Experimental report

01/08/2022

Proposal: 9-12-658 **Council:** 4/2021

Title: Controlling the Structure of Soluble Polyeletrolyte/Microemulsion Complexes (PEMECs) with Double-Hydrophilic Copolymers

Research area: Soft condensed matter

This proposal is a resubmission of 9-12-645

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Samples: PEMECs in D2O

Instrument	Requested days	Allocated days	From	To
D11	2	0		
D33	2	1	29/08/2021	30/08/2021
D22	0	0		

Abstract:

Complexes of double-hydrophilic block copolymers, with one polyelectrolyte block, and oppositely charged microemulsion (ME) droplets lead to the formation of soluble complexes (PEMECs). This allows to combine the high solubilisation capacity of microemulsions with the structuring ability of polyelectrolytes and to design larger complexes, as interesting e.g. for drug delivery. For determining their detailed structure in the size range of 1-100 nm SANS experiments are essential and in our experiments we will vary the length of the PE block in the PAA-b-PEO copolymers, the mixing ratio with the ME droplets, and size and charge of the ME droplets. By doing so we will vary systematically the size of the complexes, as well as their internal structure and loading capacity. From the SANS experiments we will deduce how the structure and properties of such soluble PEMECs depend on their composition and will become able to tailor these accordingly for potential future applications.

Controlling the Structure of Soluble Polyelectrolyte/Microemulsion Complexes (PEMECs) with Double-Hydrophilic Copolymers

In the current experiment, positively charged microemulsions ME50 (100 mM TDMAO/TTAB (5% TTAB), 50 mM 1-Hexanol, 80 mM n-decane) and ME75 (5% TTAB, 75 mM 1-hexanol, 160 mM n-decane) were complexed with negatively charged, double hydrophilic diblock copolymer of polymethacrylic acid sodium salt and poly(ethylene glycol). The double hydrophilic copolymers PEG45-100 PMANa and PEG114-50PMANa were synthesised via the atom transfer radical polymerization (ATRP). The investigated nominal charge ratio Z, was 0, 0.45, 0.5, 0.56, 0.63, 0.7 and 0.8.

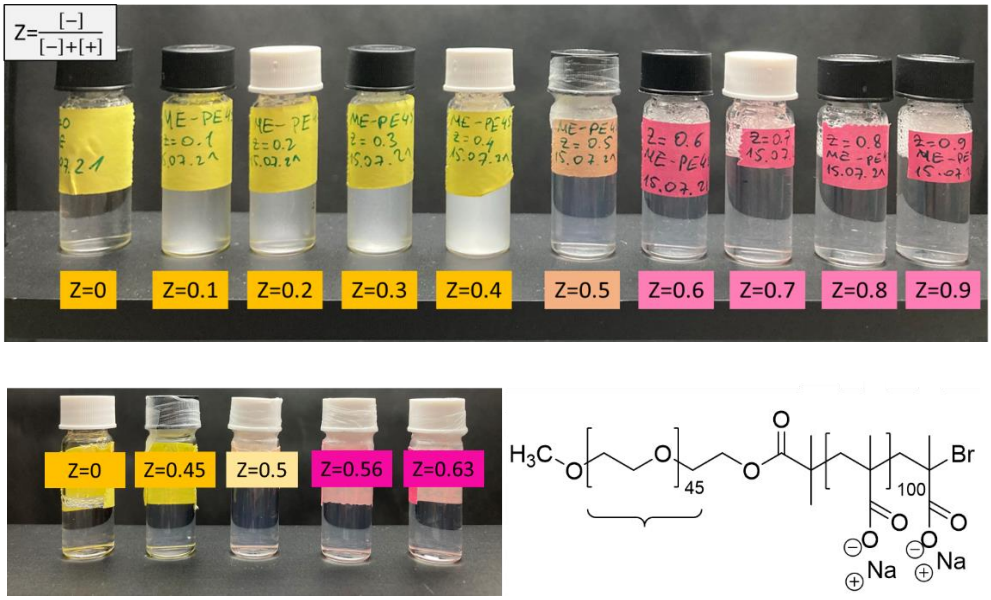

Figure 1.: Sample appearance of PEMECs ME50/PEG45-100PMANa at varying charge ratio Z and the polyelectrolyte chemical structure.

SANS data are shown in Figure 2 and in Figure 3. Pure microemulsions (Z=0) show a structure factor peak that indicates repulsive interaction and which diminishes after complexation with the polyelectrolytes at the investigated charge ratios Z. The form factor peak, however, persists, remaining at the same position and shape, indicating that the microemulsion droplet size is not influenced by the complexation with the polyelectrolytes. Formed PEMECs decrease in size with increasing Z and complexes are bigger for ME75 than for ME50. In the mid-Q region, the SANS data show slope close to Q^{-1}, characteristic for the elongated structures.

When comparing two polyanions, PEMECs based on PEG45-100PMANa tend from larger complexes, than PEG114-50PMANa, as expected due to the different chain lengths. However, at Z 0.7 and 0.8, i.e. at increasing excess of the copolymer, the differences become smaller.

