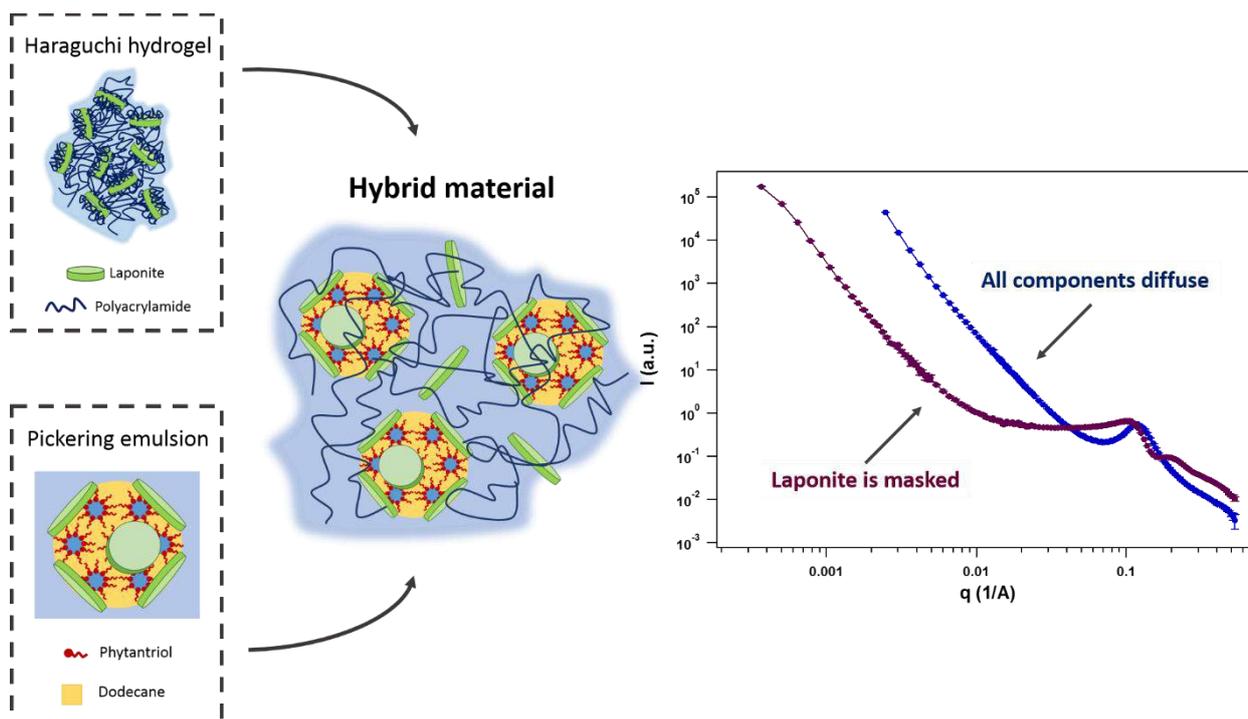
<sup>1</sup> Institut de Chimie et des Matériaux Paris-Est, Thiais, France

<sup>2</sup> Laboratoire Léon Brillouin, CEA Saclay, Gif-sur-Yvette, France

<sup>3</sup> Laboratoire Navier, Université Gustave Eiffel, Champs-sur-Marne, France

<sup>4</sup> ECE Paris, Paris, France

Hybrid materials of a polymer network with inclusions of lyotropic liquid crystalline droplets can provide versatile transport of both hydrophilic and hydrophobic substances through aqueous media. Therefore, such systems have a great potential for biotechnological and food science applications. However, weak mechanical strength of the hydrogel skeleton significantly limits the use of such composites. Haraguchi *et al.* [1] proposed to prepare hydrogels with improved mechanical properties by free radical polymerization in an aqueous suspension of Laponite clay particles. In this case, the polymer chains adsorb at the surface of the particles so that the cross-linking density of the resulting physical gel network is largely increased. We combine this effect with Pickering stabilization of droplets by Laponite particles [2] to prepare hydrogel/emulsion composites. Due to the droplets acting as multifunctional cross-links, the materials demonstrate an enhanced elastic modulus in comparison with Haraguchi hydrogels. To find out the correlation of the mechanical properties with the structure, we study the multi-scale organization of the materials using electron microscopy, X-ray Scattering and Small Angle Neutron Scattering (SANS). Thanks to the contrast variation technique, SANS allows to probe separately the arrangement of all the five different components in the system.



