Experimental report

21/04/2020

Proposal: **9-12-556** **Council:** 10/2018

Title: Polyelectrolyte Microemulsion Complexes (PEMECs) with Structures Tunable by pH

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: decane
TDMAO $C_{14}H_{29}NO(CH_3)_2$
1-hexanol
TTAB $C_{14}H_{29}N(CH_3)_3Br$
Poly(acrylic acid) sodium salt NaPA

Instrument	Requested days	Allocated days	From	To
D11	3	0		
D33	3	2	29/06/2019	01/07/2019

Abstract:

By mixing polyelectrolytes and oppositely charged colloids one can control structure and rheology of the system. In many applications, micelles are used as carriers for drug molecules, pollutants, reactants and similar substances that otherwise couldn't be dispersed in the solvent. It is therefore of great importance to investigate the behavior of 'loaded carriers' as it can be different to that of normal (empty) micelles. Oil-in-water microemulsion droplets with oppositely charged polyelectrolytes can be studied in detail by SANS measurements, because of the good contrast conditions of neutrons and having appropriate size range. As both components, microemulsion and polyelectrolyte, have pH dependent charge conditions, we will study the complex formation as a function of pH. This shall open highly interesting insights into pH-triggered complexation and droplet release as it is important for controlled uptake, delivery and release of the carriers.

Experimental Report for Exp. 9-12-556:
Polyelectrolyte Microemulsion Complexes (PEMECs)

April 21, 2020

We have measured the static scattering intensity of microemulsion – polyelectrolyte – complexes on the small angle neutron scattering (SANS) spectrometer D33 using wavelengths λ of 0.46 and 1.3 nm and sample-to-detector distances of 2.0, 7.8 and 12 m.

The O/W 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 (usually 5%) of TDMAO by the cationic surfactant Tetradecyltrimethyl ammoniumbromide (TTAB). The droplets were always saturated with Decane. These microemulsion droplets were 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: $z=[-]/([-]+[+])$.

In a first experiment we added a PEG(45)-NaPA(50) block-copolymer (PEG = polyethylene glycol, NaPA = sodium salt of polyacrylic acid, synthesised in our lab) to the microemulsion (ME50, 50 mM Hexanol, R ~ 4 nm, varying %TTAB) in an attempt to obtain larger microemulsion droplet clusters. The idea is, that a core of densely packed microemulsion droplets held together by the NaPA chains will be stabilised by a PEG corona. Since first samples prepared with the standard microemulsion containing 5% TTAB, did not show very large aggregates, the amount of charge per droplet was increased by increasing the amount of TTAB to 8, 10, 12 and 15%. The largest clusters were found for a microemulsion containing 10% TTAB, mixed with the block-copolymer in charge ratios z of 0.5 to 0.65 (see figure 1). Higher amounts of added TTAB led to instable complexes and phase separation.
The SANS data clearly show the formation of large microemulsion droplets clusters by the strong increase of scattered intensity towards low q. The microemulsion droplets themselves remain unaffected by the polymer addition as can be seen from the unchanged form factor minimum. Whether the microemulsion droplets in these aggregates arrange in the desired densely packed clusters is hard to see from the data. A small structure factor peak becomes visible, when the scattered intensity $I(q)$ is divided by the form factor of pure microemulsion droplets. The appearance of the structure factor peak is a promising first result but further detailed analysis is necessary to obtain a clear structural picture of the formed microemulsion-block-copolymer-aggregates.

