Experimental report

11/02/2022

Proposal: **9-10-1629** **Council:** 10/2019

Title: Effect of surface charges on structure and interactions of Cn-PEO micelles

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
C22H45-O-(CH2-CH2-O)100-COOH
C28H45-O-(CH2-CH2-O)100-COOH
C22H45-O-(CH2-CH2-O)100-OH
C22H45-O-(CH2-CH2-O)100-COO-
C28H45-O-(CH2-CH2-O)100-OH
C28H45-O-(CH2-CH2-O)100-COO-

Instrument	Requested days	Allocated days	From	To
D11	2	2	09/03/2021	11/03/2021
D22	2	2	08/02/2021	10/02/2021

Abstract:

Micelles formed by n-alkyl - endcapped poly(ethylene oxides) polymers are excellent model materials to study ultrasoft colloidal interactions. In previous studies the interaction could be almost perfectly described using an effective pair potential of Likos et al. The potential is a combination of a logarithmic dependence at small interparticle distances and a Yukawa-type tail derived for uncharged particles. The effective parameter in this model is the aggregation number of the micelles, which can be tuned by changing block copolymer characteristics. In the present work we propose to extend the tuneability by introducing charges on the surface of the micelles which modulates the strength and range of the interaction by an additional Coulomb repulsion. The charges are implemented by carboxy groups at terminal position of the PEO chain such that they are located on the surface of the micelles. We intend to study both the effect on inter- and intraparticle properties as a function of the degree of dissociation varied by pH. We note that beside the microscopic properties also the macroscopic rheological behavior can be adjusted such that these materials are of technological relevance.

Micelles formed by n-alkyl-poly(ethylene oxide) (C_n-PEO) and poly(ethylene-*alt*-propylene) (PEP)-PEO block copolymers in water are excellent model systems to study structure and interactions in soft colloids. The softness of the particles can be tuned simply by changing the aggregation number of the micelles which is conveniently done by variation of block copolymer parameters, e.g. size and block ratio. In earlier studies we have shown that a pair potential for star polymers derived by Likos et al. [1] yields a fairly good description of the soft interactions in such micellar systems. [2] In the present work we extend our previous studies by introducing charges at the micellar surface, resulting in an additional electrostatic repulsion. The main task of the present experiments was to examine the effect of the surface charges on both form factor P(Q) and structure factor S(Q) depending on concentration and pH. The charges were obtained by oxidation of the terminal hydroxy (OH) groups of the PEO chains to carboxy (COOH) groups which dissociate in aqueous solution. An almost quantitative oxidation could be achieved by a method reported by Bobbitt et al. [3] without any undesired polymer chain degradation.

Small angle neutron scattering experiments were done at D11 on three different polymers C_n-PEO5-COOH (*n*=22,28) and PEP3-PEO11-COOH where *n* denotes the number of carbons in the alkyl chain and 3, 5 and 11 the molecular weight in kg/mol of PEP and PEO, respectively. Micellar solutions were prepared in D_2O at three selected pH 2, 6 and 12 in order to vary the number of charges and the ionic strength. The pH was adjusted by addition of aliquots of NaOD or DCl. For each pH a series of concentrations ranging from dilute to semidilute volume fractions of $\phi = 0.15\% - 5\%$ were measured. In addition, dilute solutions of the OH terminated precursor polymers were studied as a reference. The wavelength was set at 6 Å. Three detector distances of 2, 8 and 28 meters were used with collimation lengths 4, 8 and 28m, respectively. The Q range explored was $2.5 \cdot 10^{-3} - 0.47\text{Å}^{-1}$.

