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On the effect of the nature of counterions on the self-assembly of polyoxyethylene alkyl ether carboxylic acids.[†]

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In this contribution, we investigate the effect of the type of counterion on the properties of dilute solutions of polyoxyethylene alkyl ether carboxylic acids. Two different surfactants, presenting an oleic acid alkyl chain and on-average five and nine ethylene oxide units, and terminated by a weakly anionic carboxymethyl group were studied. The surfactants were gradually ionized with sodium hydroxide, arginine, and choline hydroxide. The solutions properties were probed by light scattering, electrophoretic mobility, density and sound velocity measurements, as well as by small-angle neutron scattering. To our initial surprise, no specific effect arising from the nature of the counterion could be determined. We ascribe this phenomenon to the fact that the presence of the ethylene oxide units markedly dilute the surfactant head group charge density, reducing counterion condensation and subsequent counterion specific effects.

Introduction

Fatty acids are the oldest-man made surfactants, whose use dates back at least to time of Babylonians[1]. Fatty acids and soaps – their ionic counterpart – were obtained by the alkaline hydrolysis of triglycerides, e.g., by heating a mixture of ashes and fats. The process of hydrolysis of triglycerides, called saponification, represents also today a major route for the preparation of fatty acids[2]. Despite being readily available from renewable resources, of being easily biodegraded, and offering excellent surface active properties, fatty acids present several drawbacks, linked to their solubility in aqueous environments, which limits their use.

Fatty acids generally exhibit a high Krafft point and a very poor solubility in neutral or acidic solution. Even in alkaline condition, salts of fatty acids with multivalent cations, such as calcium or magnesium, are highly insoluble. These problems have a common origin: the high stability of solid crystal of the fatty acids and their salts. Several approaches are available, aiming at reducing the stability of the solid precipitate and thus improving the solubility of the fatty acid in solution. They include: (i) exchanging the counterion, typically sodium, with a bulkier one with a lower tendency to crystallize, such as choline, ternary ammonium salts[1,3–7]; (ii) the use of branched fatty acids[8,9]; or (iii) the insertion of few, highly flexible and bulky ethylene oxide units between the carboxylic head group and the aliphatic chains[10–13].

Polyoxyethylene alkyl ether carboxylic acids (chemical structure given in Fig. 1) are a very versatile class of surfactants[11], with generic formula $C_iE_jCH_2COOH$, with C_i being the usual nomenclature for fatty acids, and j the number of EO units. They combine in a single molecule the pH-responsive properties of the fatty acids, with the high solubility and temperature responsive behavior of nonionic polyethylene oxide alkyl ethers. Depending on the molecular architecture, i.e., the length of the aliphatic chain and the number of EO units, these surfactants self-assemble in a broad variety of structure, including vesicles, or cylindrical and globular micelles[11,13–15]. Their highly responsive behavior has been, for instance, exploited for the formulation of efficient metal-recovery systems[10,16,17].

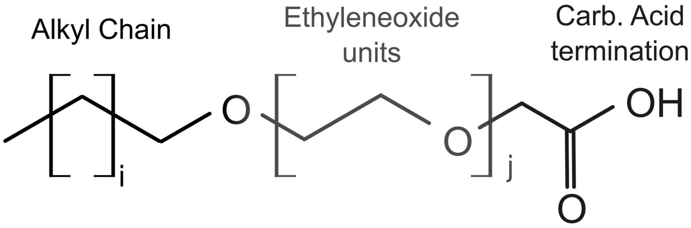

Fig. 1 Chemical formula of polyoxyethylene alkyl ether carboxylic acids, made by the hydrophobic aliphatic chain, the ethylene oxide body, and the carboxylic acid termination.

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Aim of this work is to investigate the properties of dilute solutions of polyoxyethylene alkyl ether carboxylic acids neutralized with sodium hydroxide, Choline hydroxide, and L-(+)-Arginine. In particular, we have investigated solutions of $C_{18:1}E_5CH_2COOH$ and $C_{18:1}E_9CH_2COOH$ and the effect of inorganic as well as of biologically active counterions in the micellization process. The complexity of the neutralizing agent and its adsorption on the micelle could play a role in the aggregation behavior. Moreover, the formulation can be provided with additional properties by employing biologically relevant counterions[18]. An additional point of both technical and scientific interest arises from the fact that anhydrous ethoxylated surfactants were shown to form ionic liquids when neutralized with complex counterions, such as choline[19,20]. Therefore we thought it is interesting to investigate the structure of the micelles as well as electrophoretic mobility flanked by volumetric determinations that provides a tool for the prediction of pressure effect on the involved structures.

