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Surface Charged Polymeric Micelles - A Tunable Model System Studied by SANS

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We investigate surface charged "starlike" micelles in aqueous solution formed by carboxy terminated n-octacosyl-poly(ethylene oxide) block copolymers, C_{28}-PEO5-COOH with 5 the PEO molar mass in kg/mol, by small angle neutron scattering (SANS), zeta-potential measurements and rheology. The –COOH end group was introduced by selective oxidation of the –CH_2 –OH end group of a C_{28}-PEO5-OH precursor using Bobbitt's salt. Micellar solutions of different concentrations in the dilute and semidilute range were investigated at pH 2, 6 and 12 to vary ionic strength and the number of effective surface charges Z_{eff}. Z_{eff} was further varied by using mixtures of C_{28}-PEO5-COOH and C_{28}-PEO5-OH at different mixing ratios. SANS measurements reveal that the intramicellar form factor $P(Q)$ is identical at the different pH-values which implies that the individual micellar structure is unaffected by the number of surface charges.

On the contrary, the intermicellar structure factor $S(Q)$ and the phase behavior show a strong dependence on Z_{eff}. In particular, we observe a distinct shift of the liquid - fcc crystal phase boundary. A quantitative analysis in terms of a screened Hard Sphere Yukawa otential reveals a very good agreement between experiment and theory. Because of this consistency and of the tunability of the n-alkyl-PEO starlike micelles we consider this system to be an excellent model for further studies on the interplay between steric and electrostatic interactions in soft colloids.

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