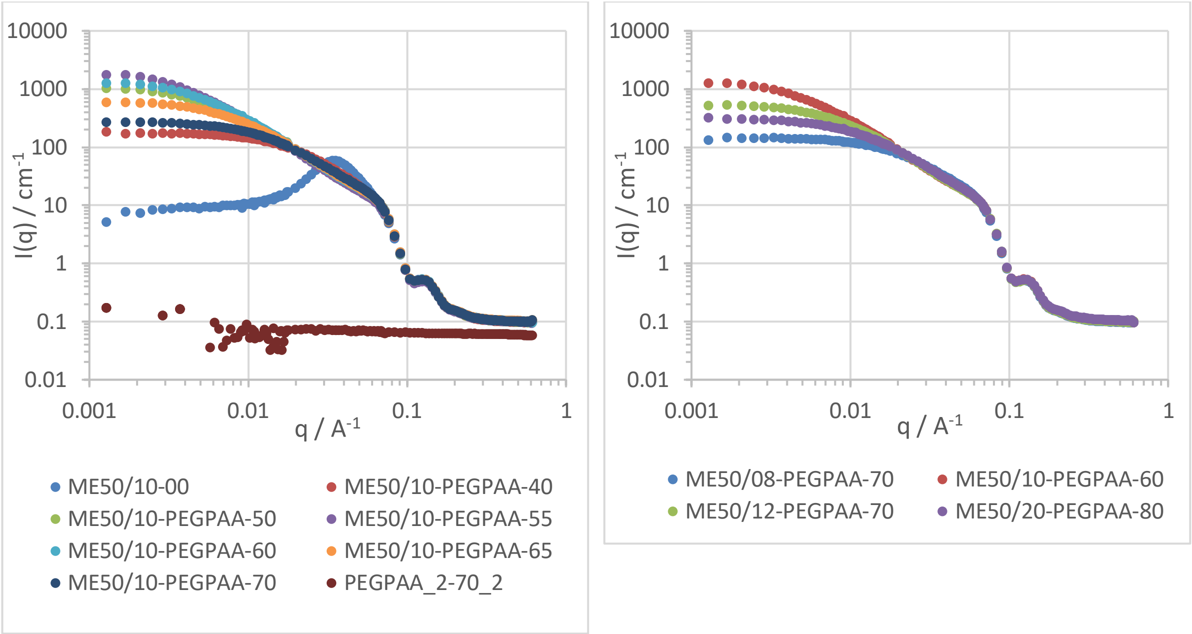

Figure 1: measured SANS data of ME50/10-PEGNaPA mixtures at different charge ratios *z* (left) and ME50-PEGNaPA mixtures with varying amount of TTAB in the microemulsion (right).

In a second experiment, we were interested in the two-phase region of the phase diagram of microemulsion-hyaluronate (HA) complexes, where a viscous coacervate phase is formed on top of a low-viscous microemulsion phase. To study the phase behaviour and the composition of the coacervate, the microemulsion (ME50, *R* ~ 4 nm, 5% TTAB) was prepared in shell contrast, using deuterated Decane d22. This microemulsion was mixed with hyaluronate of different molecular weights at a charge ratio of *z* = 0.5, where the most pronounced phase separation is expected. After equilibration, samples were carefully taken from the upper (UP) and lower phases (LP). Reference samples were prepared of the pure microemulsion and at a mixing ratio where stable microemulsion-polyelectrolyte complexes are formed (*z* = 0.7). For completeness we also included samples with another biopolyelectrolyte (Carboxymethyl cellulose, CMC) where the coacervate phase is also found, and with sodium polyacrylate (NaPA), which is undergoing a solid-liquid phase separation and no coacervate is formed here. The SANS data is shown in figure 2.

From the intensities, we can clearly see, that the upper (coacervate) phase is always more concentrated than the lower one, but also the lower phase is still containing complexes. The microemulsion droplets retain their size and shape in both phases, as can be seen from the unchanged form factor minimum. The form factor minimum can be seen very nicely in the SANS data thanks to the employed shell contrast of the microemulsion droplets. The SANS data of the coacervate phases show a structure factor peak at mid *q*, indicating densely packed droplets. It is interesting to see, that the phase behavior is similar for HA and CMC but when NaPA is added as a polyelectrolyte, the phase separation is completely different. These are very interesting first results, that certainly need further detailed analysis.