Materials and Methods

Materials

The polyethylene oxide alkyl ether carboxylic acids used in this work were obtained from Kao Chemicals and are available under the trade names AKYPO RO 50 VG and AKYPO RO 90 VG. The surfactants are of technical grade, they were used without purification but previously characterized by 1H-NMR spectroscopy[11]. The analysis indicates that the hydrophobic part consists of a 3:1 mixture of C18:1 and C16:0 aliphatic chains, that the degree of ethoxylation is 4.7 and 8.8 for RO 50 VG and RO 90 VG, respectively. The degree of carboxymethylation is for both surfactants ca. 0.9. In this work, we refer to RO 50 VG and RO 90 VG with a representative formula of $C_{18:1}E_5CH_2COOH$ and $C_{18:1}E_9CH_2COOH$, respectively. NaOH is provided by Sigma Aldrich, while Choline hydroxide and L-(+)-Arginine are products of TCI Chemicals, and were used without further purification. Heavy water (D content >99.8%) from Eurisotop (Gif-sur-Yvette, France) was used for the small-angle neutron scattering experiments.

Methods

Light scattering The time-averaged scattering from surfactant solutions was recorded on a Malvern Zetasizer Nano ZS90 of Malvern Instrument with a measurement angle of 90° and a wavelength λ of 633 nm. Temperature scans were performed within a temperature range from 10 °C to 80 °C, in 5 °C steps and allowing the sample to equilibrate for 5 minutes between each measurement.

Zeta-Potential The same Malvern Zetasizer Nano ZS90 was used to determine the electrophoretic mobility of the surfactant aggregates. The Zeta-potential (ζ-Pot) was calculated using the Smoluchowski approximation.

Densitometry The apparent molar volume and the apparent molar compressibility of the counterion were determined using an oscillating tube densitometer equipped with a sound velocity measurement chamber, the DMA 5000 M from Anton Paar. The apparent molar volume of the counterion was calculated as:

$$\overline{V_{CI}} = \frac{Mw}{d} - \frac{1000 \cdot (d - d_0)}{c \cdot d \cdot d_0} \tag{1}$$

where d and d_0 are the densities of the surfactant/counterion solution and of the pure surfactant solution, respectively; Mw is the molar mass of the counterion and c its concentration (molality). The apparent molar compressibility of the counterion was obtained as:

$$\overline{K_{CI}} = \frac{1000}{m \cdot d_0}(\beta - \beta_0) + \beta \overline{V_{CI}} \tag{2}$$

with $\beta = (d \cdot v_s^2)^{-1}$ being the isoentropic compressibility coefficient, obtained from the density of the solution and the sound velocity v_s.

Small-Angle Neutron Scattering (SANS) SANS patterns were recorded on D11 at the Institut Laue-Langevin (ILL) in Grenoble, France[21]. Three different configurations were used, with a wavelength of $\lambda = 6.0$ Å sample-to-detector distances (SD) of 1.2, 8 and 34 m and collimation of 4, 8 and 34 m, respectively, covering a q-range of 0.03 - 5 nm^{-1}, where $q = 4\pi \sin(\theta/2)/\lambda$ is the magnitude of the scattering vector and θ is the scattering angle. The differential cross-sections (absolute scaling) were obtained by comparison with the scattering from a 1 mm water sample. SANS data were fitted in absolute units using the scattering length densities and specific volumes reported in Table 1, using a model of core-shell ellipsoids extensively described earlier[11,22].

Table 1 Densities, scattering length densities (SLD), and specific volumes (v) used in for the description of the SANS experimental results.