Exemplarily, scattering curves of C_{28}-PEO5-COOH are shown in Figure 1 at pH 2 and pH 6 for four different concentrations. At pH 2 the terminal carboxy groups are not dissociated, while at pH 6, close to the equivalence point, full dissociation is assumed. Accordingly, the scattering of samples at pH 2 resembles that of micelles formed by C_{28}-PEO5-OH studied earlier. Typically, a structure factor peak evolves with increasing concentration resulting from ultrasoft colloidal interactions. On the contrary, samples at pH 6 show a considerably different behavior due to the presence of surface charges and the thus induced long ranged electrostatic interaction. This becomes obvious by a significantly more pronounced structure factor peak which appears already at a small volume fraction of $\phi = 0.15\%$. Interestingly, at $\phi = 5\%$ Bragg peaks occur in the scattering pattern which can be assigned to an fcc crystalline structure. Apparently, the electrostatic interaction leads to a liquid - solid phase transition at a much lower concentration compared to the uncharged micelles.

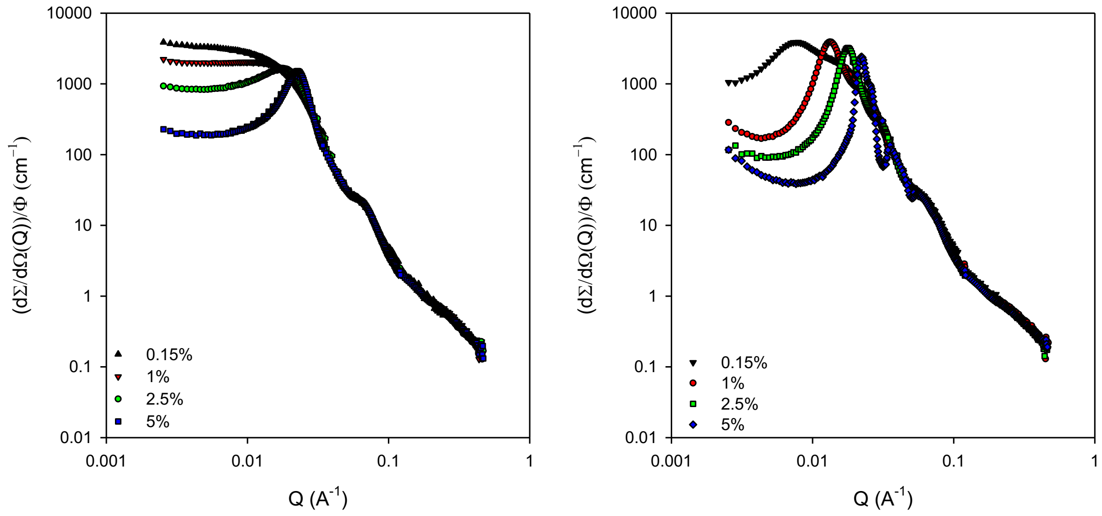

Figure 1) Scattering curves of C_{28}-PEO5-COOH at pH 2 (left) and pH 6 (right) for four different volume fractions

The dilute solutions were used to determine single micellar properties. At pH 2 and for the OH terminated samples, having no surface charges, structure factor contributions are negligible, i.e. $S(Q) \cong 1$ and $d\Sigma / d\Omega\ (Q) \propto\ P(Q)$. For comparison the two scattering curves are plotted together in Fig. 2 (left)). The two curves essentially fall on top of each other indicating that micellar properties are the same independent of the end group. To analyse the data we have used a spherical core-shell model which has already been established in an earlier study [4]. Excellent fits over the entire Q-range are obtained as shown by the solid line in Fig. 2 (left)). The global fit parameters are $N_{agg} = 164$, $R_m = 130\text{Å}$ and $R_c = 30\text{Å}$.

Fig. 2 (right)) shows a comparison of scattering curves of C_{28}-PEO5-COOH micelles at $\phi = 0.15\%$ for the three different pH values. The scattering curves exactly superimpose at intermediate and high Q range suggesting that micelles have identical intramolecular parameters. At low Q, on the other hand, the effect of charges leads to a significant structure factor contribution which is less pronounced at pH 12 because of increased ionic strength resulting from the addition of NaOD. In order to analyse the data we have combined the core shell model with the Hayter-Penfold structure factor [5] of interacting charged spheres based on the classical Yukawa potential. The additional parameters are the number of charges Z, the ionic strength $[I]$ and a hard sphere radius R_{HS}. The ionic strength is exactly calculated from the NaOD addition and can be fixed. Similarly, the intramolecular parameters which were taken from the core-shell analysis of the uncharged micelles. For pH 12 an excellent description of the scattering curves is obtained with $Z = -43$ and $R_{HS} = R_m = 130\text{Å}$. We note that the effective number of charges is significantly smaller than N_{agg}, which we refer to a counter ion condensation resulting from the relatively high ionic strength.

