Experimental report

15/02/2019

Proposal: **9-10-1513** **Council:** 4/2017

Title: Inter droplet polymer exchange in AOT based microemulsions

Research area: Physics

This proposal is a new proposal

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Samples: $D_2O + C_8D_{18} + C_{20}H_{37}NaO_7S + (C_2D_4O)_n$
$D_2O + C_8D_{18} + C_{20}D_{36}HNaO_7S + (C_2H_4O)_n$

Instrument	Requested days	Allocated days	From	To
D11	0	0		
D22	0	1	25/03/2018	26/03/2018
D33	1	0		
IN15	7	0		

Abstract:

AOT based water in oil microemulsions in the droplet phase represent perfect systems to study the effects of soft confinement. By choosing the appropriate deuteration scheme, neutron scattering allows to focus either on confinement properties or on the water soluble polymer inserted into the core of the microemulsion droplets. At low droplet volume fractions (i.e. 10%) droplet interactions can be neglected allowing to investigate structural and dynamic properties of single confined polymer chains. This was achieved in detail in our previous experiments.

Increasing droplet concentration dynamic percolation sets in and droplet collision times are reduced to several nano seconds. Besides polymer diffusion inside a single droplet, polymer dynamics between several droplets become important leading to inter droplet diffusion. The latter will be addressed in this proposal by neutron spin echo spectroscopy on polymer loaded microemulsions in the droplet phase. Different contrast situations will thereby allow to disentangle droplet and polymer dynamics taking place on similar time and length scales.

Aim

Continuing our work on polymer loaded microemulsions based on the an-ionic surfactant dioctyl sulfosuccinate (AOT) we focused on the structural properties under increasing droplet concentration. The polymer free system is thereby compared with droplets loaded with a single chain of Poly(ethylene glycol) (PEG) with a molecular weight of $1500\,\mathrm{g/mol}$. Within past experiments the soft confining geometry provided by the microemulsion was characterised by means of phase stability and its form fluctuations with small angle neutron scattering (SANS), backscattering (BS) and neutron spin echo spectroscopy (NSE). Results were discussed in experimental reports 6-02-403, 9-10-922, 9-10-1275 and publications [1–4]. Furthermore, the structure and dynamics of the confined polymer were investigated also by SANS and NSE (report 9-10-1431 and [5]). All our previous experiments worked on low droplet concentrations ($\phi = 0.1$) in order to suppress structure factor contributions in scattering experiments and strong inter droplet dynamics of the polymer. However, to reach an equilibrated system polymer exchange between microemulsion droplets has to be present. Droplet collision times can be estimated by $\tau_{\text{coll}} = \frac{V_{\text{drop}}}{\phi} \frac{\eta}{k_B T}$, with droplet volume V_{drop}, system viscosity η and thermal energy $k_B T$.[6] In the present experiment we use droplets with a radius of $r_c = 22\,\text{Å}$ dissolved in octane at $T = 35\,^\circ\text{C}$. Varying droplet concentration ϕ between 0.2 and 0.6 allows us thus to tune collision times roughly between 60 ns and 15 ns, which lies perfectly within the time scale measurable by a possibly subsequent NSE investigation.

Here we focus on the structural properties seen by SANS, studying polymer loaded microemulsions with two different deuteration schemes, leading to a so-called shell contrast (polymer invisible) or a polymer contrast (droplets invisible). The success of this contrast variation technique was shown in one of our previous works (report 9-10-1431 and [5]). After the ILL beam time samples with polymer contrast are re-measured by small angle X-ray scattering (SAXS) with our laboratory set-up. For X-rays a shell contrast is present independent of the deuteration scheme. Thus, we obtain information on the microemulsion's droplet structure for precisely the same samples investigated previously in polymer contrast.

To isolate the effect of droplet concentration on the system's structure droplet size is kept constant and polymer load is only varied from zero to one chain per droplet on average. From a preliminary investigation by dielectric spectroscopy on the polymer loaded system the percolation transition is known to be at $\phi_p = 0.33$. In static experiments like SANS this transition is usually not visible because it is a dynamic percolation process, however for a possible NSE investigation this will be important.

Experimental details

The SANS measurements were performed on D22 with a wave length of $\lambda = 5\,\text{Å}$ and detector distances of $1.2\,\mathrm{m}$ and $8.0\,\mathrm{m}$ yielding a q range of $0.008\,\text{Å}^{-1} \leq q \leq 0.846\,\text{Å}^{-1}$. The raw data was radially averaged, corrected for electronic background and empty cell scattering, and normalized to the scattering from water using standard ILL software. For all systems glass cuvettes were used as sample cells and the temperature was controlled to be 35 °C to ensure the stability of the droplet phase also for the polymer loaded samples.

