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Characterization of micellar systems by the conductivity method; Sodium salt of perfluoropolyether carboxylic acid

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Abstract: A new method for the interpretation of the conductivity of ionic surfactants is proposed. The model considers the contribution of ions and of charged micelles, and is based on the approximation of constant concentration of surfactant chains above the critical micellization concentration (CMC), and on the equilibrium constant of counterion binding to the micelles (K). These two parameters evaluated for aqueous solutions of sodium salt of perfluoropolyether carboxylic acid are as follows: $K = 35\,800\ \mathrm{dm^3\,mol^{-1}}$; $\mathrm{CMC} = 1.19 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$. The third quantity obtained by this procedure is the product of the aggregation number (N) and the size parameter ($f = e^2 L/6\pi\eta r$): $Nf = 76.5\ \mathrm{S\,cm^2\,mol^{-1}}$.

Key words: Conductivity – micelles – counterion binding – perfluorinated surfactants

Introduction

The conductivity method is a useful tool for the determination of the critical micellization concentration (CMC) of ionic surfactants [1]. The measurements are simple and accurate. In the ideal case, an ionic surfactant is completely dissociated below the CMC, and in this region the conductivity is a linear function of the concentration with the slope equal to the sum of individual ionic molar conductivities. Above the CMC, the conductivity should be constant and independent of the surfactant concentration, which implies that all excess cations and anions are in the micellar form and that the concentration of free ions is constant and that it corresponds to the CMC. However, in the real case counterions (cations in the case of anionic surfactants) dissociate from the micelles, resulting in an increase of the bulk counterion concentration and in the micellar charge. Charged micelles exhibit electrophoretic mobility, as shown for sodium dodecylsulfate by the dynamic light scattering electrophoretic method [2]. Accordingly, the conductivity (κ) should increase with the concentration (c), but with a slope lower than one below the CMC, which makes it possible to estimate the CMC from the kink in this plot [3]. Sometimes, in the CMC region the slope changes gradually causing difficulties in the accurate location of the kink. One of the reasons for this trend may be the presence of impurities or "premicellar association", i.e., the formation of small associates, the aggregation number of which increases with concentration. Above the "true" CMC the structure and the aggregation number remain constant, and only the number of micelles increases by further addition of a surfactant. In this range one may assume no significant change in the surfactant chain concentration, which is then equal to the true CMC, and is determined by chemical potential of the species.

There are several results with perfluorinated surfactants, indicating their similarities to the corresponding hydrocarbon compounds. For example, different salts of perfluorooctanoic acid showed specific conductivity behavior above the CMC. Thus, due to almost complete counterion

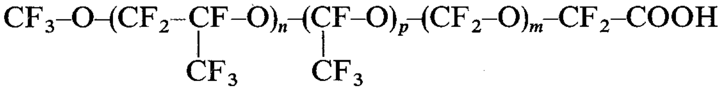
($NH_3CH_3^+$) binding the conductivity was found to be approximately constant above the CMC, while for the ammonium salt it increases because of the significant dissociation of NH_4^+ ions from the micelles [4]. The temperature dependence of the conductivity [5,6] allows for the thermodynamic analysis of the CMC data. The function lg(CMC) vs $1/T$ is not linear [3,6–8], indicating a significant change in the heat capacity due to iceberg formation, as found with both hydrocarbons [9–11] and fluorinated surfactants [8].

The aim of this study is to quantitatively interpret the conductivity data in order to accurately determine the CMC, as well as the equilibrium constant of counterion binding to ionic heads of chains incorporated in the micelles. The method will be demonstrated on the example of an aqueous solution of the sodium salt of perfluoropolyether carboxylic acid.

