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The critical micelle concentration of tetraethylammonium perfluorooctylsulfonate in water

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Abstract

The aggregation characteristics of tetraethylammonium perfluorooctylsulfonate in water were studied by several techniques: conductivity, pH, ion-selective electrodes, and surface tension. It was concluded that the aggregation process is gradual and starts with the formation of oligomers such as ion pairs that grow to give spherical micelles, which become wormlike with increasing concentration. Because of the size and hydrophobicity of the counterion, micelles quickly increase in ionization degree up to about 0.5. Differences among different critical micelle concentration values in the literature are explained on the basis of the gradual formation of micelles.

Keywords: Tetraethylammonium perfluorooctylsulfonate; Critical micelle concentration; Premicelles; Perfluorinated surfactants; Air/solution interface

1. Introduction

The physical properties of surfactant solutions, such as electrical conductivity, surface tension, light scattering, and ultrasound velocity, change at the critical micelle concentration (CMC) [1]. These changes can be abrupt or slight. In the first case, the CMC is easily determined by the intersection between two straight lines above and below the CMC. In the second case, it is difficult to obtain a precise CMC value, as several straight lines can be obtained by fitting the experimental points. Moreover, in some cases the employed property does not follow a linear relationship with concentration. To solve this problem, recently a statistical method for determining the CMC with precision, the local polynomial regression method (LPRM), was proposed [2]. This method is based on nonparametric estimation of the regression function, which has the advantage of being extremely flexible because it does not impose any parametric model on the subjacent structure of the data. Hence, this method is applicable in practically all circumstances, giving good results.

Perfluorated amphiphiles are more surface-active than normal hydrocarbon detergents. Solutions of perfluorated surfactants usually have lower CMC and attain lower surface tension values than the solutions of their hydrogenated homologues having the same chain length. They are also more temperature-resistant. These properties are the reason for using perfluorated surfactants to improve the performance of a large variety of chemical industrial products (paints, varnish, surface-finished products, etc.). Ionic perfluorosurfactants form spherical or threadlike micelles in water, depending on the nature of the counterion and the concentration of added electrolyte [3]. In particular, alkylammonium counterions are known to induce the transition from spherical to threadlike micelles in a series of perfluorosulfonic and -carboxylic acids, producing a high solution viscosity [4].

Perfluorooctanesulfonate (PFOS) salts or compounds that may degrade to PFOS have been employed since a long time ago in common uses and industrial formulations, such as fabric

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treatments, antistatic agents, paper coatings approved for food contact, shampoos, corrosion inhibitors, insecticides, and fire-fighting foams (AFFs) [5,6]. However, PFOS salts are known for toxic effects on animals, including lethality [7–10] and other biological effects [11–16].

Tetraethylammonium perfluorooctylsulfonate (TEA.PFOS) solutions have been studied in the literature using several techniques such as conductivity, kinetic data, NMR, and electric birefringence. However, there are some discrepancies. The TEA.PFOS literature CMC values range from 8.8×10^{-4} to 1.7×10^{-3} mol dm^{-3} at similar temperatures [17,18]. This 93% difference (on the basis of CMC = 0.88 mM) is higher than that reasonably expected from experimental error. Bossev et al. reported a value of 1.1×10^{-3} mol dm^{-3} at 30 °C using conductimetry measurements [18]. Micelles were reported as threadlike [17,18], but in some cases discoid micelles were suggested, the surfactant molecules being perpendicular to the disk surfaces of micelles [17].

In this article we studied the tetraethylammonium perfluorooctylsulfonate critical micelle concentration to elucidate the reason for these discrepancies.

2. Experimental

The tetraethylammonium perfluorooctylsulfonate (TEA.PFOS) was from Aldrich and was recrystallized. Water was double-distilled, deionized, and degassed before use.

The individual samples were prepared by weight. Since Bossev et al. [18] and Hoffmann and Ulbricht [19] found that the preparation of the TEA.PFOS samples in water was difficult and a long time is necessary to reach equilibrium, we shack the mixture vigorously; then it was sonicated to ensure homogeneity. Furthermore, samples were left to rest at least 4 days to reach equilibrium (one day more than Schorr and Hoffmann [17] indicated).