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## SANS contrast variation for the localization of anionic dyes in DTAB-micelles

**W. Müller**<sup>1</sup>, R. Schweins<sup>1</sup>, B. Nöcker<sup>2</sup> and K. Huber<sup>3</sup>

<sup>1</sup> Institut Laue-Langevin, Grenoble, France

<sup>2</sup> Kao Germany GmbH, Darmstadt, Germany

<sup>3</sup> University of Paderborn, Paderborn, Germany

Aqueous solutions of dye and surfactant are of major significance in practical applications such as textile dyeing, wastewater-treatment and cosmetics. Hence, numerous studies investigating dye-surfactant interaction were performed.<sup>[1]</sup> Changes in the UV/vis absorption spectrum of the dye upon surfactant-addition induced assumptions about the polarity of the environment of the dye and its location within the surfactant micelle. However, these assumptions have yet to be confirmed with measurements that unambiguously reveal a) size and shape of the dye-surfactant aggregate and b) the location of the dye within the aggregate.

Small-angle scattering (SAS) provides answers to the first question. Concerning the investigation of dye-surfactant aggregation with SAS, only one publication describing the aggregation between an anionic dye and cationic surfactants is known to us. Here, worm-like or cylindrical aggregates were described.<sup>[2]</sup> For an unambiguous localization of the dyestuff within the micelles, as it is addressed in the second question, contrast variation in small-angle neutron scattering (SANS) needs to be employed.

We studied the interaction of two commercial, anionic azo dyes (**Blue** and **Red**) with the cationic surfactant dodecyltrimethylammoniumbromide (**DTAB**) in an aqueous, alkaline buffer solution. These azo dyes self-assemble in the absence of surfactant. Whereas **Blue** forms dimers, **Red** self-assembles to higher aggregation numbers in the employed buffer. At a given dye concentration, addition of **DTAB** leads to a change in the absorption spectrum of the dye, indicating a redistribution of intermolecular interactions. Using SANS we were not only able to determine shape and size of dye-surfactant aggregates, but also to locate the dye within the dye-surfactant micelle employing contrast variation by isotopic substitution of  $h^{34}$ -**DTAB** with a mixture of  $d^{25}$ -**DTAB**/ $d^{34}$ -**DTAB**. We will present SANS-data that reveal the formation of oblate ellipsoids, cylinders or flexible cylinders from **Blue** and **DTAB**, dependent on **Blue**/DTAB-ratio, and data showing the formation of prolate ellipsoids or cylindrical structures from **Red** and **DTAB**. In all cases, the dye was found to be located on the outside of the surfactant micelle.

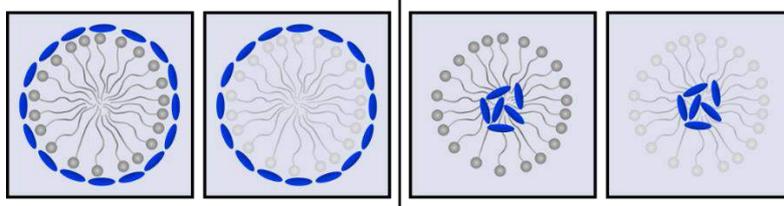


Figure 1: Sketch illustrating the principle of contrast variation in SANS by hiding the surfactant in a mixed micellar aggregate.

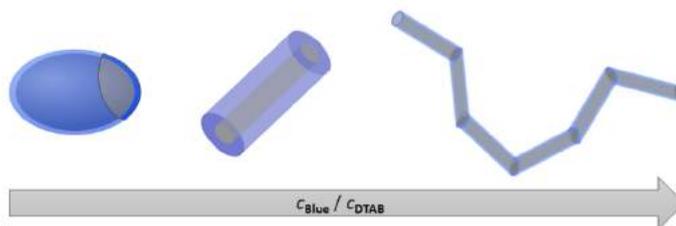


Figure 2: Shape change of **Blue**/DTAB-aggregates dependent on sample composition.

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[1] A. R. Tehrani-Bagha, K. Holmberg, *Materials*, 6 (2013), 580–608.

