The Influence of an Electrolyte on Micelle Formation in Aqueous Solutions of Sodium Monoalkyl Sulfosuccinates

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Abstract—Critical micelle concentrations were determined by conductometry for the homologous series of sodium monoalkyl sulfosuccinates $ROOCCH_2CH(SO_3Na)COONa$ (R is an alkyl radical, C_{10}–C_{15}) in the presence of sodium chloride. Coefficients of the Corrin–Harkins equation were calculated. It was shown that the formation of micelles began when a certain value of the mean ionic activity of the surface active substance was reached.

INTRODUCTION

Surface active substances are as a rule used as components of compositions containing auxiliary compounds, including electrolytes. The addition of inorganic salts is known to increase surface activity and strengthen the adsorption of surfactants at the boundary between phases. Inorganic electrolytes influence all the colloidal-chemical properties of surfactants, increase their micelle forming ability, solubilizing action, and wetting, which is extensively used for controlling surfactant properties. It was found experimentally that the introduction of electrolytes into solutions of ionogenic surfactants decreases their critical micelle concentrations (CMCs) [1, 2] according to the well-known Corrin–Harkins equation,

$$\log c_{CMC} = const - iK_g \log c,$$

where c_{CMC} is the critical micelle concentration, mol/l; i is the number of ionogenic groups in the structure of the surfactant; K_g is the constant characterizing the degree of binding of like counterions; and c is the total concentration of counterions in solution.

It was shown later that, for solutions of ionogenic surfactants that are electrolytes themselves, the mean ionic activity of surface active ions and all the counterions in solution should be taken into account [3, 4]. For instance, it was shown in [5], where the isotherms of surface tension of ammonium perfluoroligoetheralkyl monocarboxylate were measured in the presence of ammonium fluoride, that, irrespective of admixtures, all isotherms were superimposed on each other if mean activity was used instead of the concentration of the surfactant.

The overwhelming majority of works on micelle formation in solutions of surfactants are concerned with the influence of electrolytes on the behavior of cationic and anionic surfactants with singly charged cations and anions, in particular, alkyl sulfates [6, 7], sulfonates [8, 9], alkyltrimethylammonium halides, alkyltrimethylpyridinium [10], etc.

In recent years, micelle forming surfactants containing several ionogenic groups have become the object of study. In particular, so-called bola-surfactants with two ionogenic groups situated at the opposite hydrocarbon chain ends were considered [11]. Cationic surfactants containing one, two, and three trimethylammonium or pyridinium groups at one hydrocarbon radical end were studied [12, 13]. Disodium salts of sulfosuccinic acid monoesters and higher alcohols of the general formula $ROOCCH_2CH(SO_3Na)COONa$ are also anionic surfactants with two ionogenic groups [14]. However, the influence of an extraneous electrolyte on the behavior of surfactant homologues with several ionogenic groups has not been studied. This is the problem considered in the present work.

EXPERIMENTAL

Disodium salts of sulfosuccinic acid monoesters (sulfosuccinates) were synthesized from higher alcohols from C_{10} to C_{15} using the known procedure [15] and isolated and purified as described in [14]. The content of surfactants in the products was no less than 99.8%. The surface tension isotherms of their aqueous solutions contained only insignificant minima.

