Experimental report

17/10/2016

Proposal: **9-12-429** **Council:** 4/2015

Title: Nanoparticle - surfactant networks - interaction in bio-friendly gels

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Sarah SCHATTE**

Experimental team: Sarah SCHATTE
Jan SELIGER

Local contacts: Isabelle GRILLO

Samples: Vesicle Gel (Fatty Acid + Amino Acid)
Wormlike Micelle Gel (Fatty Acid + Amino Acid + NaCl)
Wormlike Gel + Nanoparticles

Instrument	Requested days	Allocated days	From	To
D22	2	0		
D33	2	0		
D11	2	2	24/11/2015	26/11/2015

Abstract:

The natural fatty acid oleic acid easily forms gels depending on charge compensation brought about by counterions. In the presence of sodium chloride, long flexible wormlike micelles are formed while with arginine, an amino acid positively charged in water, it forms short stiff cylinders in a liquid crystalline packing. In both cases, viscoelastic gels are obtained, although with very different mechanical properties and temperature sensitivity.

With this experiment, we want to determine the detailed architecture of such systems in the presence of silica nanoparticles (SiNPs) functionalized with amino acids. We will elucidate if surfactants are creating a shell around the particles, if the particles adsorb or connect to the surfactant aggregates, and how the network structure is affected by the SiNPs. In addition, the structural bridging between the two types of networks will be studied. The knowledge gained from this experiment will allow understanding and optimizing hydroferrogels where magnetic nanoparticles coated with silica can induce locomotion, impeded by the gel-forming network, leading to memory effects that can be "erased" by heating cycles.

Nanoparticle – surfactant networks – interaction in bio-friendly gels

Experiment Number:	9 – 12 – 429
Date of experiment:	24.11.2015 – 26.11.2015
Instrument:	D11
Local Contact:	Isabelle Grillo
Applicants:	Sarah Schatte (Metzke)*[1], Jan Seliger*[1], Sylvain Prévost[2], Michael Gradzielski[1] (*indicates experimentalists)
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Introduction

Rheology-modifying agents are important for many practical applications, as they can tune the macroscopic viscosity and elasticity of liquids by orders of magnitude without affecting the diffusion of solvent and small dispersed colloids while fixing in space large colloids. For instance one can obtain a solid or visco-elastic material mainly made of water (hydrogel), that is typically made up from a 3D network of solid of flexible fibres. For a number of applications (encapsulation of drugs and dyes, actuators), combining the properties of a gel with those of a colloidal suspension are very exciting, in particular if synergisms can be obtained. Sodium oleate is the basic component of the historical "soap", obtained from hydrolysis of triglycerides. Bio-friendly, this surfactant is widely used today in particular in cosmetic applications. At the same time it is rather flexible with respect to the type of aggregates that can be formed by it, also to be tuned by pH. Finally magnetic colloids have been the topic of intense research for some time and currently their incorporation within more complex colloidal systems is highly interesting scientific topic.

Aims and results of preliminary work

In a DFG-funded project (PR1473/1) entitled “Magnetic field- and temperature- responsive smart hybrid materials with rheology control: interplay between magnetic nanoparticles and a physical gel network in AC, DC and AC+DC fields probed by high frequency SANS (TISANE)” within the priority program SPP1681 “Field controlled particle matrix interactions: synthesis, multiscale modelling and application of magnetic hybrid materials”, our ultimate goal is to produce and study a ferrohydrogel, where magneto-responsive nanoparticles, coated with silica and functionalized with amino acids, are interacting with a temperature-sensitive gel-forming network. Our intent is to understand how the interaction with the network in the gel state modifies the dynamics of the particles in the presence of the external field, in order to obtain an adaptive material that modifies its fieldresponsiveness and mechanical behavior based on field- and temperature-history; final applications that can be thought of are medical (artificial muscles) and technological (actuators). Studies of phase diagrams, DLS and SLS and SAXS (SAXSess) are currently conducted in our lab, along with rheology, zetametry, densimetry, pH-titration and electric birefringence.

