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Premicellar Aggregation in Water–Salt Solutions of Sodium Alkyl Sulfonates and Dodecyl Sulfate

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Abstract—The features of premicellar aggregation in aqueous solutions of sodium *n*-octyl, *n*-nonyl, and *n*-decyl sulfonate, as well as sodium *n*-dodecyl sulfate, at a constant ionic strength maintained by adding NaCl are studied by potentiometry using modified ion-selective electrodes reversible with respect to the ions of these surfactants. For the studied surfactants, the critical micelle concentrations are refined, the compositions of the products of premicellar aggregation are determined, and the stability constants of aggregates are evaluated.

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INTRODUCTION

Micellization, adsorption, and solubilization processes in aqueous solutions of colloidal surfactants are known to be complicated by premicellar association. In spite of the universally recognized jumpwise cooperative mechanism of micellization, aggregates that are much smaller than micelles (e.g., dimers and trimers) may emerge in the region below the critical micelle concentration (CMC). This fact must be taken into account, when, e.g., implementing strict quantitative studies of micellization, calculating its thermodynamic functions, estimating physicochemical properties of systems, etc. [1].

For example, the study of monomer aggregation has appeared to be an important stage of investigating micellar polymerization of *n*-dodecylammonium 2-acrylamido-2-methylpropan sulfonate (DDA-AMPS) [2]. The use of a model implying that monomers, dimers, and micelles of sodium *n*-dodecyl sulfate (SDS) coexist in a system made it possible to determine the self-diffusion coefficients of the monomers and dimers using pulsed-field gradient FT-NMR spectroscopy [3]. Partial (12–20% of the total surfactant concentration) dimerization of amphiphilic *n*-dodecyl sulfate anions influenced the average values of the activity coefficient determined for SDS in an SDS–NaCl–water system [4] and led to additionally overestimated values calculated for the activity coefficient of *n*-dodecyl sulfate ions (DS^-) in a solution upon increasing ionic strength (I) by adding sodium chloride [5].

Various methods, such as conductometry [1, 2], potentiometry [4, 6–8], and ^{1}H NMR spectroscopy [9], are used to study aggregation in aqueous surfactant solutions. The mechanisms and forms of association in an aqueous solution of the micelle-forming DDA-AMPS monomer were studied using not only conductometry, but also capillary and rotational viscometry, isothermal translational diffusion, and atomic force microscopy [2].

Potentiometric methods employing ion-selective electrodes (ISEs) occupy a unique place in the studies of organized surfactant solutions, because they allow one to directly measure the activity (or the equilibrium concentration in case of a fixed ionic strength of a solution) of surfactant monomers or counterions in an examined system [8]. For example, the effect of NaCl as a background electrolyte on the premicellar association and the average ionic activity in aqueous SDS solutions was studied potentiometrically using a glass sodium-selective electrode [4]. Second-order electrodes were used to study the premicellar aggregation in aqueous solutions of potassium *n*-dodecyl sulfonate in the presence of KNO_3 (0.02 M) and SDS in the presence of $NaNO_3$ (0.04 M) [6]. The electrodes represented metallic mercury contacting with a paste of an insoluble salt, mercury(II) *n*-dodecyl sulfonate or $Hg(DS)_2$, and responded to *n*-dodecyl sulfonate or *n*-dodecyl sulfate ions, respectively. Standard calomel electrode was used as a reference electrode [6].

Liquid membrane electrodes (usually, those with a polyvinyl chloride (PVC) matrix) are typically used to detect surfactants. Such a PVC-membrane-based ion-selective electrode responding to DS^- ions was used to study premicellar aggregation in water–alcohol solutions containing ethanol or 1-propanol, SDS, and 10^{-4} M NaBr [10]. The fraction of an alcohol was varied from 5 to 40 vol %. The existence of dimers and trimers in the examined systems was proven and their stability constants were determined.

