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SANS analysis of aqueous ionic perfluoropolyether micelles

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Abstract. Preliminary SANS results of ionic chlorine terminated perfluoropolyether micelles in water are given. The experimental spectra have been analyzed by a two-shell ellipsoidal model for the micellar form factor and a screened Coulombic plus hard-sphere repulsion potential for the structure factor.

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The self-assembling features of perfluoropolyether (PFPE) salts with perfluoroalkyl-terminated hydrophobic tail have been described in several papers [1,2]. The subject of this work is the SANS study of aqueous micellar solutions of two salts of a PFPE carboxylic acid, which differs with respect to previously reported analogues [3] for the particularly high purity achieved for these specific samples for research purposes only. A previous work [3] examined aqueous solutions and liquid crystals of similar surfactant salts in a mixture of analogues with narrow molecular weight (MW) distribution but not yet at the purity level of the present experimental compound. The general structure of this class of carboxylic PFPE surfactants [4] is

$$Cl-(C_3F_6O)_n-(C_2F_4O)_m-(CF_2O)_q-CF_2COOX\,,$$

where, for the specific compound examined here, $n = 2$, m and q are zero, while the counter-ion X is either ammonium or potassium. The perfluoro-iso-propoxy repeated unit in the chemical structure above leads to a branched conformation of the molecule. Due to the widespread interest in fluorosurfactants mostly of perfluoroalkyl type [5,6], we believe the micellar microstructure of unusual laterally branched PFPEs to be a crucial step to be clarified for a more general view of the self-association issue. The availability of these high-purity compounds offers the opportunity of a first SANS insight into the PFPE micellar shape, size and interactions.

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1 Materials

The high-purity samples have been provided by Ausimont [4], as obtained by several purification steps allowing a purity of $> 99.5\%$ with respect to the above formula with $n = 2$ and $m, q = 0$, as confirmed by thorough analysis, for example GC-MS. Also, the experimental equivalent weight (3%–4% of typical accuracy) confirmed the expected value of 462. MilliQ-grade water has been used for solutions. As in [3], the critical micellar concentration (cmc) at 25°C, measured with an accuracy of 8% on four different samples from the same purification procedure, was 2.1×10^{-2} and 1.8×10^{-2} mol/l for the ammonium and the potassium salts, respectively. The variation of the cmc value with temperature was negligible in the range 25–30 °C. The density of aqueous solutions of the ammonium salt has been measured as a function of concentration by a PAAR DMA 5000 density meter at 28 ± 0.1 °C, thus obtaining the density of the ammonium salt ($1.836\,g/cm^3$).

2 Methods

SANS experiments were performed at the spectrometer PAXE (Laboratoire Léon Brillouin, Saclay) with a sample–detector distance of 2.55 m and an incident neutron wavelength of 5 Å with a wavelength spread of 10%. Collimation was achieved by two slits of 12 and 7 mm placed 2.5-m apart. Samples of thickness 1 mm were contained in flat quartz cells, and measured at 28 ± 0.1 °C. The scattered intensity was corrected for the empty-cell contribution and normalized to absolute scale by means of a secondary standard of known cross section [7].

3 Results

Some typical spectra are represented in Fig. 1 for ionic micellar solutions at two different concentrations for the ammonium counter-ion (0.230 M and 0.115 M) and at the concentration of 0.208 M for the potassium counter-ion. The experimental data and the fitted curves (whose meaning will be