Experimental

Chemicals

Perfluoropolyether (PFPE) carboxylic acid (Ausimont, Italy) of average molecular mass 429.6 (as obtained by potentiometric titration) has the following structure



$$CF_3{-}O{-}(CF_2{-}\underset{CF_3}{CF}{-}O)_n{-}(\underset{CF_3}{CF}{-}O)_p{-}(CF_2{-}O)_m{-}CF_2{-}COOH$$

($m \approx 0$, $p \approx 0$, $n \approx 1.6$)

The PFPE acid of narrow molecular mass distribution was prepared by distillation of raw materials produced by photooxidation. The resulting product contains isomers and also homologues of different molecular masses. Gas chromatography analysis showed that 99.5% of this acid correspond to the above formula with $0.9 < n < 2.3$. The sodium salt (NaA) was prepared by neutralization with NaOH up to pH = 7.0.

Methods

The conductivity measurements were carried out in a thermostated cell (25.0 °C) with a Jenway-4020 conductometer. The cell was calibrated with a standard KCl solution. The surfactant solutions were prepared by dilution of the concentrated stock solutions. The solutions were stirred and ultrasonicated for 10 min. The systems were homogeneous; no phase separation was observed, and the instrument readings were stable for an appreciable period of time (30 min).

The complementary static light-scattering measurements with a Brice-Phoenix light-scattering instrument were performed to gain some insight into the association of surfactant molecules.

Experimental results

The conductivity (κ) as a function of the total surfactant salt (NaA) concentration (Fig. 1) gives a constant slope up to the 1×10^{-3} mol dm^{-3}. This concentration may be taken as the CMC, but further analysis will show that a more accurate result can be obtained.

Figure 2 displays the relative light-scattering intensity measured at 45° with respect to the incident beam. The sharp increase in the intensity of the scattered light was observed at the concentration of 1.2×10^{-3} mol dm^{-3} which should correspond to CMC. Above that critical concentration the function is linear indicating the constant size of micelles in the examined concentration region.

Interpretation of data

Model

The model proposed here is based on the following assumptions:

i) The concentrations of free ions are low so that the following equation is applicable

$$\kappa = \lambda(\mathrm{Na}^+) \times c(\mathrm{Na}^+) + \lambda(\mathrm{A}^-) \times c(\mathrm{A}^-) + \lambda(\mathrm{M}) \times c(\mathrm{M})\,, \tag{1}$$

where λ is the molar conductivity, Na^+ and A^- denote the surfactant cation (sodium ion) and anion, respectively, while M stands for micellar species.

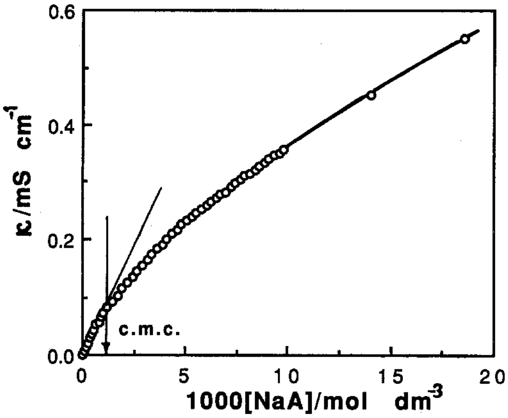


Fig. 1. The conductivity (κ) of PFPE sodium salt (NaA) solution as a function of the salt concentration at 25 °C. The straight line was obtained by linear regression for the concentrations below 8×10^{-4} mol dm^{-3}. The line above that concentration was calculated by means of Eqs. (12, 13) using $K = 35\,800$ dm^3 mol^{-1}; $fN = 76.5$ S cm^2 mol^{-1}; $c_{\text{mic}} = 1.19 \times 10^{-3}$ mol dm^{-3}. The arrow indicates true CMC, as obtained by the described interpretation.

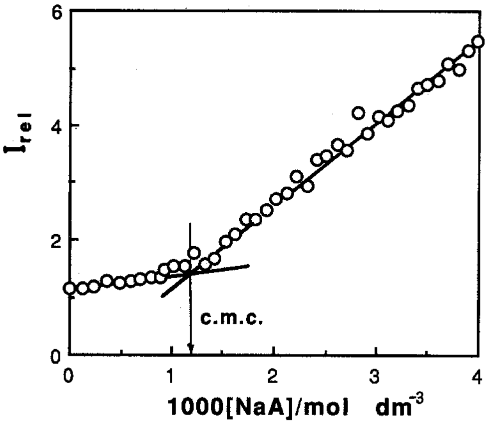


Fig. 2. The relative light-scattering intensity at 45° with respect to the incident beam as a function of PFPE sodium salt (NaA) concentration at 25.0 °C. The CMC, as obtained from the kink, is 1.2×10^{-3} mol dm^{-3}.