The CMCs of surfactants in aqueous solution and in the presence of sodium chloride were determined conductometrically at 50°C. The specific electrical conductivity of solutions was measured on an Anion 4100 (Infraspak-Analit, Russia) conductometer. The temperature 50°C was selected because the surfactants under consideration had high Kraft points.
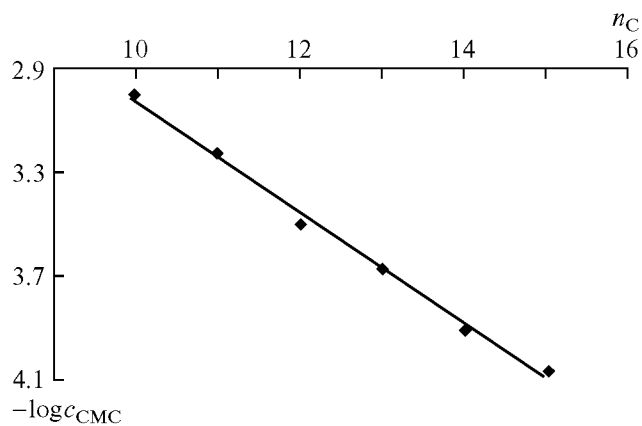
Fig. 1. Dependence of CMC of sodium monoalkyl sulfosuccinates on hydrocarbon radical length.
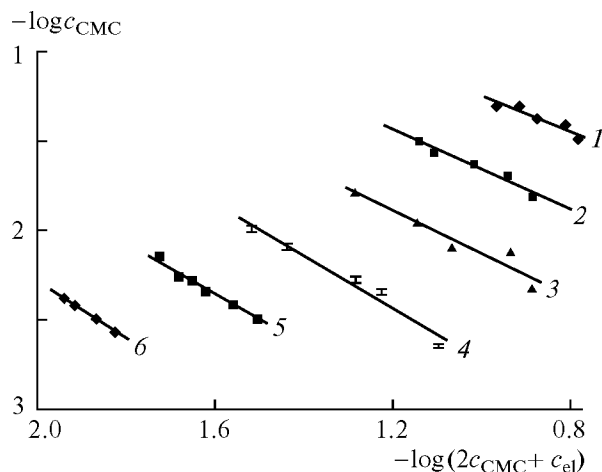

Fig. 2. Dependences of CMCs of sodium monoalkyl sulfosuccinates on the concentration of counterions in solution at $n_C = $ (1) 10, (2) 11, (3) 12, (4) 13, (5) 14, and (6) 15.

RESULTS AND DISCUSSION

The logarithms of CMCs for the homologous series well fall on a straight line (Fig. 1). The dependence of the CMCs of surfactants on the total concentration of counterions is often used to estimate the degree of binding of counterions by micelles [9, 10]. For the surfactants with doubly charged anions, this dependence is described by the equation

$$\log c_{CMC} = const - 2\beta \log c_{Na^+},$$

where β is the degree of binding of counterions and $c_{Na^+} = 2c_{CMC} + c_{NaCl}$.

The corresponding linear dependences for monoalkyl sulfosuccinate homologues are shown in Fig. 2. In the homologous series, β increases as the hydrocarbon radical grows longer (see table). The calculated β value should, however, be treated as an "apparent" degree of binding of counterions [16], because electrolyte admixtures can cause an increase in the aggregation number of surfactants and in the degree of binding.

It was of interest to apply the method of calculation of the mean ionic activities of surfactants [3, 17] to systems with sodium monoalkyl sulfosuccinates and

an additional electrolyte. Surfactants dissociate in solutions as

$$ROOCCH_2CH(SO_3Na)COONa$$

$$\longrightarrow ROOCCH_2CH(SO_3^-)COO^- + 2Na^+.$$
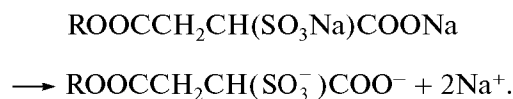
In the presence of sodium chloride, the ionic strength of the solution is

$$I = 3c_{surfactant} + c_{NaCl},$$

where $c_{surfactant}$ and c_{NaCl} are the molar concentrations of the surfactant and salt, respectively. At $I < 0.1$ mol/l, activity coefficients were calculated in the second Debye–Hückel approximation,

$$\log f_\pm = -|z_1 z_2| A I^{1/2}/(1 + I^{1/2}),$$

where z_i is the charge of ion i, I is the ionic strength of the solution, and A is the coefficient depending on temperature; at 50°C, $A = 0.54$ [18]. The mean ionic concentration of surfactants is $\bar{c}_\pm = (c_{Na^+}^2 c_{surfactant})^{1/3}$, where c_{Na^+} is the concentration of the counterion in solution, $c_{Na^+} = 2c_{surfactant} + c_{NaCl}$.