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## **D11+: renewal of the archetypal SANS**

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**S. Prévost**<sup>1</sup>

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The longest pinhole Small Angle Neutron Scattering diffractometer, D11, is in user operation since 1972 at the Institut Laue-Langevin in Grenoble, France. For half a century, scientific experiments covering the classical  $q$ -ranges of SANS and VSANS have been successfully conducted covering all fields of soft matter, magnetism, structural biology, cultural heritage etc. Within the upgrade programme Endurance II, a new multi-tube detector covering  $2 \text{ m}^2$  has been installed in 2021 and a new collimation will be installed in 2023, while the primary guides dating back from the construction of ILL will be overhauled. In Spring 2024, D11 will restart user service with an expected gain in brilliance of a factor 3. We present the performances of the new detector and the design for the future collimation.

# Microscopic insight on thermally driven concentration fluctuations and component dynamics in polymeric mixtures of industrial interest

**N. Shafqat**<sup>1,2</sup>, A. Alegria<sup>1,3</sup>, N. Malicki<sup>2</sup>, S. Dronet<sup>2</sup>, F. Natali<sup>4</sup>, L. Mangin-Thro<sup>4</sup>, L. Porcar<sup>4</sup>, J. Kohlbrecher<sup>5</sup>, A. Arbe<sup>1</sup> and J. Colmenero<sup>1,3,6</sup>

<sup>1</sup> *Centro de Física de Materiales (CSIC-UPV/EHU) and Materials Physics Centre (MPC), Paseo Manuel de Lardizabal 5, 20018 San Sebastian, Spain*

<sup>2</sup> *Manufacture Francaise des Pneumatiques MICHELIN, Site de Ladoux, 23 place des Carmes Dechaux, Cedex 9 F-63040, Clermont-Ferrand, France*

<sup>3</sup> *Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología (UPV/EHU), Apartado 1072, 20080 San Sebastian, Spain*

<sup>4</sup> *Institut Laue-Langevin, 71 avenue de Martyrs, Grenoble Cedex 9, 38042, France*

<sup>5</sup> *Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*

<sup>6</sup> *Donostia Internation Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 San Sebastian, Spain*

Being the main component of tires, Styrene-Butadiene Rubber (SBR) is the synthetic polymer with highest production worldwide (>5.4 millions tons in 2012). All possible kinds of routes are explored by tire companies to optimize the end-use properties of SBR. One of them consists of mixing it with other systems displaying different dynamical behaviour. This route allows tuning essential parameters like e.g. the average glass-transition temperature  $T_g$  of the final system. In mixtures, the self-concentration ingredient is believed to be the main reason for the dynamic asymmetry retained by the components, while thermally driven concentration fluctuations (TCFs) are thought to be behind the usually observed broad distribution of mobilities [1]. Blends of SBR and polystyrene oligomers (PS), as an example of a simplified industrial system, have been investigated to obtain detailed information about the segmental dynamics of both components within the blends [2,3]. In this contribution we present another binary mixture, blends of styrene-butadiene rubber with polystyrene of 500g/mol, lower size than that investigated in our previous works [2-4]. We have used small angle neutron scattering (SANS, D22 at ILL), diffuse scattering (D7 at ILL), and elastic fixed window neutron scan experiments (EFWS, IN13 at ILL). We studied blends of SBR/PS with SBR weight fraction of 80, 65, 50 and 20%. The SBR is the low- $T_g$  (faster) component and the PS or plasticizer is the high- $T_g$  (slower) component. The strategy used in this work is to investigate blends of polymers, where PS component is deuterated and the SBR protonated to follow SBR hydrogen self-motions in the blend and the inverse labelling to follow the PS component by the EFWS experiments. EFWS provides insight on the individual displacements of the components at a time of about 80ps. This informs us about the heterogeneities in the atomic displacements at such time. The EFWS can be also used to determine a 'microscopic' glass transition temperature for each of the blend components which can be directly compared with calorimetric results. As complementary experiment, by means of D7 we measured the ratio between coherent and incoherent contributions to the differential scattering cross-section to determine the range of Q where we could safely consider that the IN13 results mainly reflect incoherent dynamics of the hydrogenated blend component. From SANS, we obtained very valuable information, directly determining the correlation length and amplitude of TCFs; this allow us to define the phase diagram and assure that for the composition range investigated, in the supercooled liquid state the blend is in the miscible state.

Last, we will show preliminary results of SANS experiments performed at PSI (SANS-I) on SBR/PS blends, varying the properties of the high- $T_g$  component.

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