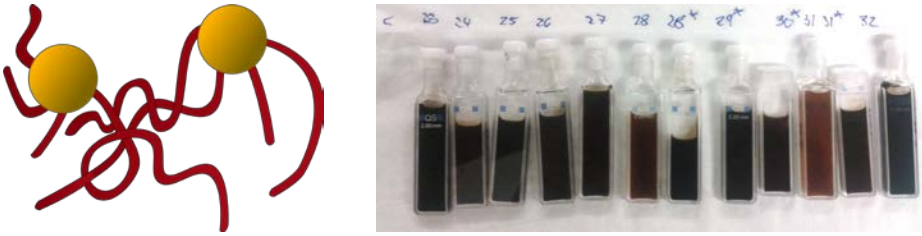

Figure 1-2: left: Sketch of nanoparticles attached to nodes of wormlike-micelles. right: Viscoelastic ferrogels that do not flow under gravity can be obtained using amino acids, oleates and silica coated magnetic nanoparticles of different shell sizes.

Our hydrogels are formed by mixing oleate salts (the pKa of oleic acid has been estimated at 9.85 [1]) with positively charged amino acids, the latter taking on the role of counter-ions of the carboxylate surfactant. The effects of the three positively charged amino acids AA (L-lysine "K", L-arginine "R" and L-histidine "H") have been compared, with arginine being the most interesting one. The system can be tuned via the molar ratio amino acid / fatty acid salt, the pH (to be changed by addition of HCl or NaOH) and the temperature (5 – 65 °C). Heated above 45 °C the solutions become low viscous, and when cooled down below 15 °C the gel becomes a white waxy solid. Our first aim now was to understand how the gel properties and structure will be influenced by the presence of silica-coated magnetic nanoparticles.

Experiment

In our SANS experiments different approaches to synthesize monodisperse silica shells were compared. The resulting particles were measured in D2O to match the magnetic core, in a sodium oleate solution (D2O) and a micellar gel made from amino acids and oleates to observe stability and agglomeration behavior in those systems, as well as influences on the gel structure.

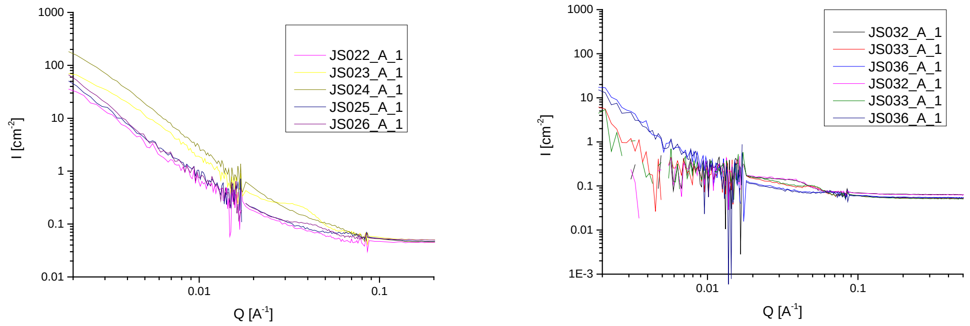

Figure 3-4: SANS data of non-successful synthesis approaches using a sonifier tip (right) and arginine as base (left) in an undisturbed μ-emulsion reaction. Data represent silica-coated magnetic nanoparticles in D2O.

Two of the three tested synthesis approaches were unsuccessful as seen in Figure 3-4. Due to the magnetic properties, the synthesis cannot be stirred magnetically without separating nanoparticles from the reaction medium (reverse μ-emulsion). Using a sonifier tip constantly during the reaction time did not lead to monodisperse shells in the planned size range of 5-15 nm. An undisturbed μ-emulsion approach using arginine as the base to catalyze thee hydrolysis of the silica precursor as seen in Figure 4 was also not successful in giving monodisperse shells in the planned size range.