An example of the dependence of specific conductivity on concentration and the mean ionic activity of a surfactant, sodium monotridecyl sulfosuccinate, is shown in Fig. 3. The CMC noticeably decreases as the concentration of sodium chloride grows (Fig. 3a), whereas the mean activity values corresponding to the beginning of micelle formation in solution approach each other significantly (Fig. 3b). Similar behavior was observed for the other homologous series members. It follows that the formation of micelles in solutions of ionogenic surfactants, including the formation of
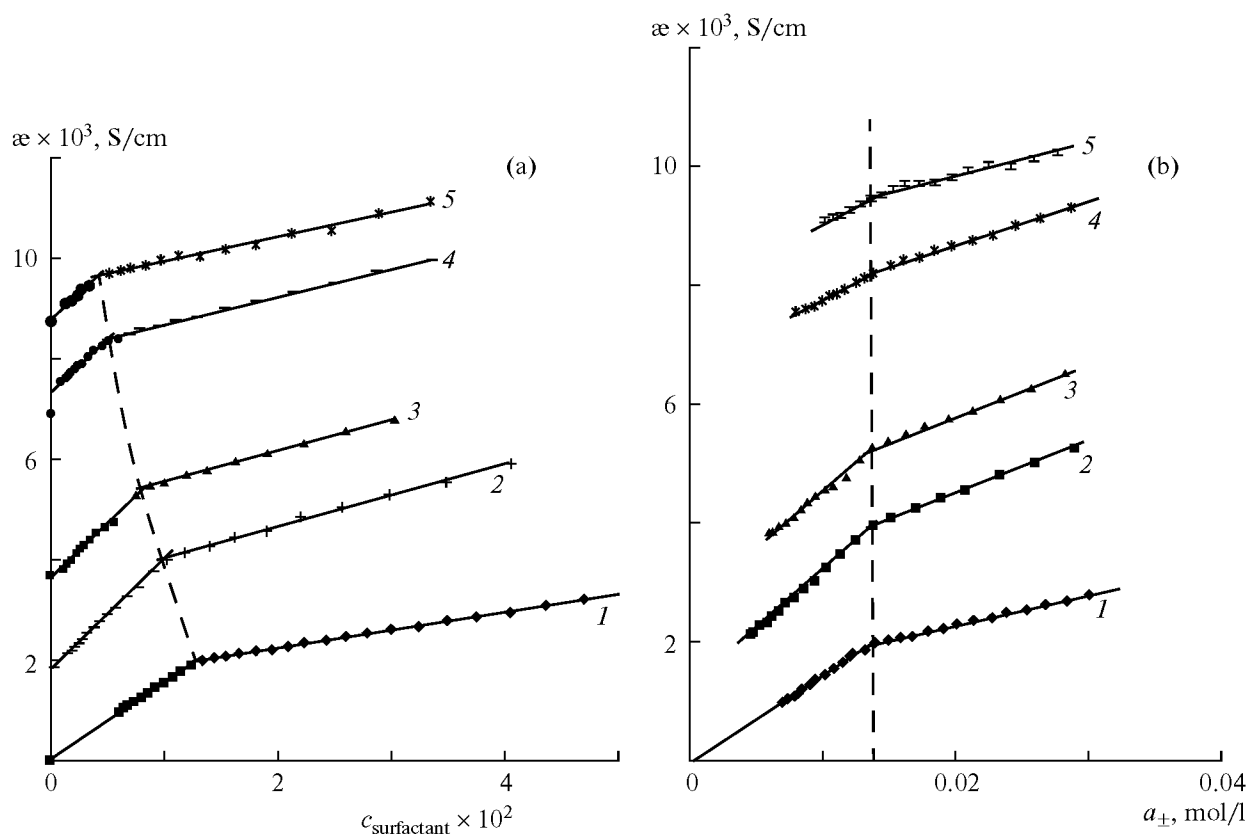
Degrees of counterion binding calculated by the Corrin–Harkins equation at $T = 50°C$

n_C	β	n_C	β
10	0.48 ± 0.11	13	0.74 ± 0.09
11	0.51 ± 0.07	14	0.75 ± 0.02
12	0.59 ± 0.10	15	0.80 ± 0.08

Fig. 3. Dependences of specific conductivity on (a) surfactant concentration and (b) mean surfactant ionic activity at various NaCl contents: (*1*) 0, (*2*) 0.01, (*3*) 0.02, (*4*) 0.04, and (*5*) 0.05 mol/l.

micelles in the presence of electrolytes, begins when a certain mean surfactant ionic activity is reached.

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