ii) Below the CMC the ionic surfactant is completely dissociated and no micelles exist, so that the conductivity is simply related to the total surfactant concentration, [NaA]

$$\kappa = (\lambda(\text{Na}^+) + \lambda(\text{A}^-)) \times [\text{NaA}] \,. \tag{2}$$

The slope of κ vs [NaA] plot (below the CMC) and the literature value of $\lambda(\text{Na}^+)$ together with Eq. (2) yield the molar conductivity of anions.

iii) The CMC will be defined here as the concentration of free monomers in the presence of micelles, so that

$$c(\text{A}^-) = c_{\text{mic}} \,, \tag{3}$$

where c_{mic} denotes critical micellization concentration. Since the monomer concentration shows a decrease when surfactant is added above CMC, the $c(A^-)$ value in Eq. (3) is an average in the examined concentration range.

iv) In the presence of micelles, counterions (cations) are partially associated with surfactant ionic heads according to

$$\text{Na}^+(\text{aq}) + \text{A}^-{}_{(\text{mic})} \rightarrow \text{NaA}_{(\text{mic})} \,, \tag{4}$$

where aqueous and micellar forms are denoted in brackets.

The equilibrium constant of the counterion association reaction K may be defined as

$$K = [\text{NaA}_{(\text{mic})}]/c(\text{Na}^+) \times [\text{A}^-{}_{(\text{mic})}]$$
$$= (N - z)/z \times c(\text{Na}^+) \,, \tag{5}$$

where N is the micelle aggregation number and z denotes the absolute value of the micelle charge number.

iv) Concentration of free counterions is

$$c(\text{Na}^+) = c_{\text{mic}} + z([\text{NaA}] - c_{\text{mic}})/N \,. \tag{6}$$

v) Concentration of micellar species is

$$c(\text{M}) = ([\text{NaA}] - c_{\text{mic}})/N \,. \tag{7}$$

vi) Molar conductivity of charged micellar species is given by

$$\lambda(\text{M}) = zeLu_M \,, \tag{8}$$

where e, L, and u are proton charge, the Avogadro constant, and electrophoretic mobility, respectively.

For spherical micelles of radius r in the medium of viscosity η the electrophoretic mobility, u_M, is equal to

$$u_M = ze/6\pi\eta r \,. \tag{9}$$

For micelles of any shape, one can write

$$\lambda(\text{M}) = z^2 f \,, \tag{10}$$

where coefficient f for spherical micelles is given by

$$f = e^2 L/6\pi\eta r \,. \tag{11}$$

Equations (1, 3, 6, 7, 10) yield the conductivity κ above the CMC

$$\kappa = c_{\mathrm{mic}}(\lambda(\mathrm{A}^-) + \lambda(\mathrm{Na}^+)) + [([\mathrm{NaA}] - c_{\mathrm{mic}}) z/N] \times [\lambda(\mathrm{Na}^+) + Nf(z/N)] \,. \quad (12)$$

Following Eqs. (5 and 6), the relative micellar charge number z/N is equal to

$$z/N = \{[(Kc_{\mathrm{mic}} + 1)^2 + 4K([\mathrm{NaA}] - c_{\mathrm{mic}})]^{1/2} - Kc_{\mathrm{mic}} - 1\}/[2K([\mathrm{NaA}] - c_{\mathrm{mic}})] \quad (13)$$

The conductivity data should be interpreted in two steps. At first, one uses the values below the CMC and obtains, by linear regression, the molar conductivity of the surfactant. With the literature data for molar conductivity of counterions one gets the λ value for the surfactant chains. The second step concerns data above the CMC. Equations (12 and 13), by nonlinear regression analysis yield the best values of CMC, fN and of the counterion association equilibrium constant K.

