Experimental report

16/03/2017

Proposal: **9-12-421**

Council: 4/2015

Title: Interconnecting charged microemulsion droplets via oppositely charged polyelectrolyte effect of polyelectrolyte structure

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
TDMAO $C_{14}H_{29}NO(CH_3)_2$
TTAB $C_{14}H_{29}N(CH_3)_3$ Br
1-Hexanol $C_6H_{13}OH$
d-decane $C_{10}D_{22}$

Instrument	Requested days	Allocated days	From	To
D22	3	0		
D33	3	0		
D11	3	3	09/11/2016	12/11/2016

Abstract:

By adding oppositely charged polyelectrolyte to ionic oil-in-water (O/W) microemulsions a network of microemulsion droplets is formed that is interconnected by electrostatic binding. Such network formation allows to control viscosity and internal mobility of the droplets (e. g. relevant for the release of solubilised active agents). A very important parameter for their understanding is the mesoscopic structure and in particular the interactions between the droplets which are modified by the presence of the polyelectrolyte. This question can only be addressed properly by SANS measurements as only contrast variation allows to determine exclusively the arrangement of the droplets within the droplet/polyelectrolyte complexes. Within the planned SANS experiments we will address especially the role of polyelectrolyte structure as we will vary the type of polyanion employed and also of the size of the droplets. This shall yield a comprehensive understanding of how the architecture of the polyelectrolyte and the curvature of the microemulsion droplets control the properties of such complex systems.

Experimental Report for Exp. 9-12-421:
Interconnecting charged microemulsion droplets via oppositely charged polyelectrolyte effect of polyelectrolyte structure

March 16, 2017

We have measured the static scattering intensity of microemulsion – polyelectrolyte – complexes on the small angle neutron scattering (SANS) spectrometer D11 using a wavelength λ of 0.6 nm and sample-to-detector distances of 1.5, 8 and 34 m.

The microemulsion system used in this study consists of the zwitterionic surfactant Tetradecyldimethyl aminoxide (TDMAO), the cosurfactant Hexanol and decane as oil. By employing different amounts of cosurfactant the size of the microemulsion droplets can be varied. A positive charge can be introduced to the system by substituting small amounts of TTAB by the cationic surfactant Tetradecyltrimethyl ammoniumbromide (TTAB). Figure 1 shows the scattering profiles of microemulsions containing 5% of TTAB and different amounts of Hecanol, all were saturated with Decane. The different accessible sizes of the droplets, as well as their quite monodisperse nature and the repulsive interaction introduces by the TTAB are well visible in the SANS data.

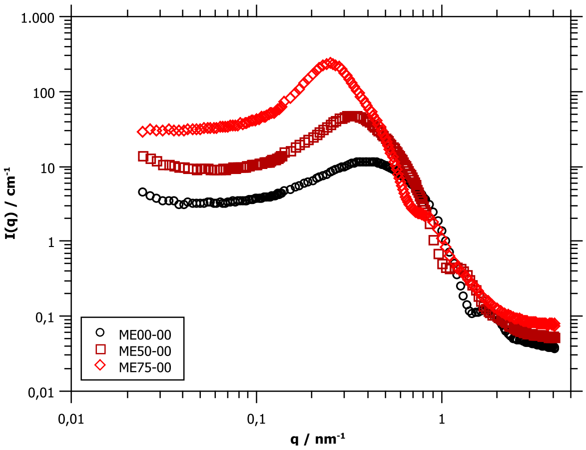

Figure 1: I(q) of pure microemulsions containing 5% TTAB and different amounts of Hexanol, showing the different accessible sizes

These microemulsion droplets are now mixed with polyelectrolytes to obtain colloidal assemblies where phase behaviour and structure depend on a large number of structural and system parameters such as: radius R, concentration, and number of charges of the microemulsion droplets, flexibility, molecular weight and charge density of the polyelectrolyte; and very importantly the mixing ratio that can be characterized by the ratio of the concentration of polyelectrolyte charges to the total charge concentration: z=[-]/([-]+[+]).

To this solution different amounts of sodium polyacrylate (NaPA) were added which led to a variation of z. We studied samples with the medium sized droplets mixed with NaPA of 60 kg/mol in the polyelectrolyte excess region with z-values of 0.70, 0.80 and 0.90 because they were the most stable mixtures. The scattering curves given in Figure 2 show that the structure of the microemulsion droplets is not affected by the addition of the polyanion, as the curves are not affected at high q. However, in the low q-regime an increasing scattering intensity is observed that can be attributed to the envisioned formation of complexes.