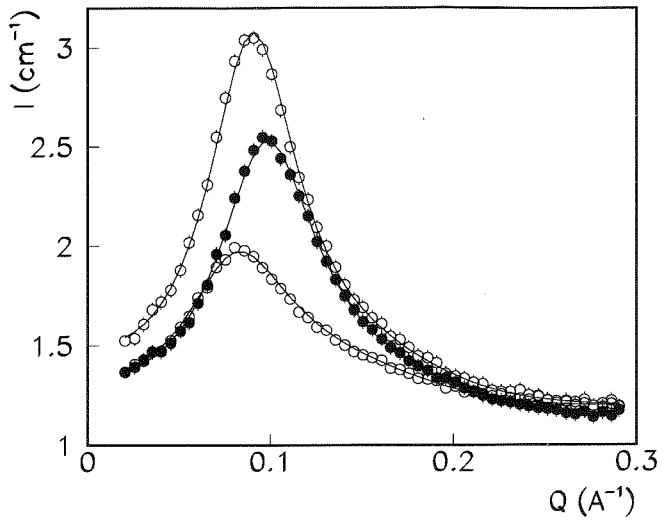

Fig. 1. Experimental scattered intensity at $T = 28\,°C$ of ammonium (*open points*) and potassium (*full points*) PFPE micellar solutions. Concentrations: 0.230 M (*upper curve*) and 0.115 M (*lower curve*) for the ammonium salt and 0.208 M for the potassium salt. The *continuous lines* represent the fitted curves

explained below) are plotted as scattered neutron cross section per unit volume of the sample, $I(Q)$, vs. the scattering wave vector $\boldsymbol{Q}$. The experimental spectra are characterized by a sharp structural peak at around $0.1\,\text{Å}^{-1}$, a manifestation of strong interactions between the charged particles. A decrease of concentration for the ammonium surfactant leads to a strong decrease of the peak maximum.

To have insight into the solution microstructure, SANS data have been analysed assuming an ellipsoidal two-shell model for the micellar particle structure factor $P(Q)$ and an analytical solution of a multicomponent ionic liquid in a mean spherical approximation (MMSA) for the interparticle structure factor $S(Q)$ of the charged micelles in solution. $S(Q)$ is the result of a screened Coulombic repulsion between micelles in addition to hard-sphere repulsion. The treatment of the data is based on the algorithm of Hayter and Penfold [8], which proved [9] to be very useful. The total scattered intensity $I(Q)$, under the previous hypotheses, can thus be written:

$$I(Q) = C_M N\,(\Sigma b_i - V_m \varrho_s)^2\, P(Q) S(Q)\,,$$

where C_M is the number density of the surfactant molecules ($C_M = C - \text{cmc}$, with C being the surfactant concentration), N is the average surfactant aggregation number of the micelle, Σb_i is the total scattering length of all the atoms in the surfactant molecule, V_m is the surfactant molecule volume and ϱ_s is the scattering density of the solvent.

The micellar solution is assumed to be composed of surfactant molecules at the cmc and monodispersed ellipsoidal micelles with a mean surfactant aggregation number N and an effective micellar charge Q^*. The micelles are two-shell aggregates composed of an inner region, the hydrophobic core (made up of close-packed surfactant tails) with principal axes a, b, b and the hydrophilic layer, composed of head groups (CO_2^-), a fraction of counter-ions (NH_4^+ or K^+) and hydration water molecules, with a thickness t. The volume of the surfactant molecule has been obtained by the MW and density measurements reported above. The volume of the ammonium surfactant is $433\,\text{Å}^3$. The volume of the surfactant hydrophobic tail, $384\,\text{Å}^3$, has been evaluated by subtracting the volumes of the counter-ion [10] and of the polar head (CO_2^-, $V = 35.3\,\text{Å}^3$ estimated by the universal force field method [11]) from the volume of the ammonium salt. The scattering lengths of the tail, head group and counter-ion have been also calculated.

Table 1. SANS results at 28 °C

C (M)	Q^*	N	t (Å)	b (Å)	D (Å)	a/b	n_W
			NH_4^+				
0.230	19	57	3.7	13	42	2.2	9
0.115	17	39	4.0	15	39	1.1	11
			K^+				
0.208	17	40	4.1	12	39	2.0	12
0.101	14	31	4.1	14	36	1.1	13

A fitting procedure of the experimental data to the theoretical model has been performed. The four free fitting parameters are Q^*, N, t and b. The quality of the fit was deduced by the reduced χ^2 value, which is close to 1, so the agreement between the experimental data and the fitted curve is very good. The numerical results are reported in Table 1 for the four samples studied at two different concentrations for both ammonium and potassium micelles. In Table 1 the average micelle diameter D, the axial ratio a/b and the number of interfacial water molecules for a surfactant molecule n_W are also reported in addition to the free parameters.

