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Thermodynamics and Structure of Micelles in Aqueous Solutions of Sodium Decyl Sulfate in the Region of the Third Critical Micelle Concentration

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Abstract—Using data on heat capacity of sodium decyl sulfate solutions near the third critical micelle concentration, obtained earlier via high-precision scanning calorimetry, the temperature dependences are calculated for the thermodynamic functions of the corresponding micellar transition and the components of its Gibbs free energy. It is shown that the considered intermicellar transition, interpreted as the micellar shape transforming from cylindrical to lamellar as the concentration grows, occurs at an equilibrium molality of 0.33 and a temperature of 323 K. Correlations between the thermodynamic functions of the transition with structural changes in the micelles and the key micellar parameters are discussed.

Keywords: polymorphic transition, third critical micelle concentration, aggregation numbers and structure of cylindrical and lamellar micelles, components of the Gibbs free energy of transition

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INTRODUCTION

Physical processes related to changes in the micelle structure in ionic surfactant solutions mimic some hard to understand processes that occur in nanosystems (e.g., in biology and medicine) [1]. Among these processes are polymorphic intermicellar transitions. Our earlier studies focusing on the thermodynamics of polymorphic micellar transitions were conducted for diluted solutions of an anionic surfactant, sodium decyl sulfate (SDS), near critical micelle concentrations CMC_{1-2} ($m = 0.12$) and CMC_2 ($m = 0.22$). These CMCs correspond to the transition that occurs upon the asymmetrization of spherical micelles (CMC_{1-2}) and the transition of spheroidal micelles into cylindrical ones (CMC_2) in aqueous SDS solutions [2, 3].

The heat-capacity properties of SDS solutions at higher concentrations ($m = 0.28$ – 0.42) and temperatures (275–363 K) were studied in [4] via adiabatic differential scanning calorimetry. Krafft point T_{Kr} was found to be 280 K. Analysis of typical changes in the abovementioned properties and partial molar heat capacities (PMHCs) in particular allowed identification of regions corresponding to a new micellar transition in SDS solutions that had never been studied before and followed CMC_2 (i.e., at $m = 0.30$ – 0.38 and

293–343 K). Its equilibrium parameters were also identified: CMC_3 ($m = 0.33$) and $T_0 = 323$ K. In accordance with the models that were used, this new transition was interpreted as the shape of micells transforming from cylindrical to lamellar as concentration of the solution rose [5].

SDS is a mesogenic surfactant. According to the phase diagram of an SDS–water system, the nematic hexagonal lyomesophase is formed over a broad range of temperatures (283–353 K) starting with 40 wt % SDS. It is important that transition to the lamellar phase occurs at higher SDS concentrations (≈ 67 wt %); the lamellar phase is known to form from a micellar solution containing aggregates of bilayer lamellar micelles [6]. This is a strong argument in favor of the existence of cylindrical and lamellar micelles in more diluted SDS solutions and their transition occurring gradually as their concentration grows.

In this work, we use calculated PMHC values of SDS in these solutions [4] to determine the temperature dependences of thermodynamic functions of the polymorphic transition corresponding to CMC_3 and the components of its Gibbs free energy, estimate the key parameters of micelles, and discuss correlations with structural changes that occur inside micelles.

EXPERIMENTAL

The heat-capacity properties of SDS solutions with the specified concentrations and temperatures were determined and the respective calculations (including the PMHC values) made in [4]. Data on the substances that were used, how they were purified, the parameters of the SCAL-1 calorimeter that was employed, the experimental conditions and those of calibration, and results from calorimeter testing were also presented in [4].

The way of determining the thermodynamic functions of different transitions in solutions using data on heat capacity [7, 8] was applied earlier to polymorphic transitions in micellar systems [2, 3]. In this approach, the thermodynamic functions of intermicellar transition are calculated using the Kirchhoff, Clausius, and Gibbs–Helmholtz equations, the integral forms of which are written as

$$\Delta H(T) = \Delta H_0 + \int_{T_0}^T \overline{\Delta C_{p2}} dT, \quad (1)$$

$$\Delta S(T) = \Delta H_0/T_0 + \int_{T_0}^T (\overline{\Delta C_{p2}}/T) dT, \quad (2)$$

$$\Delta G(T) = \Delta H_0 - T(\Delta H_0/T_0) + \int_{T_0}^T \overline{\Delta C_{p2}} dT - T \int_{T_0}^T (\overline{\Delta C_{p2}}/T) dT, \quad (3)$$

where T_0 is the temperature of the equilibrium transition; ΔH_0 is the enthalpy of transition at temperature T_0 ; $\Delta H(T)$, $\Delta S(T)$, $\Delta G(T)$ are the partial molar (PM) thermodynamic functions at temperature T ; and $\overline{\Delta C_{p2}}$ is the difference between the PMHC of surfactant molecules in the solution that have aggregated to form micelles of lamellar and cylindrical shapes at identical T , P , and m parameters.