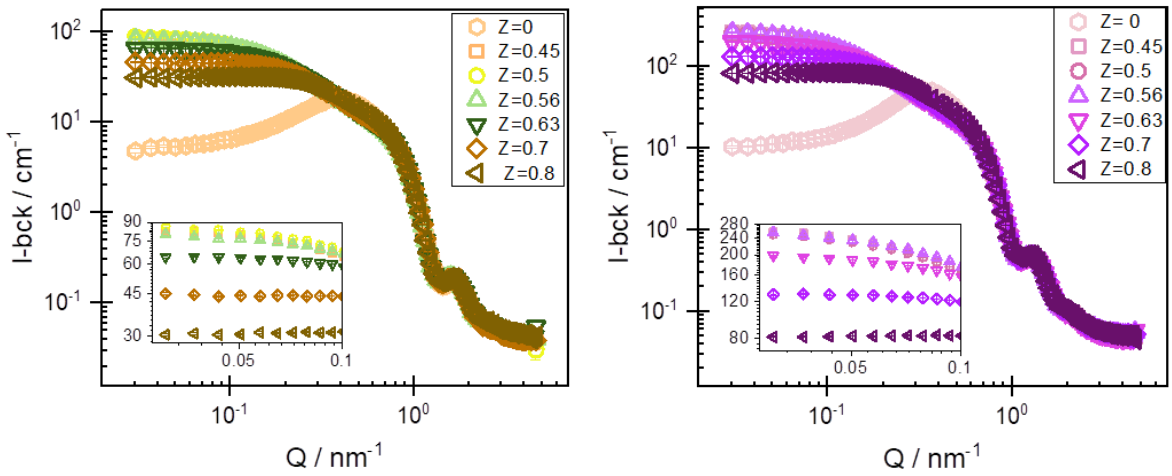

Figure 2. SANS data of PEMEC based on PEG45-100PMANa and ME50 (left) and ME75 (right). Insets show the low q-range.

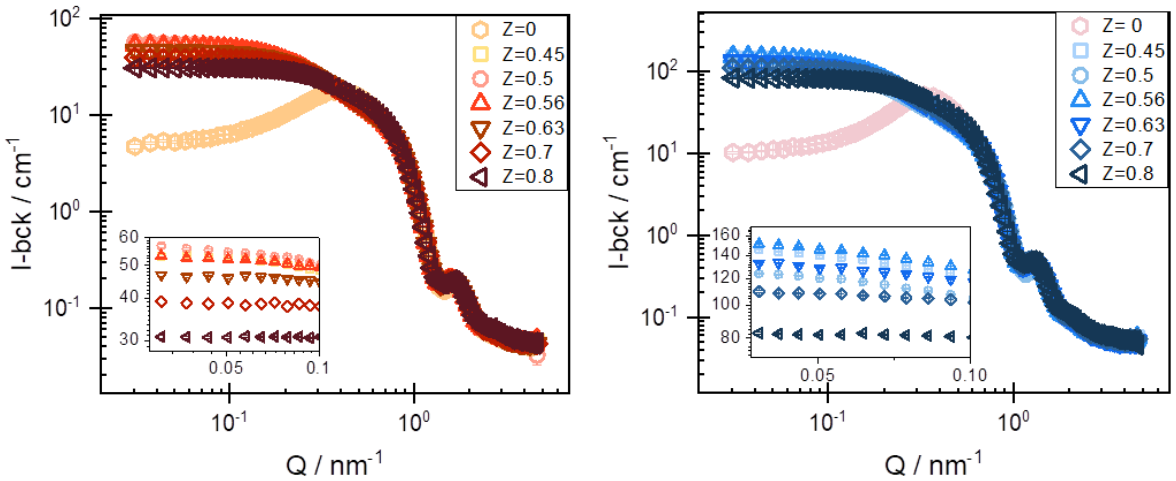

Figure 3. SANS data of PEMEC based on PEG114-50PMANa and ME50 (left) and ME75 (right). Insets show the low q-range.

The scattering curves of the pure microemulsions were fitted with a sphere form factor and applying the Hayter-Penfold Rescaled Mean Spherical Approximation (RMSA) structure factor for charged spheres, see Figure 4. Fitted radii are 3.1 and 4.1 nm for ME50 and ME75, respectively, and SANS data described well by this model.

For the complexes with the double hydrophilic copolymer, we are currently adapting scattering models in which a certain number of microemulsion droplets is confined into the core of the complex aggregate and surrounded by the PEO chains. This model then shall give the number of droplets per aggregate, how densely are packed within the complexes and how the complex

size depends on the choice of the copolymer, as well as on the mixing ratio of droplets to copolymer. This information then will be of central importance to gain an understanding of the assembly principles applying to this new type of ionically assembled colloidal systems.

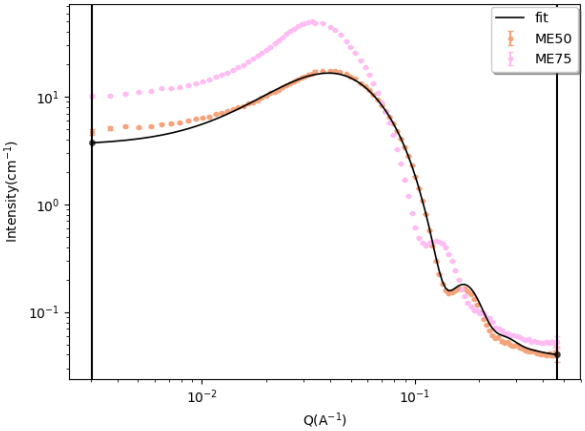

Figure 4. Microemulsions with fitted sphere form factor, applying the Hayter-Penfold Rescaled Mean Spherical Approximation (RMSA) structure factor.