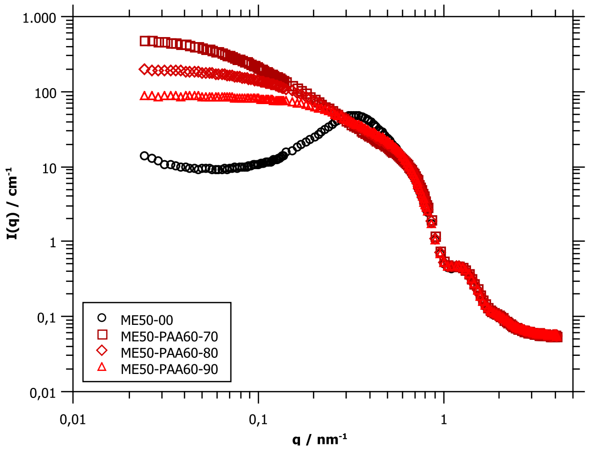

Figure 2: I(q) of pure microemulsion and samples with different amounts of polyelectrolyte (NaPA) added. The changed interactions between the droplets can be seen at low q.

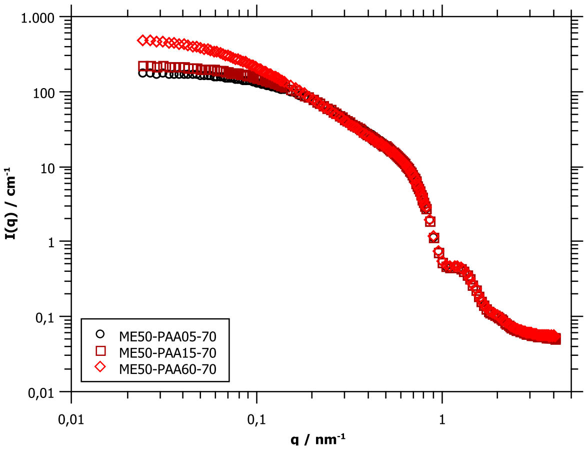

Figure 3: I(q) of microemulsion droplets mixed with Na-PA of different molecular weights but keeping the same mixing ratio.

The pronounced linear part in the scattering curves at low to medium q suggests the formation of elongated structures. Apparently the formed complexes are more elongated the closer the sample is to the phase boundary. The complexes become smaller the more polyelectrolyte is added.

Figure 3 shows the measured SANS curves of the same microemulsion droplets mixed with Na-PA of different molecular weights (5, 15 and 60 kg/mol). It can be seen that the molecular weight affects the size of the formed complexes. As expected, longer polyelectrolyte chains form bigger complexes.

The same effect can be observed for complexes are formed with smaller or larger droplets.

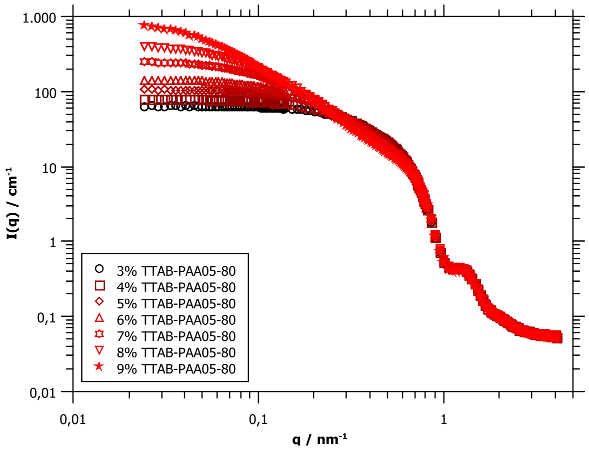

Figure 4: I(q) for microemulsion droplets with different charge density mixed with NaPA of 5 kg/mol at a mixing ratio of z = 0.8

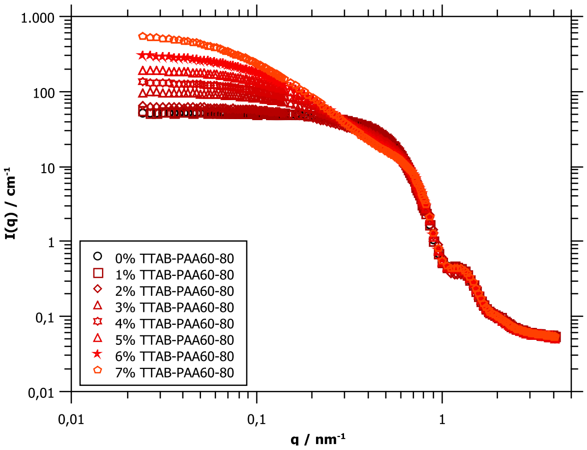

Figure 5: I(q) for microemulsion droplets with different charge density mixed with NaPA of 60 kg/mol at a mixing ratio of z = 0.8.