Results of interpretation

Initial slopes of the conductivity functions (Fig. 1) resulted in the molar conductivity of the sodium salt of PFPE of 73.6 S cm^2 mol^{-1}. Using a literature [12] value of λ for Na$^+$ at 25 °C (50.1 S cm^2 mol^{-1}), the molar conductivity of the surfactant anion was obtained as 23.5 S cm^2 mol^{-1}. This value is reasonable when compared with ions of similar sizes. The linearity and the reasonable λ value confirm the assumption of practically complete dissociation of the surfactant below the CMC.

The data above the CMC were evaluated from Eqs. (12 and 13) by the nonlinear regression analysis ("ANOVA and REGRESSION ANALYSIS," STATGRAPHICS) and the following values produced the best fit:

$K = (35\,800 \pm 1800)$ dm^3 mol^{-1};

$c_{\mathrm{mic}} = (1.19 \pm 0.05) \times 10^{-3}$ mol dm^{-3}

$fN = (76.5 \pm 5.8)$ S cm^2 mol^{-1}

Correlation coefficient: $R^2 = 0.9989$

Discussion

Sodium salt of PFPE acid showed an increase in the conductivity above the kink in κ vs c plot, which means that charged micelles were formed and that no phase separation occurred. In the case of precipitation at temperatures below the Krafft point, the composition of the separated phase should be stoichiometric, the concentration of ions should be equal to the solubility and, consequently, the conductivity should remain constant, which was not the case.

In this work, the concept of the counterion association equilibrium constant was introduced. Since the ionic strength was not markedly changed in the experiments, it was reasonable to assume that the value of K should not vary significantly with the surfactant concentration. This assumption is supported by the agreement of the theoretical line with the experimental points (Fig. 1). However, the slight change in the charge number may be expected, as is indeed demonstrated in Fig. 3, showing that the calculated relative charge decreases with the total surfactant concentration. This finding indicates that the interpretation of conductivity data, based on the assumption of the constant electrophoretic mobility of the micelles (i.e., constant charge number), is an approximation [6]. The critical micellization concentration of the surfactant salt obtained by the interpretation of the conductivity data, $(1.19 \pm 0.05) \times 10^{-3}$ mol dm^{-3}, agrees well with the finding by light-scattering measurements (1.2×10^{-3} mol dm^{-3}). The linearity of the light-scattering intensity (Fig. 2) indicates a constant

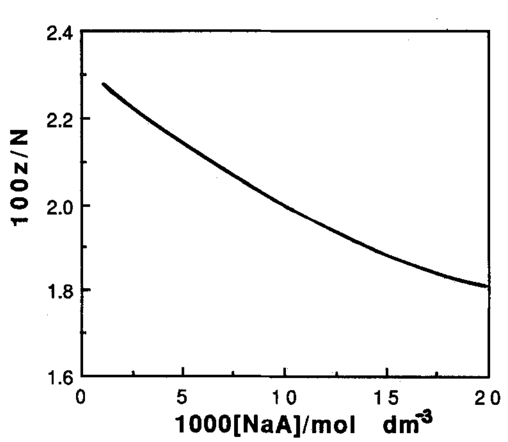


Fig. 3. The relative charge of micelles (z/N) as calculated by Eq. (13) for the PFPE sodium salt (NaA) as a function of the concentration. The corresponding values of the parameters are given in the legend of Fig. 1.

micellar size over the entire concentration region as it is required by the proposed model (constant r and f, Eqs. (9–11)).

The interpretation proposed in this work is based on the approximation of the constancy of the monomer concentration above the CMC. However, it was established that the increase in the ionic surfactant concentration is followed by a (slight) decrease in the free surfactant chain concentration, which is due to the counterion effect stabilizing the charged micelles [14–16]. This behavior influences the proposed interpretation to a certain degree, but for a surfactant characterized by a low CMC, and consequently low counterion concentrations, no significant effect is expected. In fact, the monomer concentration, as obtained by the regression analysis, represents the average value for the examined concentration range.

