Experimental Report

24/09/2013

Proposal:	**9-10-1275**	**Council:**	10/2012

Title: Form fluctuations of polymer loaded spherical microemulsions

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples:
Poly(ethyleneglycol) (C2H4O)n; deuterated and protonated
D2O-AOT-decane-d22 microemulsion

Instrument	Req. Days	All. Days	From	To
IN15 Standard	8	8	25/03/2013	02/04/2013
D11	1	1	08/04/2013	09/04/2013

Abstract:

Spherical microemulsions have been widely used to study confined dynamics. In addition polymer loaded microemulsions serve as a model system for the interaction of bio molecules with cell membranes. With this work we want to investigate the surfactant dynamics of a spherical water-AOT-decane microemulsion, modified by Poly(ethyleneglycol) (PEG). Our preliminary investigations suggest, that the polymer is located at the surfactant shell and modifies its relaxation behaviour. Based on this investigations, two different molecular weights of PEG are chosen, ensuring radii of gyration below and above the droplet core radius. Complementary to rather indirect preliminary measurements by X-ray and light scattering as well as dielectric spectroscopy the neutron spin-echo experiments will give us the opportunity to quantify directly the bending modulus of the surfactant shell. With additional SANS experiments the position of the polymer inside the droplets and the radii of gyration can be verified.

Aim

After recent investigations on structural as well as dynamic properties on droplet phase microemulsions with the ionic surfactant AOT, we wanted to extend our work on polymer loaded droplets by adding the water soluble polymer Poly(ethylene glycol) (PEO). As stated in experimental report 6-02-403 the droplet phase exist over a wide temperature range and includes a huge variety of droplet sizes. Within the work of experimental report 9-10-922 neutron spin echo spectroscopy revealed the membrane dynamics of the surfactant shell and resulted in a bending modulus of around $\kappa = 0.3 k_B T$ for temperatures down to $-8\,^{\circ}\mathrm{C}$. To investigate the influence of added polymer our aim was now to measure the membrane dynamics by neutron spin echo spectroscopy of droplets with water core radii close to the polymer's radius of gyration and significantly higher. To ensure the structural properties of the system and determine the polymer's radius of gyration, small angle neutron scattering (SANS) is performed as well. The chosen system was a D_2O, AOT, d-octane microemulsion with and without d-PEO ($M_N = 1300\,\mathrm{g\,mol^{-1}}$) to measure a shell contrast. The molar ratio of water to surfactant W was chosen to be 12 and 20 resulting approximately in droplet core radii of $2\,\mathrm{nm}$ and $3\,\mathrm{nm}$ respectively, fitting well to the predicted polymers radius of gyration of $1.5\,\mathrm{nm}$. The amount of polymer given to the system was calculated to result in $Z = 1$ to $Z = 3$ polymer chains per droplet on average.

Experimental details

The SANS measurements were performed on D11 with a wave length of $\lambda = 4.5\,\text{Å}$ and detector distances of $1.2\,\mathrm{m}$, $8.0\,\mathrm{m}$ and $20.0\,\mathrm{m}$ yielding a q range of $0.004\,\text{Å}^{-1} \leq q \leq 0.67\,\text{Å}^{-1}$. The raw data were radially averaged, corrected for electronic background and empty cell scattering, and normalized to the scattering from water using standard ILL software.

For the NSE experiments on IN15 we used neutron wave lengths of $\lambda = 6\,\text{Å}$ and $\lambda = 9\,\text{Å}$ and measured at angles of 4°, 7°, 10°, 13° and 3°, 6°, 9° respectively. The overall investigated q range was therefore $0.026\,\text{Å}^{-1}$ to $0.266\,\text{Å}^{-1}$ with Fourier times up to $11\,\mathrm{ns}$ for $\lambda = 6\,\text{Å}$ and $36\,\mathrm{ns}$ for $\lambda = 9\,\text{Å}$. Instrumental resolution was determined with graphite which is a coherent elastic scatterer. All spectra were corrected for background scattering from the pure solvent and the sample holder. The multi-detector signal was sub-grouped into 2 - 9 q-values per scattering angle.

For both experiments glass cuvettes were used as sample cells and the temperature was controlled to be $35\,^{\circ}\mathrm{C}$ to ensure the existence of the droplet phase also for the polymer loaded samples.

