50 years of D11

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Structure and interaction of surface charged polymeric micelles

Soft colloids are ubiquitous in synthetic and biological material as e.g. vesicles, dendrimers, microgels, polymergrafted nanoparticles, micelles, star polymers and certain proteins. They display a dual character between a polymer and the archetypical hard sphere colloid. Due to this hybrid nature, soft colloids macroscopically show interesting structural [1] and dynamical [2] properties resulting from its unique microscopic structure. Flow behavior of crowded solutions, (visco-) elastic properties of jammed states as gels and glasses and finally (crystal) structure and stability of other highly ordered phases [3] crucially depend on "softness", which is intimately related to the details of molecular structure.

We established micelles formed by n-alkane-PEO-OH amphiphilic block copolymers as an easy and elegant model system to tailor colloidal softness [4]. Parameters to tailor the "softness" start on a microscopic level by selecting the chemical nature of the hydrophobic block, by varying the solvophobic-to-solvophilic block ratio [1], the absolute block molecular weights [2], polydispersity of the hydrophobic block [3], and/or the interfacial tension [4].

In the present work, we introduce surface charges on the micelles resulting in electrostatic interactions in addition to the inherently present steric repulsion. The charges are implemented by oxidation of the terminal hydroxy group of the PEO block into a carboxy group by means of Bobbitt's salt [5]. Since carboxylic acids are weak acids, the number of charges on the particles depends on pH. The range and strength of the electrostatic repulsion can be easily modified by varying the effective number of charges via change in pH and/or ionic strength. Thus, the structural properties of micellar solutions can be effectively adjusted.

Here we present a study on the intra- and interparticle structure of C28-PEO5k-COOH polymer micelles in D2O over a broad range of concentrations by SANS as a function of the number of surface charges and ionic strength. We demonstrate that the micellar form factor remains the same independent of the number of charges. However, in contrast to neutral micelles, the charged micelles typically reveal structure factor contributions even at very dilute concentration, arising from the dominating long-range electrostatic repulsion. Structure factors in the liquid state are analyzed using established effective interaction potentials [7]. By increasing the concentration a liquid to crystal transition is observed for all systems, but for charged micelles at a much lower concentration compared to the uncharged micelles.

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