Commercial PVC-membrane-based ISEs designed for detecting inorganic anions can be used to obtain a response to surfactant anions after their exposure in solutions of corresponding surfactants [5, 7, 8]. Due to the high affinity of surfactant monomers to lipophilic membranes, the modified ISEs lose their primary electrode function and exhibit high selectivity coefficients with respect to an individual surfactant ion in the presence of inorganic anions [5, 11]. Modification of commercial EM-NO_3-01 nitrate-selective electrodes based on a PVC membrane, which contained tetra-*n*-decylammonium salt, NO_3^-, as an ion exchange system, yielded electrodes reversible with respect to *n*-alkyl sulfate and *n*-alkyl sulfonate anions. These ISEs were used for potentiometric determination of the activity coefficients of surfactant anions in aqueous and water–salt premicellar solutions [5]. The modified DS^--selective electrodes were used to study the premicellar aggregation in aqueous SDS solutions [7, 8]. $(DS^-)_2$ dimers were found to be the prevailing product of the premicellar aggregation; the determined logarithm of the dimerization constant equal to 2.18 ± 0.05 showed a rather good agreement with the value determined by measuring electrical conductivity (2.50) [1] and the value obtained by ^{1}H NMR spectroscopy (2.32 ± 0.12) [9].

This study is a continuation of the above-cited investigations. The goal of the work was to investigate the features of premicellar aggregation in water–salt solutions of sodium *n*-decyl, *n*-nonyl, and *n*-octyl sulfonates, as well as sodium *n*-dodecyl sulfate, using modified commercial EM-ClO_4-01 perchlorate-selective electrodes with a PVC membrane containing $(C_{10}H_{21})_4N^+ClO_4^-$, and to determine the compositions and stability constants of the aggregates as depending on the structure of the surfactants.

EXPERIMENTAL

The following reagents were used in this study: sodium *n*-decyl sulfonate (n-$C_{10}H_{21}SO_3Na$) and sodium *n*-octyl sulfonate monohydrate (n-$C_8H_{17d}SO_3Na \cdot H_2O$) with basic substance contents of ≥98% (Acros), sodium *n*-nonyl sulfonate (n-$C_9H_{19}SO_3Na$) (Fluka), sodium *n*-dodecyl sulfate ($C_{12}H_{25}OSO_3Na$) with basic substance contents of ≥99% (Sigma), and NaCl of reagent grade. All solutions were prepared in bidistilled water with a specific conductivity of $1.5 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

To prepare modified electrodes responding to the surfactant anions, commercial EM-ClO_4-01 electrodes were exposed and stored in 0.001 M solutions of sodium salts of the corresponding anionic surfactants. The internal solutions of the electrodes contained the surfactants (0.001 M) and NaCl (0.005 M). Prior to the measurements, the electrodes were exposed in bidistilled water for 1 h. The electromotive force (EMF) was measured at 25.0 ± 0.1°C using a compensating circuit with an uncertainty of ±0.3 mV. An EVL-1MZ silver chloride electrode was used as the reference one; a 1.0 M NH_4NO_3 solution in an agar gel played the role of a salt bridge. The potentiometric data were processed using the CLINP 2.1 software (www.chemo.univer.kharov.ua/kholin/climp.html) [12].

RESULTS AND DISCUSSION

The electrode response of the modified surfactant-selective electrodes was studied in solutions with a constant ionic strength maintained by adding calculated amounts of NaCl. The concentration of NaCl as a background electrolyte was chosen based on the selectivity coefficients, which had been previously determined using the method of mixed solutions [5]. The I value was 0.20 M for the n-$C_8H_{17}SO_3Na$–NaCl system, 0.10 M for the n-$C_{10}H_{21}SO_3Na$–NaCl and $C_9H_{19}SO_3Na$–NaCl systems, and 0.01 M for the SDS–NaCl system.

The concentration dependences of the electrode parameters experimentally found for the ISEs in a wide range of surfactant concentrations (Fig. 1) were used to determine the parameters of the electrode function (from segment I), refine the CMC values as the abscissa of the intersection points between the linear segments I and II, and study the premicellar aggregation of surfactant ions in a narrow concentration range near the CMCs.