Results

Shell contrast systems

The obtained data for shell contrast samples, with and without polymer, are depicted in figure 1. For low droplet concentrations, i.e. $\phi \leq 0.3$ the typical scattering curve of a spherical core-shell particle is obtained, with a pronounced minimum around $q = 0.1\,\text{Å}^{-1}$. In general the polymer loaded samples exhibit a more shallow, smeared minimum indicating an increased polydispersity of the droplet radii. At higher q-values scattering data from polymer free and loaded systems are almost identical. At small q-values a plateau emerges with increasing ϕ, being less dominant for polymer loaded samples, a clear sign of an upcoming structure factor contribution.

With a pure form factor model it is possible to describe data for $q \geq 0.05\,\text{Å}^{-1}$ for empty and loaded droplets. The resulting core radius (water core + surfactant head groups) is consistently $r_c = 22.8\,\text{Å}$ with

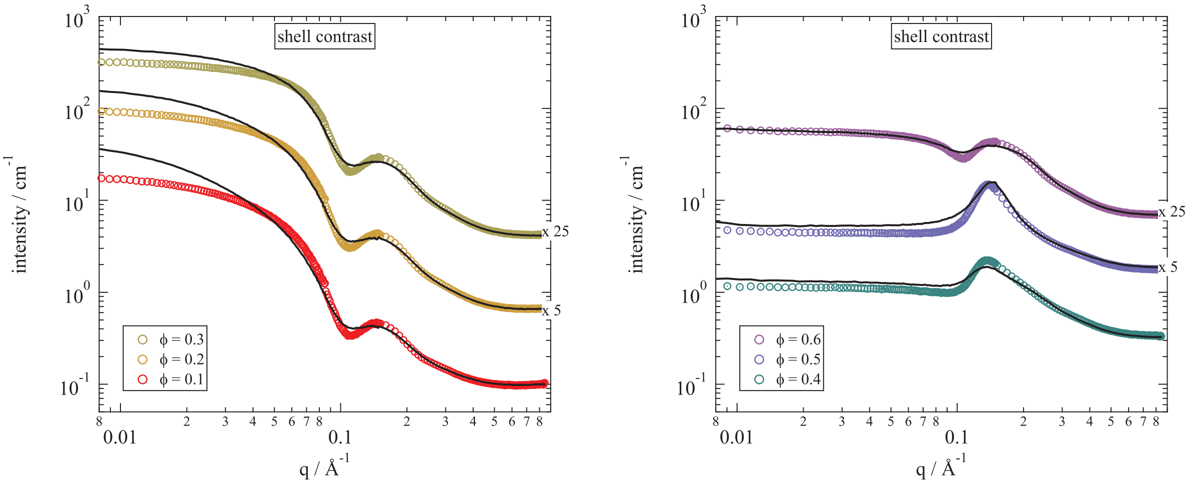

Figure 1: SANS data of the investigated microemulsions with shell contrast. Polymer free systems are depicted as coloured data points while the respective polymer loaded ones are given by solid black lines. For a better visibility data are shifted vertically by the given factors. Error bars are smaller than symbols.

a shell thickness (surfactant tail groups) of $l = 8.6\,\text{Å}$. The relative radius polydispersity is $\sigma_0 = 0.20$ and $\sigma_1 = 0.24$ for the polymer free and loaded system respectively, thus addition of polymer leads to a significant increase.

For high droplet concentrations $\phi \geq 0.4$ scattering data seems less likely to originate from a droplet phased microemulsion. The before observed maximum at $q = 0.15\,\text{Å}^{-1}$ shifts slightly to smaller values and becomes the dominating feature. Differences between polymer free and loaded systems almost vanish. A model description of highly concentrated polydisperse droplet systems is challenging because an exact solution for the combination of form factor $f(q)$ and structure factor $S(q)$ is only available for solid particles without a shell.[7] The two available approximations for the scattered intensity

$$I_d(q) \propto S(q) \cdot \langle f(q) \rangle^2 + \langle f^2(q) \rangle - \langle f(q) \rangle^2$$
$$I_a(q) \propto S(q) \cdot \langle f(q) \rangle^2$$

both fail for high polydispersities and droplet concentrations.[7] For a qualitative discussion of the emerging structure factor we therefore calculate an effective structure factor by $S_{\text{eff}}(q) = I(q)/\langle f(q) \rangle^2$.

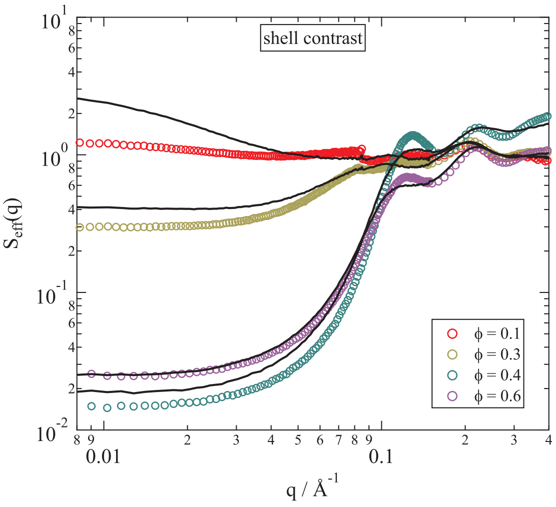

Figure 2: Effective structure factor calculated from scattering data. Polymer free systems are depicted as coloured data points while the respective polymer loaded ones are given by solid black lines.