ΔH_0 is calculated by comparing the response signals obtained during temperature scanning in the calibration and working experiments [3, 8]:

$$\Delta H_0 = u_x \delta_k \Delta t \mu_2 / M, \quad (4)$$

where $\delta_k = (P_c/u_c)$ is sensitivity of the calorimeter; P_c is the power of the calibration current; u_x and u_c are response signals of the electric potential in the working and calibration experiments; Δt is the length of calibration; μ_2 is the molar weight of the substance in solution in an operating cell; and M is the weight of the substance. The scan rate was $v = 0.5$ K/min. Calibration at equilibrium transition temperature $T_0 = 323$ K in particular was done with power $P_c = 25 \times 10^3$ nW at $\Delta t = 605.65$ s. Sensitivity δ_k was 33.40279 nW/mV. The parameters of the experiment were SDS concentration $m = 0.33$ at 323 K, solution density $\rho = 1.00098$ g/cm³,

and $M = 0.02668$ g. Response signal u_x (recorded below the baseline) was -10634.0 mV.

Under the equilibrium conditions of the polymorphic transition ($m = 0.33$ and 323 K),

$$\begin{aligned} \Delta H_0 &= -2099.01 \text{ kJ/mol}, \\ \Delta S_0 &= \Delta H_0/T_0 = -6.498 \text{ J/(mol K)}, \\ \Delta G_0 &= 0. \end{aligned} \quad (5)$$

The errors in determining ΔH_0 were actually the instrument bias (identical to the bias in determining specific heat capacities C_p of solutions: $C_p^0 + \delta_k u_x v / M$). It is well known that heat capacity can be determined with high accuracy via the high-precision scanning calorimetry of solutions (the error is no greater than several units to the fourth decimal place). We used specialized WScal software that considered the volume of solvents displaced from the solution. The errors grew substantially for calculations of the $\Delta H(T)$ values and were mainly due to errors in approximating the apparent molar heat capacity needed to calculate PMHC [4]. In this work, the total errors are estimated at 3–5%.

RESULTS AND DISCUSSION

Thermodynamic Functions of the Transition and the Micelle Aggregation Number

From a thermodynamic viewpoint, the extrema on isotherms and isoconcentrates of the PMHC of surfactants $(\partial \overline{C_{p2}}/\partial m)_{p,T} = 0$ and $(\partial \overline{C_{p2}}/\partial T)_{p,m} = 0$. At concentrations greater than CMC_1 (and especially CMC_2), where the intermicellar space contains almost no surfactant ions, all changes that occur as the shape transforms are related to changes in the packing density and architecture of surfactant ions in the surface layer of micelles. When SDS concentration m grows from 0.30 to 0.38, cylindrical micelles can be rearranged into lamellar bilayer micelles with smaller specific surface area a and greater packing density $q = V_c/(al_c)$, where V_c and l_c are the volume and length of the hydrocarbon substituent in the SDS molecule [5].

Figure 1 shows dependence $\overline{C_{p2}}(T)$ of the PMHC of SDS in a solution with equilibrium concentration $m = 0.33$ of transition CMC_3 throughout the considered temperature range, taken from [4]. It was noted earlier that the Krafft point corresponds to the minimum at 280 K.

If we analyze the process of micelle shape transformation at $m = \text{const}$ in the context of elevated temperature, we would expect the packing of the surface layer of micelles to be loosened and a plate–cylinder transition to occur. However, Fig. 1 shows that PMHC $\overline{C_{p2}}$ falls at temperatures above 293 K (the onset of the transition), where 100% of the surface-active SDS ions aggregate into lamellar micelles. The nascent

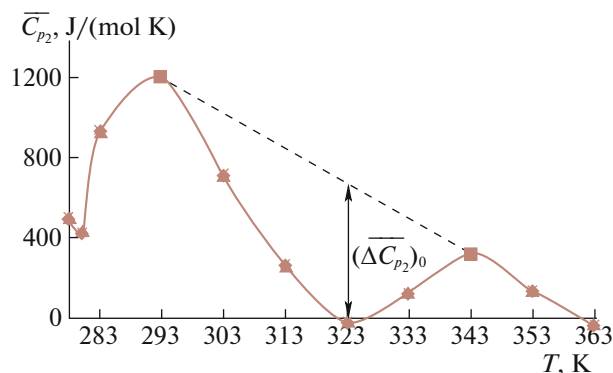


Fig. 1. Temperature dependence of partial molar heat capacity of SDS in a solution with equilibrium concentration $\text{CMC}_3 = 0.33 \text{ mol/kg}$.