Compound	Density [g cm^{-3}]	SLD [10^{-4} nm^{-2}]	v [nm^3]
$C_{16}/C_{18:1}$	0.80	-0.37	0.464
$(OCH_2CH_2)_{4.7}OCH_2COOH$	1.25	1.33	0.341
$(OCH_2CH_2)_{8.8}OCH_2COOH$	1.22	1.04	0.618

Results and Discussion

A series of experiments were performed on dilute surfactant solutions gradually neutralized with three different strong bases: sodium hydroxide, Choline hydroxide, and arginine. It is important to highlight that these class of surfactants exhibit very low values of critical micelle concentration, irrespective of their degree of ionization[11] and that, accordingly, all experiments were performed at a surfactant concentration significantly above the critical micelle concentration. To follow the neutralization reaction between the weekly acidic surfactant and the strongly alkaline counterion, the pH values of the mixtures were recorded and are reported in Fig. 2. The data evidence the same behavior for sodium and choline hydroxide and a slightly different one for Arginine. The difference arises from the fact that sodium and Choline hydroxide are strong bases, which as fully dissociated at the given experimental conditions, while the pKa of the Guanidine unit of Arginine is close to 12[23] (recent reports hint towards a stronger dissociation constant[24]).

While pH titrations provide a first insight into the acid-base reaction between the counterion and the surfactant head group,

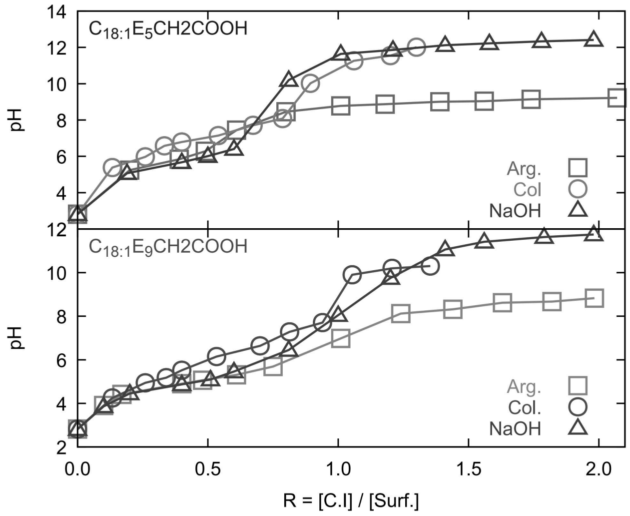

Fig. 2 Dependence of the pH of a 5 wt% solution of $C_{18:1}E_9CH_2COOH$ (top) and $C_{18:1}E_9CH_2COOH$ (bottom) as a function of the neutralization ratio, defined as the ratio of the concentration of the counterion and the surfactant.

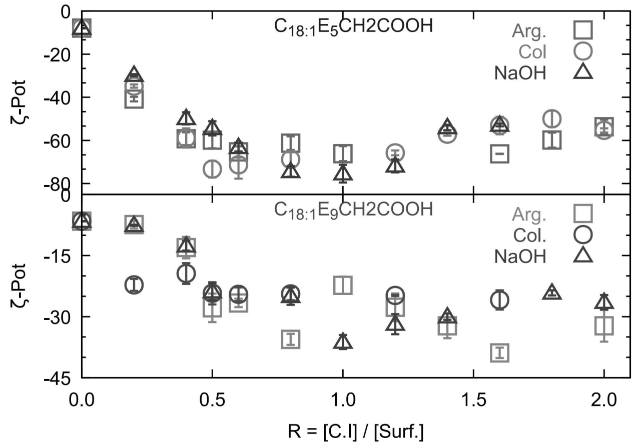

Fig. 3 Dependence of the ζ-Potential of the surfactant aggregates (5 wt% solution) of $C_{18:1}E_9CH_2COOH$ (top) and $C_{18:1}E_9CH_2COOH$ (bottom) as a function of the neutralization ratio, defined as the ratio of the concentration of the counterion and the surfactant.

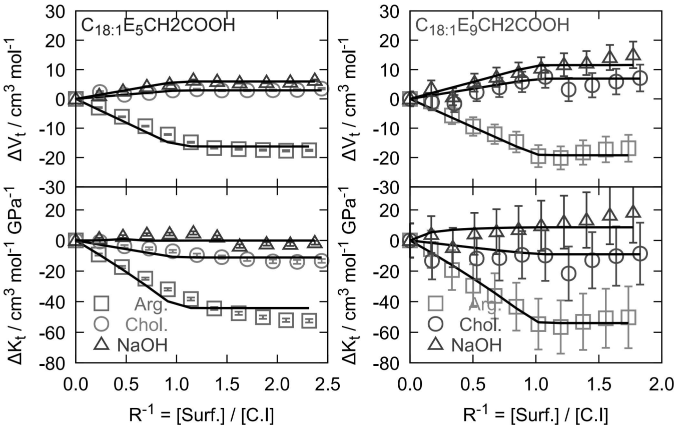

Fig. 4 Change of apparent molar volume and compressibility of different salts when transferred from a purely aqueous environment to a surfactant solution at different surfactant concentration. Full lines are best fits according to a simple 1:1 reaction (see text for full details). Experiments were performed at a constant salt concentration of 0.04 mol kg^{-1}.