In the premicellar region (Fig. 1, segment I, linear part), total concentration $c(R^-)$ of the potential-determining surfactant ions at I = const coincided with their equilibrium concentration $[R^-]$ and the electrode response of the surfactant-selective electrodes was described by the following equation:

$$E = E^{\otimes} - k\log[R^-],$$

where $E^{\otimes}$ is the constant component of the cell EMF and k is the angular coefficient of the electrode function, the value of which ranged from 54 to 59 mV for our modified electrodes, thereby confirming their applicability for further experiments.

Table 1 lists the CMC values in water–salt solutions of the surfactants calculated using the corresponding experimental dependences shown in Fig. 1. Our data are in satisfactory agreement with the values available at present.

Ten to fifteen experimental EMF values were obtained in a narrow range of surfactant concentrations near the determined CMC values. The EMF values were processed mathematically using the CLINP 2.1 software, which enabled us to refine an aggregation model simultaneously with the calculation of the equilibrium constants. Eleven different aggregation mod-

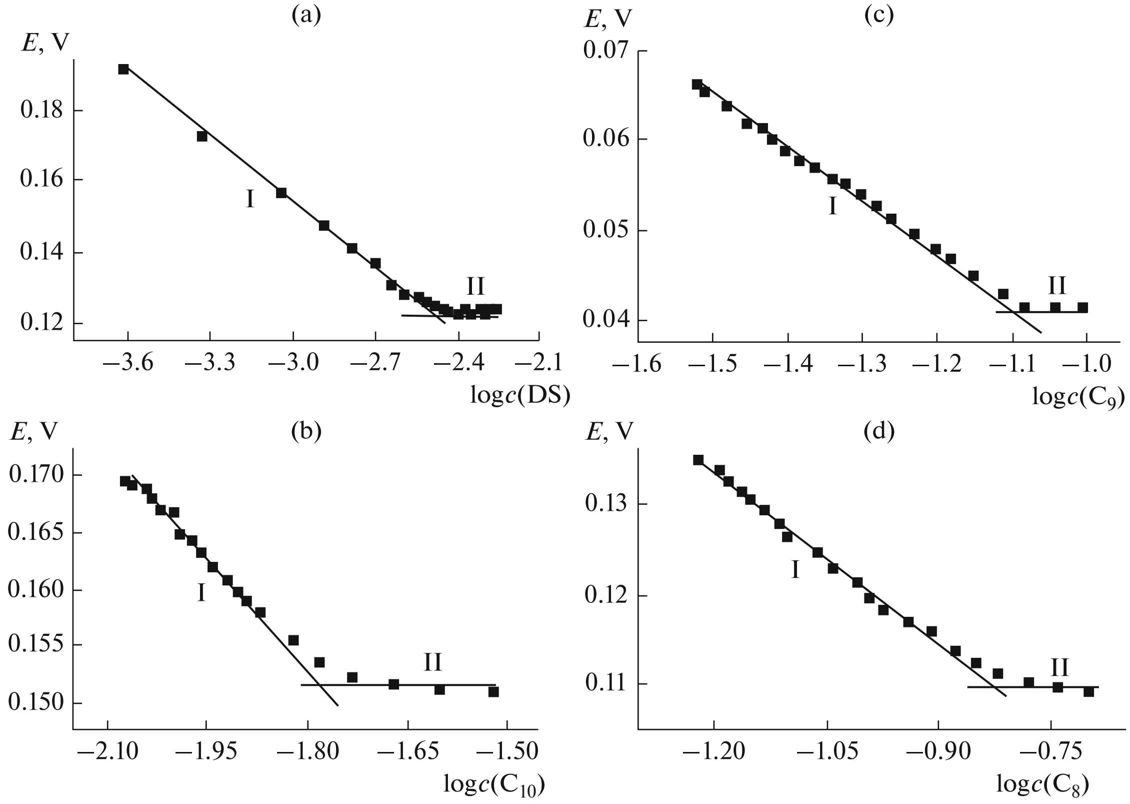

Fig. 1. The electrode responses of surfactant-selective electrodes as functions of logarithmic overall surfactant concentration in the presence of NaCl: (a) SDS, (b) sodium *n*-decyl sulfonate, (c) sodium *n*-nonyl sulfonate, and (d) sodium *n*-octyl sulfonate.