In this work the concept of "true" critical micellization concentration was defined as (average) monomer concentration above the CMC. This value was found to be at 1.19×10^{-3} mol dm^{-3}, and does not necessarily correspond to the kink in the κ vs. c presentation. Figure 4 displays the data in the concentration region near the CMC. It is clear that the deviation from the straight line starts below that concentration, indicating the onset of association below the "true" CMC. These associates, formed in the narrow concentration region, are not "regular" micelles with a defined structure, i.e., being characterized by the same chemical potential as those in the higher concentration region.

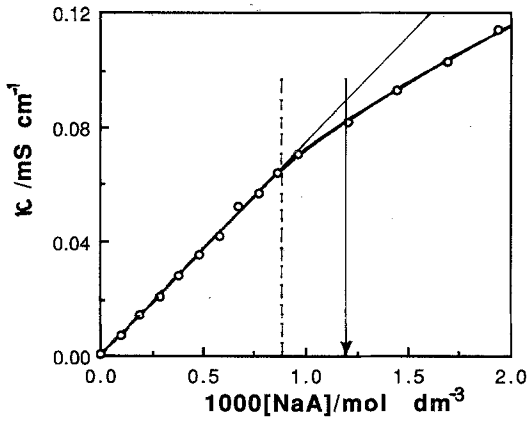


Fig. 4. The same plot as in Fig. 1, but the scales were expanded in order to present clearly the properties in the vicinity of the CMC. The true CMC is denoted by arrow, while dashed line

The size parameter fN has no simple meaning, but one may expect it to assume a higher value for larger micelles. The volume of a micelle should be proportional to the aggregation number N while the radius of the spherical micelles may be taken as proportional to the cube root of the volume. Consequently, according to Eq. (11) the product fN should be higher for larger micelles. The size parameter fN is determined by the size and shape of the micelles; it corresponds to their aggregation number and diffusion coefficient so that it deserves further analysis. Generally, it can be concluded that fN should be higher for larger micelles. For aqueous systems at 25 °C, Eq. (11) reads

$$N = 8.3\,(fN/S\,\mathrm{cm}^2\,\mathrm{mol}^{-1})\,(r/\mathrm{nm})\,. \qquad (14)$$

For micelles of sodium salt of PFPE acid the fN value was found to be 76.5 S cm^2 mol^{-1}, which yields an aggregation number of 17 if the micelles are spheres with radius of 2 nm [13]. The fN value could also be analyzed on the basis of the surfactant density. Assuming the density of surfactant to be 1.7 g cm^{-3}, the analysis shows that the micelles are highly hydrated.

The presented work demonstrates the possibility of the use of the conductivity method for the characterization of surfactant systems. The conductometry yields an accurate CMC value, defined as the (average) surfactant monomer concentration. This CMC may be higher than the one corresponding to the onset of micelle formation. However, one may expect this difference to be negligible for most of the systems. For the sodium salt of PFPE acid the CMC, evaluated from both conductivity and light scattering data, agrees well with the value obtained from the surface tension measurements [17]. By using the above interpretation, in addition to the CMC, one may obtain the micellar charge and the equilibrium constant for counterion association with the charged heads of chain constituents of the micelles. The measurements at different temperatures may provide other useful information. For example, the Krafft point temperature may be obtained from κ vs c plots; if the solid phase is formed the conductivity should be constant above the solubility and should not increase in the concentration region above the kink, as in the case of micelle formation. The temperature dependency of the counterion dissociation equilibrium constant provides the enthalpy change of this process, which can be compared with the calorimetry results.

The presented interpretation of the conductivity data is a step further with respect to the model based on constancy of the micelle electrophoretic mobility [6]. However, the shortcoming of the proposed model is the approximation of relative constancy of monomer concentration above the CMC, which is applicable for the narrow concentration range. Further work should incorporate an empirical relationship between monomer and total surfactant concentration, based on potentiometry data with selective electrodes. For the PFPE anions such an electrode could not be prepared so that another surfactant should be chosen for that purpose. The second possibility–to incorporate the theoretical relationship describing the monomer concentration change–is less promising due to the necessary approximations which could not be avoided.

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