little information on specific interactions between the surfactant aggregate and the counterion is obtained. Accordingly, ζ-potential measurements were carried out and are shown in Fig. 3. No notable difference in the trends of zeta potential between the three different counterions can be detected, indicating that, at ambient temperature, no specific binding of counterions takes place at the micelle/solution interface. Notably, the data referring to $C_{18:1}E_5CH_2COOH$ indicate the presence of a shallow minimum around equimolarity, which can be explained by a more pronounced counterion condensation taking place in the counterion excess regime. This effect is not observed for the $C_{18:1}E_9CH_2COOH$ case. It was previously shown that, even at full degree of ionization, the fraction of condensed counterions on $C_{18:1}E_9CH_2COOH$ micelles is less than 30% of the charges[10], significantly less than what usually observed for strongly ionic surfactant micelles, such as sodium dodecyl sulfate (SDS) or tetradecyl ammonium bromide, where typical values of 70∼80 % of the charges are compensated by counterions[25,26]. This peculiar behavior of $C_{18:1}E_9CH_2COOH$ arises from the large number of EO units, which causes a significant dilution of the charges at the micellar surface. For the sake of comparison, SDS exhibits a headgroup density approx. 0.56 nm^{-2}, while the one of $C_{18:1}E_9CH_2COOH$ is 0.28 nm^{-2}[10]. It is reasonable to assume that this effect is significantly less pronounced for aggregates of $C_{18:1}E_5CH_2COOH$, and that a counterion condensation occurs due to the lower number of EO units and the subsequent higher density of head groups at the surfactant aggregate surface.

Further insight into the interactions between the counterion and the surfactant micelles can be obtained by density and sound velocity measurements. In detail, the acid-base reaction between the surfactant and the salt is followed, and the apparent partial molar volume and compressibility, calculated according to:

$$V = \xi \cdot V_0 + (1-\xi) \cdot V_i \tag{3}$$

where V_0 and V_i are the apparent partial molar volumes of the counterion in water and in large excess of the surfactant, respectively. ξ is the degree of conversion of the acid-base reaction and is calculated assuming a infinitely large binding constant. The apparent partial molar compressibility of the counterion follows from its classical thermodynamic relation:

$$K = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{V}\left(\xi \cdot K_0 + (1-\xi) \cdot K_i + \frac{\partial \xi}{\partial P}(V_i - V_0)\right) \tag{4}$$

with K_0 and K_i being the apparent partial molar compressibilities of the counterion in water and in large excess of the surfactant, respectively. Due to the very large equilibrium constant of the reaction, the term $\partial\xi/\partial P \approx 0$ can be neglected. For the ease of comparison, the apparent molar volumes and compressibilities of the counterions, rescaled by their respective quantities in pure water, are shown in Fig. 4. Note that these quantities reflect the change of the apparent molar property when the salt is transferred from