In figure 2 a selection of resulting effective structures factors is shown. For the calculation the fitted pure form factor mentioned above was used, scaled accordingly to the increasing droplet fraction. For high droplet concentrations and q-values data oscillates not around one, but exhibits an increasing trend. This again is an indication that these systems have left the droplet phase because their scattered intensity decays weaker than q^{-4} typical for spherical droplet scattering. However, the increasing peak feature at $q^* = 0.12\,\text{Å}^{-1}$ is related to a distance $d = 2\pi/q^* = 50.6\,\text{Å}$, which matches quite well two times the droplet radius, thus precisely what one would expect for a system of densely packed spheres. The polymer loaded systems behave quite similar, only at low ϕ an additional power law feature is observed at the lowest q-values. This is well known for small polymer loaded droplets and is caused by irregularly aggregating droplets.[3]

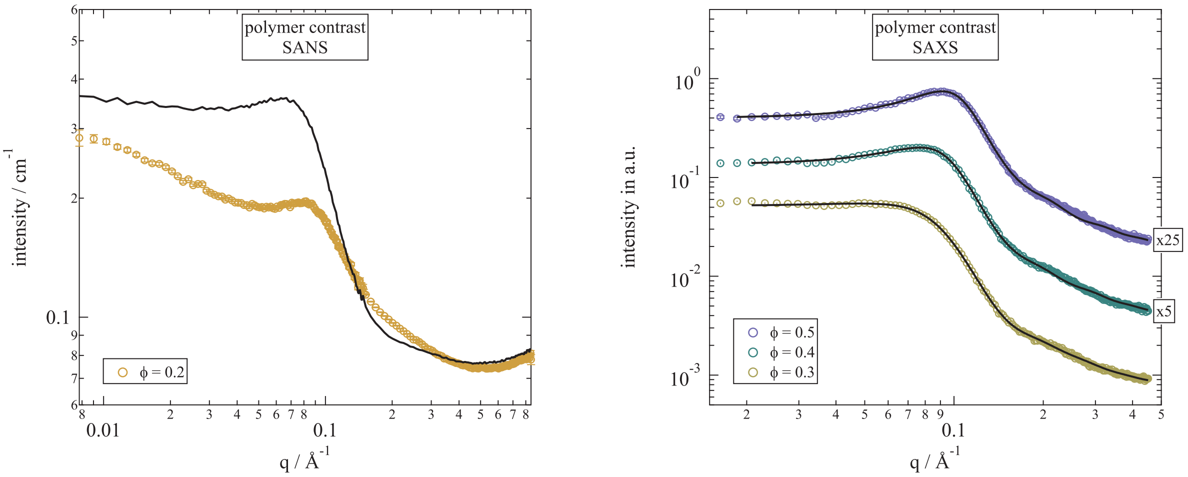

Figure 3: Left panel: SANS data of $\phi = 0.2$ sample with polymer contrast. Polymer free systems is depicted as coloured data points while the respective polymer loaded one is given by solid black line. Right panel: SAXS data of polymer loaded systems with polymer contrast. Black solid lines are fits of a spherical core-shell model with hard-sphere structure factor.

Polymer contrast systems

Evaluation of scattering data from polymer contrast systems is even more challenging. On the left hand side of figure 3 exemplary data for the polymer free and loaded $\phi = 0.2$ sample is shown. In our recent study on low droplet concentrations remaining scattering from the fully deuterated microemulsion (i.e. polymer free system) could be simply subtracted from the polymer loaded sample, because scattering from the bare system and the polymer did not add up coherently.[5] At increased droplet concentration this seems to be different. Around $q = 0.2\,\text{Å}^{-1}$ scattered intensity from the fully deuterated system is stronger than from the polymer loaded droplet, thus in the polymer loaded system additional interference effects have to be present reducing intensity in this q-region. We will need to develop a more sophisticated method of data evaluation in order to explain this observation.

However, SAXS investigations on the polymer loaded samples with polymer contrast seem promising (right hand side of figure 3). Data shown for chosen droplet concentrations can nicely be described by combination of a spherical core-shell form factor and a hard-sphere structure factor. Thus, the microemulsion systems are still in the droplet phase confining the water soluble polymer. This is an important information for the ongoing process of model development for data evaluation mentioned above.

References

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