From the reported results we observe similarities and differences between the ammonium and potassium micelles. In fact, in both cases the micelles, with average diameter 40 Å are composed of an inner fluorinated tail of 13 Å (b) and an interfacial layer of 4 Å (t) which contains the surfactant carboxylic polar heads (each surrounded by 10 water molecules). Thus, in the concentration range investigated, the fluorinated chain of the surfactant defines the micellar inner core size and the carboxylic head defines the micellar interfacial thickness, as also found for the hydrogenated micelles in similar surfactant concentrations [12]. The axial ratio varies from 2 to 1 for both counter-ions when the surfactant concentration decreases; thus the aggregates are sharply prolate ellipsoids at higher concentration and become more spherical at lower concentration.

The net micellar surface charge depends weakly on the counter-ion and changes slightly vs. concentration for both counter-ions. The average aggregation number is 60 and 40 for an ammonium counter-ion at high and low surfactant concentrations respectively, whereas it is 40–30 for potassium (same trend vs. concentration). The latter parameter depends strongly on the counter-ion, as also found for hydrogenated micelles [13].

In conclusion, ionic chlorine terminated perfluoropolyether micelles have been studied by SANS. The Hayter–Penfold model for the inter-micellar structure factor and the two-shell ellipsoidal model for the micellar form factor (successfully used for hydrogenated aggregates) well describe also the microstructure of the micelles presented in this work.

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References

1. C.M.C. Gambi, M.G. Giri, M. Carlà, D. Senatra, A. Chittofrati: Phys. Rev. E **56**, 4356 (1997)
2. P. Baglioni, C.M.C. Gambi, R. Giordano: Physica B **234–236**, 295 (1997)
3. F. Caboi, A. Chittofrati, P. Lazzari, M. Monduzzi: Colloids and Surfaces A: Physicochem. Eng. Aspects **160**, 47 (1999)
4. G. Marchionni, A. Staccione (Ausimont S.p.A.). U.S. Patent 5.143.589 (1992)
5. Erik Kissa. *Fluorinated surfactants* (Marcel Dekker, Inc. 1994), Surfactant Science Series Vol. 50
6. E. Giannetti, M. Visca (Ausimont S.p.A.): U.S. Pat. 4.864.006 (1988)
7. J. Teixeira: *Structure and Dynamics of Strongly Interacting Colloids and Supra-molecular Aggregates in Solution*, ed. by S.-H. Chen, J.S. Huang, P. Tartaglia (Kluwer Academic Publisher, Dordrecht 1992)
8. J.B. Hayter, J. Penfold: Mol. Phys. **42**, 109 (1981)
9. Y.C. Liu, P. Baglioni, J. Teixeira, S.-H. Chen: J. Phys. Chem. **98**, 10208 (1994)
10. Yizhak Marcus: *Ion Properties* (Marcel Dekker, Inc. 1997), p. 46
11. A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard-III, W.M. Skiff: J. Am. Chem. Soc. **114**, 10024 (1992); with additional parameters (for dummy atoms) from L.A. Castonguay, A.K. Rappe: J. Am. Chem. Soc. **114**, 5832 (1992), and A.K. Rappe, K.S. Colwell: Inorg. Chem. **32**, 3438 (1993)
12. D. Bendedouch, S.-H. Chen, W.C. Koehler: J. Phys. Chem. **87**, 2621 (1983)
13. S.-H. Chen: Ann. Rev. Phys. Chem. **37**, 351 (1986)