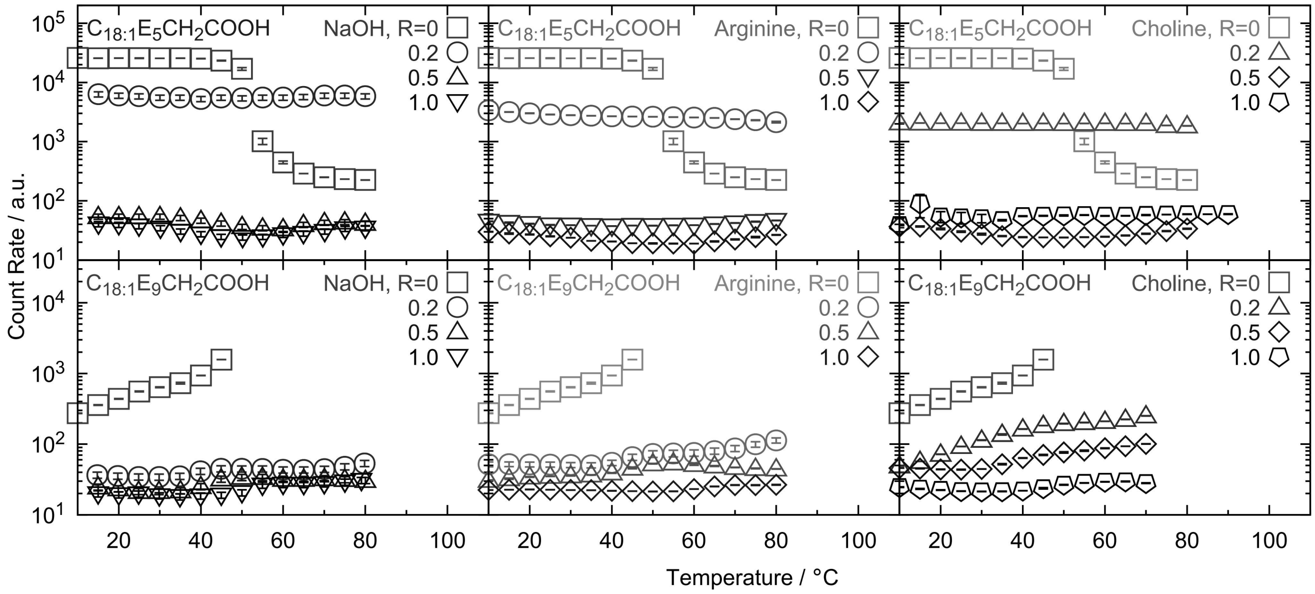

Fig. 5 Dependence of intensity of light scattered at an angle of 90° from 5wt% solutions of $C_{18:1}E_9CH_2COOH$ (top) and $C_{18:1}E_9CH_2COOH$ (bottom) with different degrees of neutralization ratio, defined as the ratio of the concentration of the counterion and the surfactant, as a function of temperature.

a purely aqueous solution to a surfactant solution.

Despite the simplest possible model has been chosen, it is able to reproduce the features of all measured curves. The obtained values are reported in the supporting information. No significant difference between the interaction of the counterion with $C_{18:1}E_5CH_2COOH$ or $C_{18:1}E_9CH_2COOH$ can be observed. In particular, negative values of ΔV_t were found for Arginine, while small, slightly positive values were found for NaOH and Choline. It is well established that positive and negative changes in the apparent molar volume of transfer are related to hydrophobic and electrostatic interactions, respectively. On this basis, one can argue that the arginine transfer reflects mainly the neutralization of this weak base while for Choline and sodium hydroxide the little changes are likely related to dehydration effect on the micellar aggregates as soon as the neutralization of the carboxylic acid occurs.

A further relevant aspect of polyoxyethylene alkyl ether carboxylic acids, is their temperature-dependent phase behavior, particularly rich for the nonionized species. Accordingly, the temperature-dependent behavior of surfactant solutions containing different amounts of counterions was probed by monitoring the intensity of the laser light scattered at an angle of 90°. The values are shown in Fig. 5, and are proportional to the mass of the aggregates. To start with, the scattering intensity of the acidic form of $C_{18:1}E_9CH_2COOH$ is significantly lower than that of $C_{18:1}E_5CH_2COOH$. The difference stems for the smaller head group of the latter component, which, in its nonionic and partially ionic form was shown to assemble in bilayered structures[27,28], while $C_{18:1}E_9CH_2COOH$ forms cylindrical micelles in its nonionic form[11]. The sudden decrease in scattering intensity observed for $C_{18:1}E_5CH_2COOH$, with R=0, arises from the formation of a dense precipitate, which coexists with a translucent surfactant solution. A similar effect was observed for $C_{12}E_5CH_2COOH$[11]. In contrast, with increasing temperature, the solutions of $C_{18:1}E_9CH_2COOH$ with R=0, become increasingly turbid, consequence of micellar growth, typically observed for similar nonionic alkyl ether surfactants[29,30].
The turbidity of $C_{18:1}E_5CH_2COOH$ solutions, regardless of the type of counterion and the degree of neutralization R (except for R=0), is temperature independent. In contrast, micellar growth is observed for most of the mixtures of $C_{18:1}E_9CH_2COOH$ probed in this study, and the effect is more marked when Choline is the counterion. This observation indicates that Choline favors micellar growth at high temperatures, in contrast to sodium, and to a less extent also to arginine.