Results

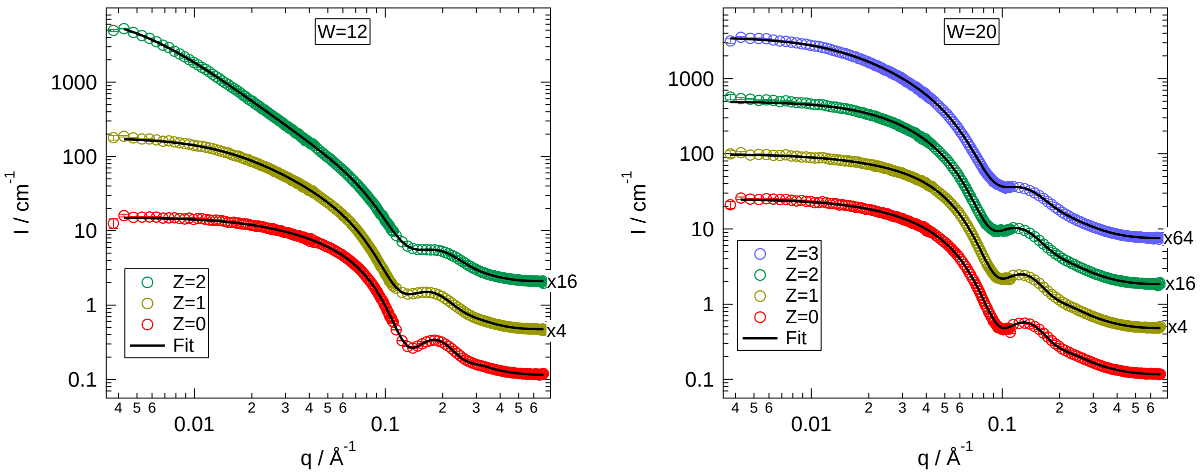

Figure 1: SANS data of the measured samples with $W = 12$ (left) and $W = 20$ (right) and different polymer content. Fitted model is described in the text

The measured SANS data is depicted in figure 1. The most prominent differences between the two series are the position of the minimum, indicating the droplet radius and the low q behaviour, sensitive to aggregation of droplets. To describe the data a spherical core shell model was used as form factor, together with a Ornstein-Zernike structure factor to take possible droplet clustering into account [1].

As also shown in figure 1 the model is fully capable to describe the measured data over the whole investigated q range. As expected the fitted radii of the $W = 20$ sample are bigger than the ones from the $W = 12$ sample in consistency with the results from van Dijk et al. [2] (fig. 2). Under addition of polymer the polydispersity of the droplet rises strongly, an effect which is more pronounced for the smaller droplets. Also the clustering is strongly affected by the polymer and the droplet size. While for the $W = 20$ series the correlation length of the Ornstein-Zernike structure factor stays almost constant around 50 Å, it increases strongly for the $W = 12$ series up to 200 Å for the $Z = 2$ sample.

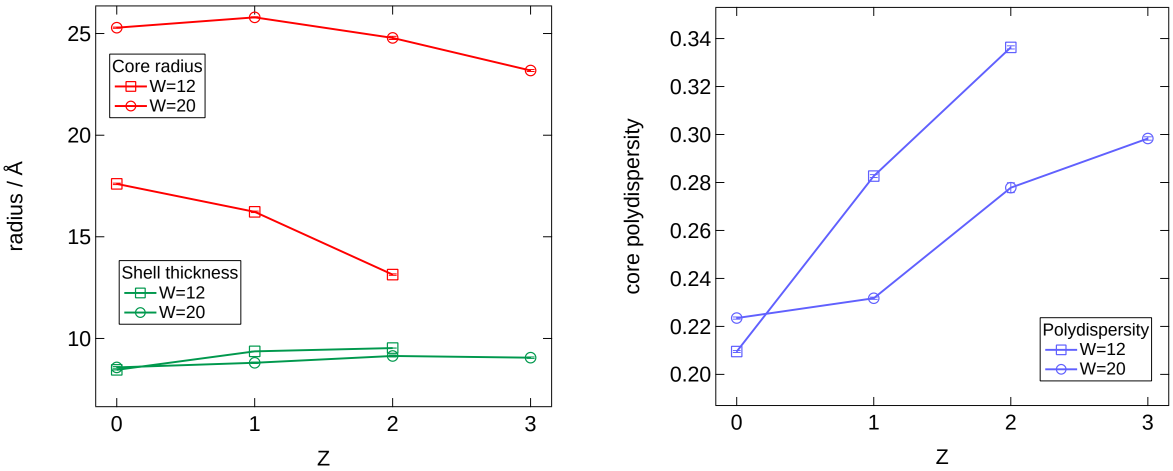

Figure 2: Fitted droplet radii and shell thickness (left) and polydispersity (right) of the sample

Summarising the SANS measurements we can confirm that all prepared samples are microemulsions in the droplet phase whose radii and shell thickness were determined precisely. The polymers influence to the structural features of the droplet are a moderate decrease in droplet radius and a pronounced tendency to clustering, especially for smaller droplets. In addition the polymers radius of gyration was measured to be 12 Å.