Further, we studied the effect of the charge density of the droplets. As can be seen in the scattering curves in figure 4 and 5, the charge density strongly affects the interaction between microemulsion

droplet and polyelectrolyte. This study was done for two different molecular weights of Na-PA but always containing the same mixing ratio between droplets and PA units.
It can be easily seen, that the droplets with no or low charge density don't interact with the polyelectrolytes, while large complexes are built at high charge densities. The shorter polyelectrolyte (Na-PA of 4 kg/mol) allows stable complexes at even higher charge densities.

To investigate the nature of the formed complexes further, a dilution series was studied. Figure 6 and 7 show the smallest microemulsion droplets, mixed with Na-PAA of 60 kg/mol in two different charge ratios: one at microemulsion- and one at polyelectrolyte excess. Both samples were prepared at a concentration of 400 mM surfactant (95% TDMAO + 5% TTAB) and diluted in several steps down to 5 mM of surfactant.
The form factor minimum in the high q region indicates that the structure of the microemulsion droplets is stable over the whole concentration range.

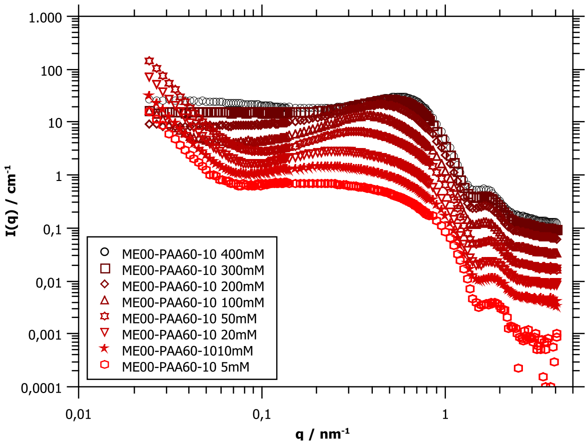

Figure 6: dilution series of complexes with small microemulsion droplets and Na-PA (60 kg/mol) at microemulsion excess.

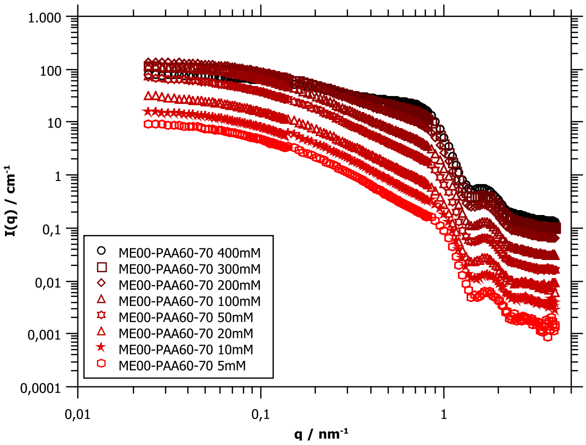

Figure 7: dilution series of complexes with small microemulsion droplets and Na-PA (60 kg/mol) at polyelectrolyte excess.

Figure 6 shows the dilution of a sample at microemulsion excess. At concentrations of 100 mM surfactant and low a rise in the intensity at small q can be seen, which indicates larger structures. To our understanding, this shows the transition from a space filling network at high concentrations into single clusters at lower concentrations.
In Figure 7, which shows the dilution of a sample at polyelectrolyte excess, no such transition is visible. Apparently the polyelectrolyte concentration in this sample is high enough to allow a continuous network formation at all concentrations.

To conclude, in this experiment we have studied a wide range of parameters, including the mixing ratio, length of polyelectrolyte, size and charge density of droplets and concentration. The results will allow to derive a detailed understanding of the effects of these parameters on the arrangement of the microemulsion droplets and how they couple together to yield polyelectrolyte modified microemulsions. This is a key step for exploring and developing such novel systems further for interesting applications.