This micellar growth is examined in more detail using small-angle neutron scattering (SANS), which allows us to probe colloidal structures in the size range of 1 ∼ 100 nm. The SANS of 1 vol% solution of $C_{18:1}E_9CH_2COOH$ were analyzed in absolute units using a model of core-shell prolate ellipsoids interacting via a charged hard sphere potential[31]. All the details of the model, including the implementation of molecular constraints, can be found elsewhere[11]. The experimental data and the fitted curves are shown in Fig. 6, the obtained parameters are given in the supporting information. The micellar growth of the nonionic form of $C_{18:1}E_9CH_2COOH$, indicated by the turbidity data, can be observed also in the SANS patterns, exhibiting a significant increase of the forward scattering intensity, and with a micellar length growing from approx. 17 to almost 50 nm, when the sample is heated. It is noteworthy that the model of flexible rodlike micelle would be more appropriate for the current case. Nonetheless, using a single model to describe the whole data series allows for a better comparison of the obtained parameters. A significant reduction in micellar size is observed as soon as the surfactant is,

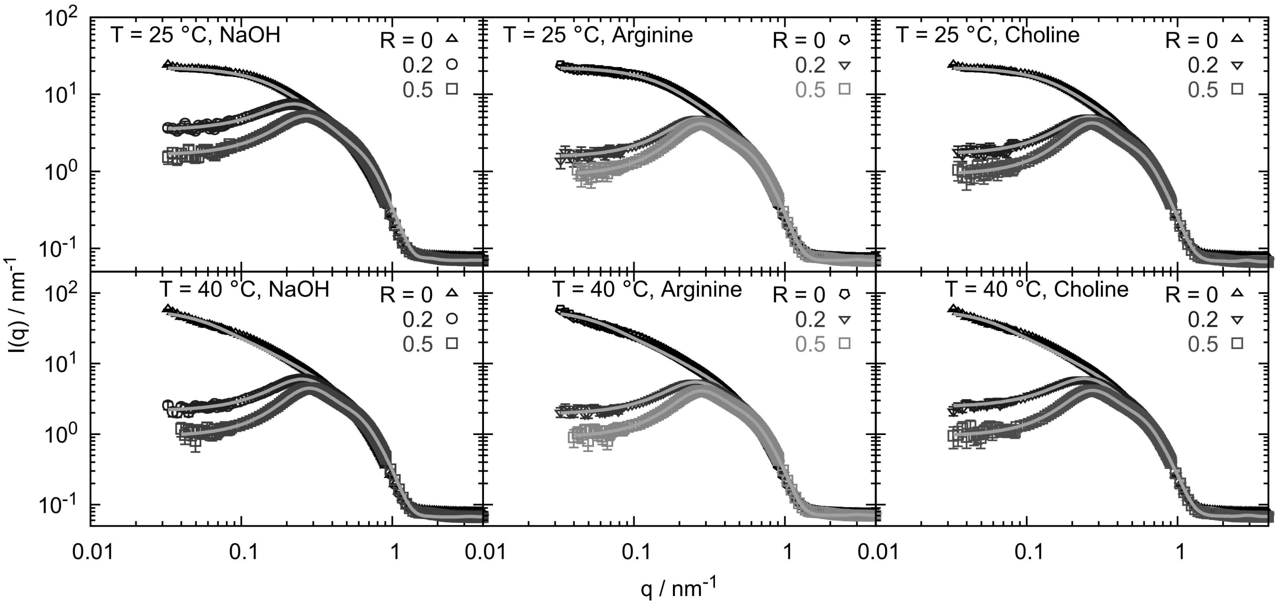

Fig. 6 Small-angle neutron scattering pattern of $C_{18:1}E_9CH_2COOH$ 1 vol% solutions partially neutralized, from left to right, with NaOH, Arginine, and Choline. The patterns were recorded at 25 (top) and 40 °C (bottom).