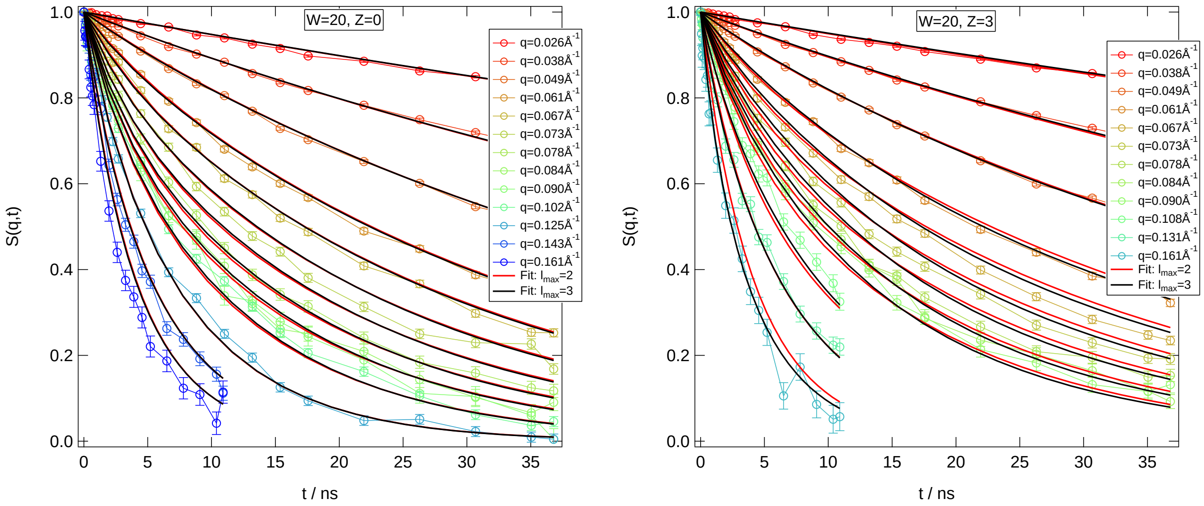

Figure 3: Intermediate scattering function for two samples with $W = 20$ for selected q values. The fits include either the $l = 2$ mode (red lines) or the $l = 2$ and the $l = 3$ mode (black lines).

Figure 3 shows exemplarily the results of two spin echo measurements for the $W = 20$ samples with and without polymer. To describe the data we choose a model suggested by Farago et al. in which the droplet shape fluctuations are expanded in spherical harmonics $R(\theta, \phi, t) = R_0 + R_0 \sum_{l,m} u_{l,m}(t) Y_{l,m}(\theta, \phi)$ with mean droplet radius R_0 and dimensionless, time dependent amplitudes $u_{l,m}(t)$. The resulting scattering function reads then as follows [3]:

$$I(q,t) \propto \left\langle \exp\left(-D_{tr} q^2 t\right) \left[f_0(qR) + \sum_{l \geq 2} \frac{2l+1}{4\pi} f_l(qR) \langle |u_l|^2 \rangle \exp\left(-\frac{t}{\tau_l}\right) \right] \right\rangle \tag{1}$$

The function $f_0(qR)$ and $f_1(qR)$ consist mainly of Bessel functions (for details see [3]), while D_{tr} is the translational diffusion coefficient, R the mean droplet radius and τ_l the relaxation time of the respective mode. With R and its polydispersity known from the SANS experiments the only fitting parameters are D_{tr}, the u_l and the τ_l which should be the same for all measured q values. Implying this a global fitting procedure was used which fitted simultaneously all measured intermediate scattering functions of one sample with either only a $l = 2$ mode (three fitting parameters) or with a $l = 2$ and $l = 3$ mode (five fitting parameters).

In the case of the polymer free sample it can be seen that including the third mode does not change the fit significantly and the data can be reasonably described by using only the second mode. For the polymer loaded droplets this changes, fits which include also the third mode can descibe the data significantly better, especially at q values around the minimum of the form factor ($q = 0.095\,\text{Å}^{-1}$) and the high q values. For the smaller droplets of the $W = 12$ series (not shown here) it is always sufficient to use only the $l = 2$ mode.

With the fitted relaxation times it is now possible to calculate the bending modulus κ by [4]:

$$\kappa = \frac{1}{48} \left(\frac{k_B T}{\pi p^2} + \frac{\eta_w R^3}{\tau_2} \frac{23\eta_o + 32\eta_w}{3\eta_w} \right) \tag{2}$$

Here p is the polydispersity and R the droplet radius both determined by SANS. The viscosities of water η_w and η_o were calculated according to [5] and [6] respectively and τ_2 is the relaxation time of the second mode determined by neutron spin echo spectroscopy. The resulting bending modulus and its variation with the polymer content Z is depicted in figure 4. For the polymer free samples the bigger droplets reveal to be less floppy than the small ones. Adding polymer leads to a massive decrease in the bending modulus almost independent from polymer content and droplet size.

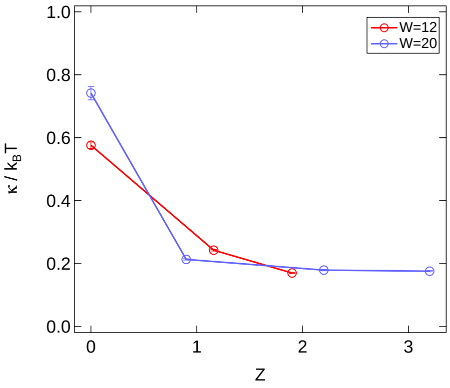

Figure 4: Calculated bending modulus for both W series in dependence from the number Z of polymer chains per droplet

References

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[6] Dymond J, Øye H. *Journal of Physical and Chemical Reference Data*, 23(1):41–53, 1994.