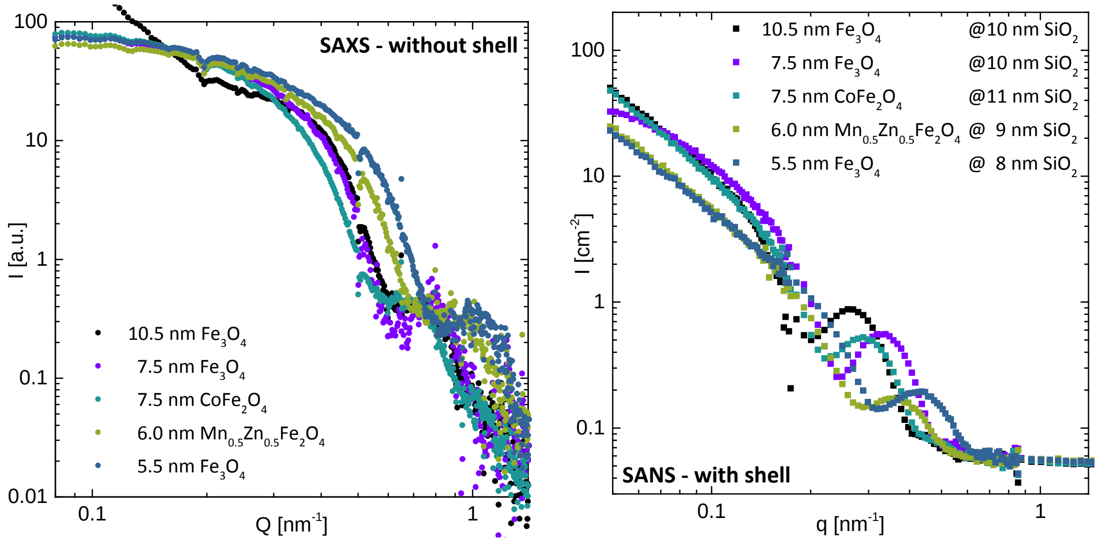

Figure 5-6: SAXS data of magnetic nanoparticles without shell (left, in cyclohexane) and SANS of particles with shell measured in D2O (right).

The third approach using a similar synthesis to the one used for particles in Figure 4, was successful. Here, ammonia was used as base in an undisturbed µ-emulsion reaction. Figure 5 and 6 show the particle cores measured in SAXS and the shells measured in SANS (in D2O – contrast match with core). In comparison to SAXS data (lab instrument, SAXSess, Anton Paar) from magnetic cores without shell, measured in cyclohexane, we can clearly see the contrast match of the core. Only the silica shell at lower q can be seen. The shell thickness obtained by this synthesis method can be calculated as 8 - 11 nm. The oscillations can be attributed to very monodisperse shells, but the lack of a plateau in the Porod region at low q also suggests agglomerates.

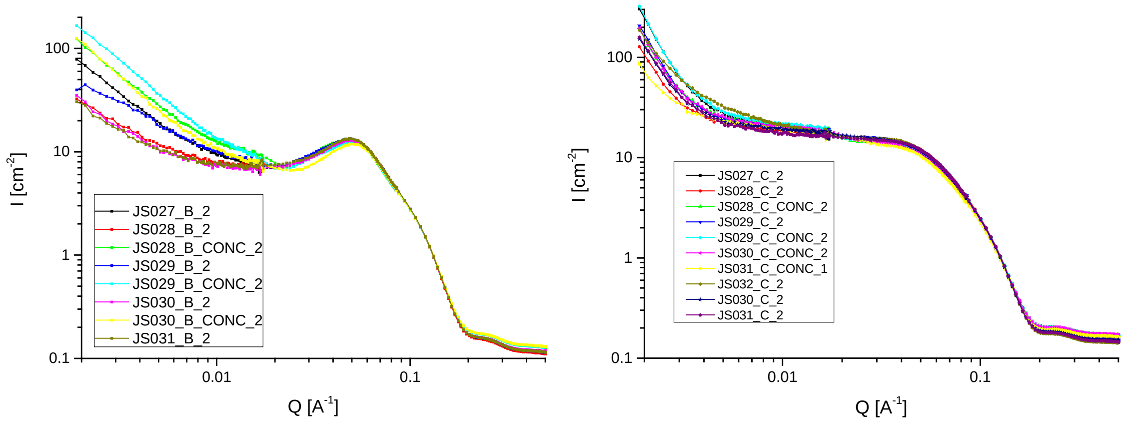

Figure 7-8: Silica coated magnetic nanoparticles in sodium oleate solution (left) and micellar gel (right). Solvent: D2O

SANS of the particles in sodium oleate solution shows stable particles with small agglomeration effects, but the vesicular structure is kept. The same is true for the worm-like micellar structures in corresponding ferrogels as seen in Figure 7 and 8.

References

[1]J. R. Kanicky and D. O. Shah, “Effect of Degree, Type, and Position of Unsaturation on the pKa of Long-Chain Fatty Acids,” Journal of Colloid and Interface Science, vol. 256, no. 1, pp. 201, 2002.