els were considered. We took into account either the formation of only one aggregate (dimer R_2^{2-}; trimer R_3^{3-}; and surfactant ion–counterion associates with compositions NaR, NaR_2^-, Na_2R^+, or Na_2R_2) or the coexistence of two possible aggregates. The formation of aggregates from a larger number of asymmetrically charged ions was not taken into account, because this process is energetically unfavorable in diluted solutions [1]. The adequacy of describing the experimental data was assessed using Pearson's test χ^2 [12].

The calculation results are presented in Table 2 as concentration yields α_i of the simulated aggregates of different compositions (α_i denotes the fraction of the equilibrium concentration of an aggregate relative to the overall surfactant concentration). The aggregate the fraction of equilibrium concentration of which was highest at a surfactant concentration almost coinciding with the CMC (these values are shown in bold in Table 2) was chosen as the main product of the premicellar aggregation (the prevalent form). Under this approach, for SDS and sodium *n*-decyl sulfonate, the prevalent form was the R_2^{2-} dimer; for sodium *n*-nonyl sulfonate, it was the neutral NaR associate; and, for sodium *n*-octyl sulfonate, it was the associate with a composition Na_2R^+. It can be seen that the probability

Table 1. CMC values in water–salt solutions of anionic surfactants (25°C)

Surfactant	*I*(NaCl), M	CMC, M	
		our results	literature data
n-$C_{12}H_{25}OSO_3Na$	0.01	3.3×10^{-3}	3.8×10^{-3} [13]
n-$C_{10}H_{21}SO_3Na$	0.10	0.016	0.0219 (30°C, [13])
n-$C_9H_{19}SO_3Na$	0.10	0.078	not found
n-$C_8H_{17}SO_3Na$	0.20	0.148	0.14 (without NaCl, [13]), 0.154 (without NaCl, [14])

Table 2. Fractions of the equilibrium concentrations of simulated aggregates with different compositions relative to the overall surfactant concentration in water–salt premicellar solutions of sodium *n*-alkyl sulfonates and sodium *n*-dodecyl sulfate

Surfactant (I, M)	Surfactant concentration range, 10^{-2} M, $n = 6–7$	α_i, %					
		R_2^{2-}	NaR	R_3^{3-}	Na_2R^+	NaR_2^-	Na_2R_2
n-$C_{12}H_{25}SO_4Na$ (0.01)	0.12–0.3	4–**5**	5–2	4–0.5	<0.1	<0.1	<0.1
n-$C_{10}H_{21}SO_3Na$ (0.10)	0.8–2.1	2–**5**	0	0.4–2	0.1–1	1–2	1–2
n-$C_9H_{19}SO_3Na$ (0.10)	3.6–7.3	5–11	16–**17**	3–9	17–14	6–11	7–10
n-$C_8H_{17}SO_3Na$ (0.20)	11–14	0	0	3–5	10–**11**	5–6	5–6

of dimer formation decreases with a reduction in the number of carbon atoms in a surfactant anion and a rise in the ionic strength of the solution, while associates with counterions become the prevalent forms of the premicellar aggregates.