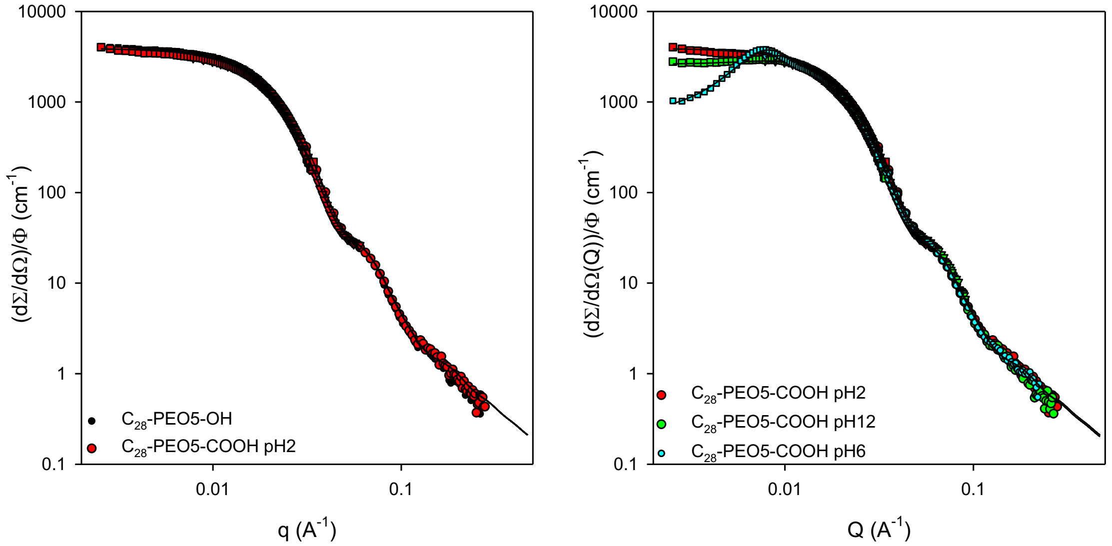

Figure 2) left: Superposition of scattering curves of C_{28}*-PEO5-OH and* C_{28}*-PEO5-COOH (pH 2) at* $\phi = 0.15\%$*, solid line shows a fit with a spherical core shell model; right: scattering curves of* C_{28}*-PEO5-COOH at* $\phi = 0.15\%$ *for pH 2, 6 and 12, solid lines are fits with the core - shell model taking into account S(Q) contributions of charged spheres by the Hayter - Penfold approach.*

It is also possible to fit the scattering data at pH 6, however, with parameter $R_{HS} \gg R_m$ which we presently do not fully understand. This applies also to the higher concentration data at pH 6 and 12. An analysis of these data with more recent models [6] is currently in progress.

Summarizing our results, we have studied the effect of surface charges of polymer micelles on structure and interaction. The scattering data reveal that single micellar properties are identical independent of end-group and pH. In contrast, a significant change of micelle interaction was found due to the presence of the long-ranged electrostatic repulsion. The dissociation of the carboxy end-group adjusted by pH and the ionic strength were found to be important tuning parameters. A more quantitative evaluation of the data is necessary for a full understanding of such systems.

[1] Likos et al., Phys. Rev. Lett., **1998**, *80*, 4450.

[2] Amann, Dissertation, WWU Münster 2017.

[3] Bobbitt et al., Organic Reactions, (NY) **2010**, *74*, 103.

[4] Zinn et al., Soft Matter, **2014**, *10*, 5212.

[5] Hayter and Penfold, Molecular Physics, **1981**, *42*, 109.

[6] M. Heinen et al., J. Chem. Phys. **2011**, *134*, 044532.