Several difficulties were found in ensuring the attainment of equilibrium. It was necessary to perform some controls and to confirm that the measurements were reproducible. As an example, we prepared each concentration separately and then it was sonicated and left to rest for 4 days. Next we checked that the results of measurements were constant with the time: after the first measurement, another one was made several hours after and then another after 1 day.

When error intervals were computed, the Student t function was employed with a confidence level of 0.90. To obtain the average of several measurements having different errors, the linear unbiased minimum variance estimation method [20] was employed. This method uses the inverse of the square of the error of each measurement as its statistical weight in the average.

The specific conductivity (κ) was measured with a Kyoto Electronic C-117 conductivity meter calibrated with KCl solutions and literature data [21,22]. Solutions were vigorously shaken during conductivity measurement in a thermostatic bath at 293.15 ± 0.01 K. The κ data were analyzed by the local polynomial regression method [2] to determinate the inflection point.

We also used the $\Delta\kappa = \kappa_{\text{measured}} - \kappa_{\text{extrapolated}}$ vs total surfactant concentration (C) representation, where κ_{measured} and $\kappa_{\text{extrapolated}}$ are the measured value of the specific conductivity at each C and the κ value extrapolated at the same concentration from the data below the CMC. This representation magnifies the difference in slopes below and above the CMC. Conductivity data were also studied by the differential conductivity $\Lambda^{\text{d}} = 1000\partial\kappa/\partial C$ vs C_{average}, where $\partial\kappa/\partial C = 1000(\kappa_2 - \kappa_1)/(C_2 - C_1)$ and $C_{\text{average}} = (C_2 - C_1)/2$; C_1 and C_2 being two successive total surfactant concentrations whose respective specific conductivities are κ_1 and κ_2. This representation allows obtaining additional information from conductivity data [23,24].

The pH determinations were made at 293.15 K with a CRISON GLP 22 pH meter and a CRISON glass electrode. Five minutes after the immersion of the electrode in each sample a series of 10 measurements were made. Measurements were performed on the pH and the potential (mV) scale.

Since tetraethylammonium perfluorooctylsulfonate is a salt of a strong surface-active acid and a weak base (TEAOH), its hydrolysis give acid solutions:

$$\text{TEA}^{+} + \text{H}_2\text{O} \leftrightarrow \text{TEAOH} + \text{H}^{+}. \tag{1}$$

So there is some tetraethylammonium hydroxide (TEAOH) in solution in equilibrium with TEA^{+} and H^{+} ions.

The apparent constant of acidity of the TEA^{+} ion $K_{\text{a}} = [\text{H}^{+}]^2/C$ is very sensitive to changes of the polarity in the environments of the hydrolyzable species. The measured K_{a} value involves contributions of the value for the nonaggregated TEA^{+} ions in monomeric solution in water and of the counterions in the Stern layer at the aggregates' surface. The importance of these contributions depends in turn on the proportion of both species in solution. The contribution of TEA^{+} ions included in the aggregates' Stern layer is affected by the polarity of this region [25,26], which in turn is strongly affected by its structure [27,28]. This structure (nature of head groups and counterions, degree of micelle ionization, distance between polar head groups) is in turn affected by the general micelle structure (spherical, wormlike, or disklike shape). The Stern layer of anionic micelles attracts H^{+} and repels OH^{-} [29], and the difference between the local pH in this layer and that in the bulk solution may be as large as 2 pH units [30,31]. As a consequence, values of pK_{a} may vary up to about 1.3 units when a weak acid is anchored at the micelle Stern layer [32].

The ion-selective measurements were made with a GLP 22 pH meter with a saturated calomel reference electrode (CRISON) and a perfluorooctanesulfonate ion-selective electrode to determine the concentration of free (nonaggregated) PFOS^{-} ions at each total surfactant concentration C, and a dodecyltrimethylammonium ($\text{C}_{12}\text{TEA}^{+}$) ion-selective electrode to determine the free TEA^{+} ion concentration. The construction of both surfactant ion-selective electrodes may be found in the literature ((PFOS^{-}) [33]; ($\text{C}_{12}\text{TEA}^{+}$) [34]). Although the primary ions for both ion-selective electrodes were not PFOS^{-} and TEA^{+}, their response to these ions was good, as frequently occurs with ion-selective electrodes [35]. To ensure equilibrium 30 min were waited before the first determination, and then a