even to a small extent, ionized. While the rotational axis has been kept constant to 2 nm to reduce the number of free parameters[11], we observe a drastic reduction of the equatorial axis, regardless of the counterion type or the temperature. The temperature-induced micellar growth observed in the turbidimetric experiments is confirmed by the SANS analysis, with a slightly more pronounced growth when Choline is the counterion. Apart from this minor effect, the SANS experiments show that the nature of the counterion has a remarkably little effect on the structural behavior of $C_{18:1}E_9CH_2COOH$. Moreover, from the structural parameters of core size and shell thickness, the amount of water in the micellar shell can be estimated. For the nonionic species, it decreases from 60 to $50\%_{vol}$ when the temperature is increased from 25 to 40 °C. Upon addition of the counterion, the shell hydration increases to approx. $60\%_{vol}$ for sodium, and to above $70\%_{vol}$ for choline and arginine. These values correspond to an average number of 2 water molecules per EO group (the carboxymethyl termination is counted as it was one ethylene oxide unit), for the nonionic species at high temperature, to above 7 water molecules per EO unit for the surfactant neutralized with choline and arginine. The relatively low hydration of the uncharged surfactant can be justified by the presence intra-micellar hydrogen bonds between the carboxylic acid termination and the ethylene oxide unit, effectively reducing the need of hydration water in the shell.

These results are in contrast with similar studies performed on simple, non-ethoxylated fatty acids[4,5,7,32]. Evidently, the presence of even a few ethylene oxide units strongly alters the responsiveness of the fatty acid to the type of counterion. The different behavior can be rationalized considering three main causes. Firstly, the surfactant head group can be simplified in two segments, the weakly anionic, pH-responsive carboxymethyl termination, and the nonionic, temperature-responsive oligo ethylene oxide block. The latter imparts to the surfactant an amphiphilic character even in acidic conditions. Moreover, it reduces the importance of the carboxylic acid termination on the overall surfactant properties. In fact, polyoxyethylene alkyl ether carboxylic acids are water-soluble even in very acidic conditions and the effect of pH on the self-assembly is reduced with increasing number of EO units[11]. The second reason which can be identified is the fact the presence of the ethylene oxide block causes a “dilution” of the charged head group on the micelle surface. Such a dilution causes a reduction of the counterion condensation on the micelle surface, and, consequently, decreases the sensitivity of the surfactant to the counterion type. Further consequences are the better tolerance of polyoxyethylene alkyl ether carboxylic acids to divalent ions[33] or a decreased pK_a value of the head group when compared to classical fatty acids[12]. Finally, the high conformational entropy of the flexible ethylene oxide block has been shown to significantly affect the properties of similar systems[20,34,35]. In fact, multiple sodium – ether-oxygen interaction where shown to effectively dilute the charge of small cationss, which, for certain aspects, behave similarly to larger counterions[34].

Conclusions

In this contribution, we have investigated the properties of dilute solutions of polyoxyethylene alkyl ether carboxylic acids neutralized with three different bases, namely sodium hydroxide, Choline hydroxide, and arginine. Potentiometric titrations, electrophoretic mobility, density, and sound velocity measurements, combined with a structural study performed by light and neutron scattering provide a comprehensive insight into the behavior of these mixtures.

In contrast to the numerous studies which demonstrate that the nature of the counterion has a remarkable effect on the self-assembly behavior of related fatty acids, we could not evidence any ion-specific effect in the investigated series. This result, somehow surprising, highlights the effect of the introduction of even a few ethylene oxide units in the surfactant head group. In a simplified view, the surfactant head group can be subdivided in a nonionic part, the EO block, and a ionic one, the carboxymethyl termination. For the case of fatty acid, the whole amphiphilic behavior is dictated by the carboxylic acid, with strong effects arising from its degree of ionization and type of counterion. In contrast, the effect of the carboxylic acid is 'diluted' by the presence of the nonionic block. Moreover, the oligo ethylene oxide acts as a spacer, reducing the distance between the ionic terminations and the overall surface charge density. The immediate consequence is a reduced tendency of counterion condensation on the surfactant micelle interface, and thus a minor sensitivity of the surfactant on the nature of the counterion.

Finally, this study sheds light on an important aspect of the self-assembly properties of simple fatty acids, and of polyoxyethylene alkyl ether carboxylic acids. We rationalize the observation as the result of the presence of, even a few, ethylene oxide units in the surfactant head group, and the resulting dilution of the charged units. The observations also explain the origin of the resistance of polyoxyethylene alkyl ether carboxylic acids towards hard water conditions, which represents an important technical aspect of this class of surfactant, and similarly related anionic ethoxylated surfactants.

Conflicts of interest

There are no conflicts to declare.

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