This conclusion was confirmed by a decrease in the equilibrium concentration of the potential-determining monomer relative to the total surfactant concentration near the CMC, with this decrease being observed only in water–salt solutions of SDS and sodium *n*-decyl sulfonate (Fig. 2). The approximation equations for the dependences shown in Fig. 2 have the following forms:

$$[DS^-] = (0.852 \pm 0.008)c(SDS)$$

and

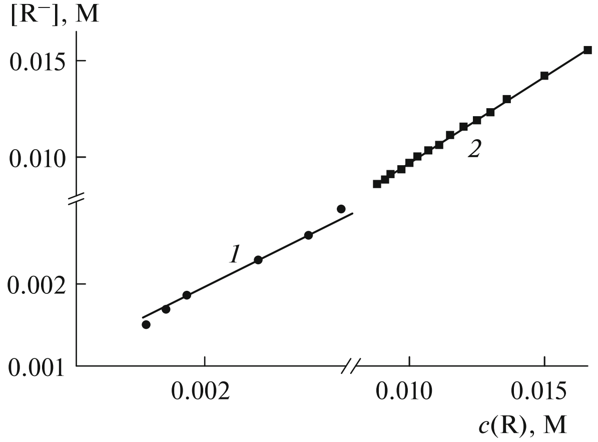

Fig. 2. The equilibrium concentrations of monomer anions as functions of the overall surfactant concentration: (*1*) sodium *n*-dodecyl sulfate ($I = 0.01$ M) and (*2*) sodium *n*-decyl sulfonate ($I = 0.10$ M).

$$[C_{10}H_{21}SO_3^-] = (0.895 \pm 0.004)c(C_{10}H_{21}SO_3Na).$$

A steep slope of a straight line gives grounds to infer that the degree of binding of surfactant anions into dimers is smaller. Hence, the stability constant of the resulting dimers for *n*-decyl sulfonate ions is lower than that for DS^- ions. This fact is supported by the calculated values of the constants (Table 3).

The dimerization constant obtained for DS^- ions in premicellar SDS–NaCl solutions ($I = 0.01$ M) is an order of magnitude lower than those estimated by different methods for "pure" SDS solutions (2.18 [7, 8], 2.50 [1], and 2.32 [9]). This result is in absolute agreement with the ideas about the effect of a background electrolyte (ionic strength of a solution) on a shift in the equilibrium under consideration: increased concentration of Na^+ counterions partially shields the charges of surfactant anions and reduces the degree of anion binding into dimers. The same conclusions were drawn by van Voorst Vader [6], who studied the premicellar aggregation in aqueous SDS solutions in the presence of 0.04 M $NaNO_3$. The stability constant obtained for $(DS)_2^{2-}$ dimers in his study was $K = 10$; i.e., $\log K = 1.0$.

It follows from our data (Table 3) that, as the length of the hydrocarbon radicals in alkyl sulfonates decreases from C_{10} to C_8, the composition of the aggregation product varies; however, the logarithmic the aggregation constants remain close to each other.

It should be noted that the existence of Na_2R^+ species is not impossible, because the formation of Na_2DS^+ ions was recorded in the gas phase by sputtering ionization mass-spectroscopy in the electric field [15]. On the other hand, $Na(DS)_2^-$ ions were also detected in that study. Hence, allowance for these anions in our model is legitimate, although, according

Table 3. Logarithmic stability constants of aggregates in water–salt premicellar solutions of sodium *n*-alkyl sulfonates and sodium *n*-dodecyl sulfate

Surfactant (*I*, M)	Main aggregation product	Equilibrium	log*K*
n-$C_{12}H_{25}OSO_3Na$ (0.01)	R_2^{2-}	$R^- + R^- \rightleftarrows R_2^{2-}$	1.15 ± 0.05
n-$C_{10}H_{21}SO_3Na$ (0.10)	R_2^{2-}	$R^- + R^- \rightleftarrows R_2^{2-}$	0.50 ± 0.05
n-$C_9H_{19}SO_3Na$ (0.10)	NaR	$R^- + Na^+ \rightleftarrows NaR$	0.56 ± 0.01
n-$C_8H_{17}SO_3Na$ (0.20)	Na_2R^+	$R^- + 2Na^+ \rightleftarrows Na_2R^+$	0.49 ± 0.09

to our calculation results, the probability that they are formed in a solution is rather low (Table 2).

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