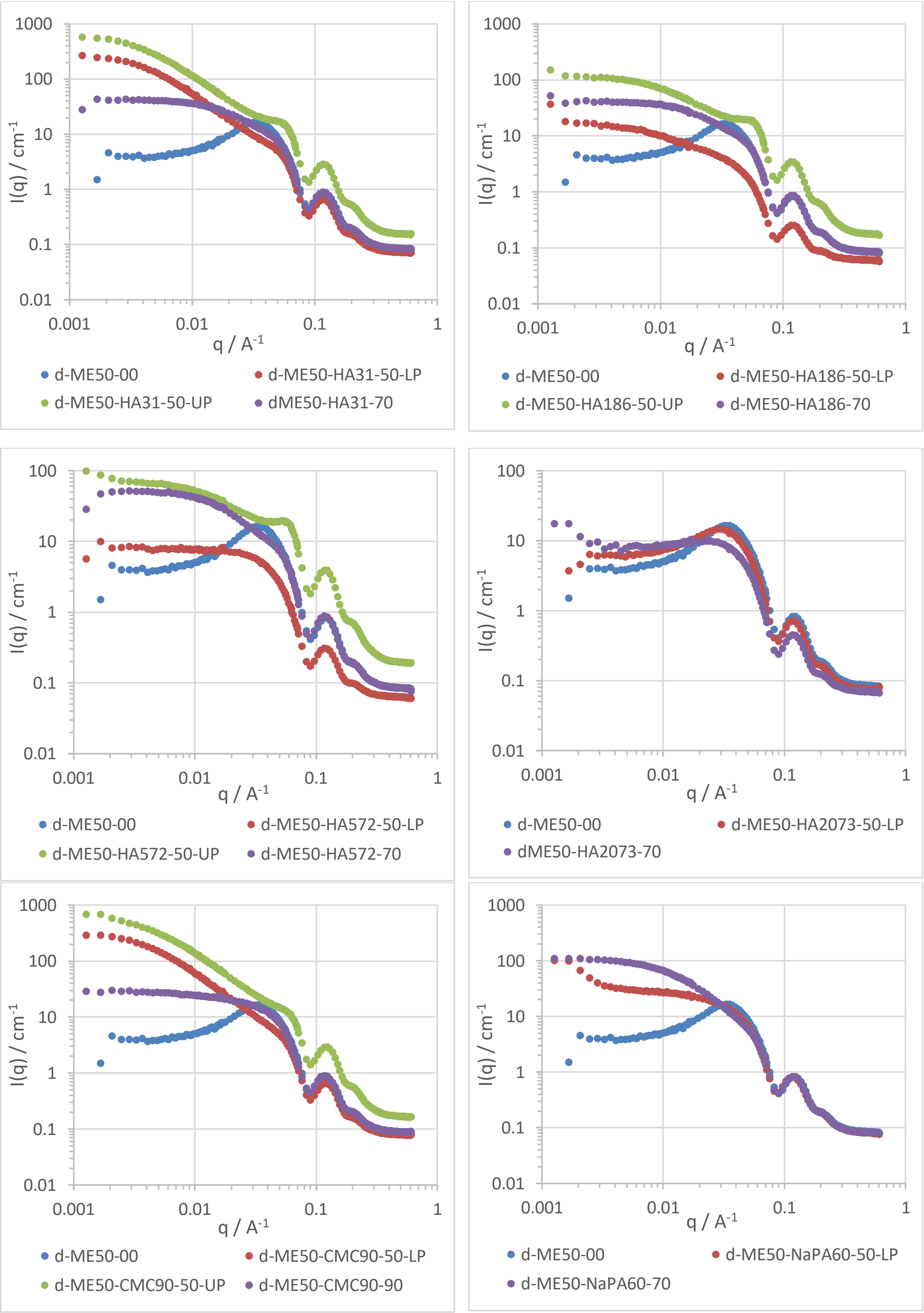

Figure 2: measured SANS data of biphasig microemulsion-polyelectrolyte complexes in shell contrast. For HA2073 and NaPA60, the upper phase was too small to be measured in SANS.