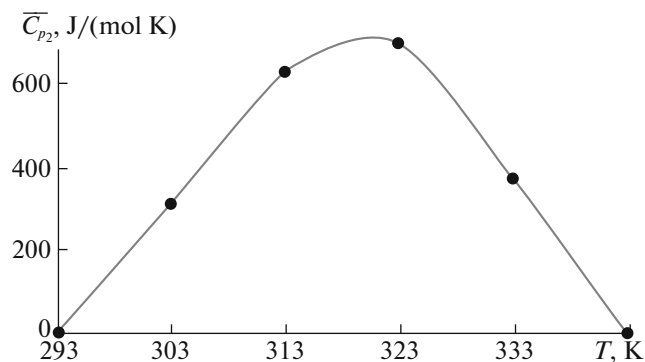


Fig. 2. Temperature dependence of partial molar heat capacity of intermicellar transition in an SDS solution at $\text{CMC}_3 = 0.33 \text{ mol/kg}$.

micelles with cylindrical surfaces are therefore more densely packed. At the end of the transition (343 K), all surface-active SDS ions have aggregated into cylindrical micelles. At the equilibrium point ($T_0 = 323 \text{ K}$), equal percentages of these ions aggregate into micelles of both shapes. The solution now contains, in addition to negatively charged micelles, only a small percentage of free Na^+ ions: $(1 - \beta) = (1 - N/n)$, where n is the aggregation number of surfactant ions in a micelle; N is the number of counterions; and β is the degree of counterion bonding.

The $\Delta\overline{Cp}_2(T)$ values are determined from Fig. 1 according to the y -coordinates between experimental curve $\overline{Cp}_2(T)$ and the dashed line drawn from the point where the transition starts (293 K) to the point where it ends (343 K) [4, 5]. This extrapolation $(\overline{Cp}_2)_0 = 6341.31 - 17.55T$ represents the hypothetical PMHC that SDS molecules aggregated into plate-like micelles would have if there were no transition-related processes. Of course, it is the additivity of PMHC that is meant.

The extrapolation is the baseline of PMHC scanning; it is in our case negatively sloped, as opposed to other studied intermicellar transitions in SDS solutions (CMC_{1-2} and CMC_2) [2, 3]. As already noted, this means the PMHC of SDS molecules in cylindrical micelles at the margins of transition is almost 300% lower than in lamellar micelles: $\overline{Cp}_2(343 \text{ K})/\overline{Cp}_2(293 \text{ K}) = 0.27$ (Fig. 1). This happens even though the landing area in a cylindrical micelle is twice that in a lamellar micelle ($a_{\text{cyl}} > a_{\text{lam}}$; $n_{\text{cyl}} < n_{\text{lam}}$), according to the packing equation in [9]. The surface architecture of micelles when their shape is rearranged presumably depends not only on surfactant ions but on the layer of counterions as well (the Stern layer). This layer must be dense and planar for lamellar micelles, and rarefied and uneven for the distorted cylindrical surface: Na^+ ions can be partially incorporated into the voids between the head sulfate groups of surfactant

ions, and thus sterically hinder ion mobility. This is accompanied by changes in the interionic distance, the thickness of the electrical double layer (EDL), and the number of water molecules; and thus the redistribution of the competing contributions of hydrophobic and electrostatic energies.

Figure 2 shows the temperature dependence of PMHC transition $\Delta\overline{Cp}_2(T)$ at CMC_3 $m = 0.33$. The area under the curve is the characteristic heat effect of the process,

$$\int_{T_i}^{T_f} \Delta\overline{Cp}_2(T) dT = [\Delta H]_{T_f}^{T_i} = \Delta H(T_i) - \Delta H(T_f) \quad (6)$$

and is equal to 20.090 kJ/mol. Here, $T_i = 293 \text{ K}$ and $T_f = 343 \text{ K}$ are the temperatures of the initial and final transition. The area under curve $\overline{Cp}_2(T)$ lies below the PMHC baseline (Fig. 1), $\overline{Cp}_2(343 \text{ K}) < \overline{Cp}_2(293 \text{ K})$, so the characteristic enthalpy of the process is negative.

Integrals (1)–(3) were calculated without approximating the corresponding subintegral functions using the mean value theorem. The mean value of the subintegral function was calculated as that of a quadratic function on each integration interval. The superiority of this approach was demonstrated in [10].

Thermodynamic functions $\Delta H(T)$, $\Delta S(T)$, and $\Delta G(T)$ of the transition are shown in Fig. 3. The enthalpy and entropy of the transition behave symbatically. Exothermicity declines (energy is absorbed) and entropy grows along with temperature. The fraction of surface-active SDS ions aggregated into lamellar micelles predominates during the first part of the transition (293–323 K). These ions are more thermodynamically stable: more cylindrical micelles are destroyed, and the exothermicity of the process ($\Delta H = -14.92 \text{ kJ/mol}$; $T\Delta S = -13.9 \text{ kJ/mol}$ at 293 K) wins the competition for negative ΔG . In contrast, the entropy factor makes a slightly greater contribution to

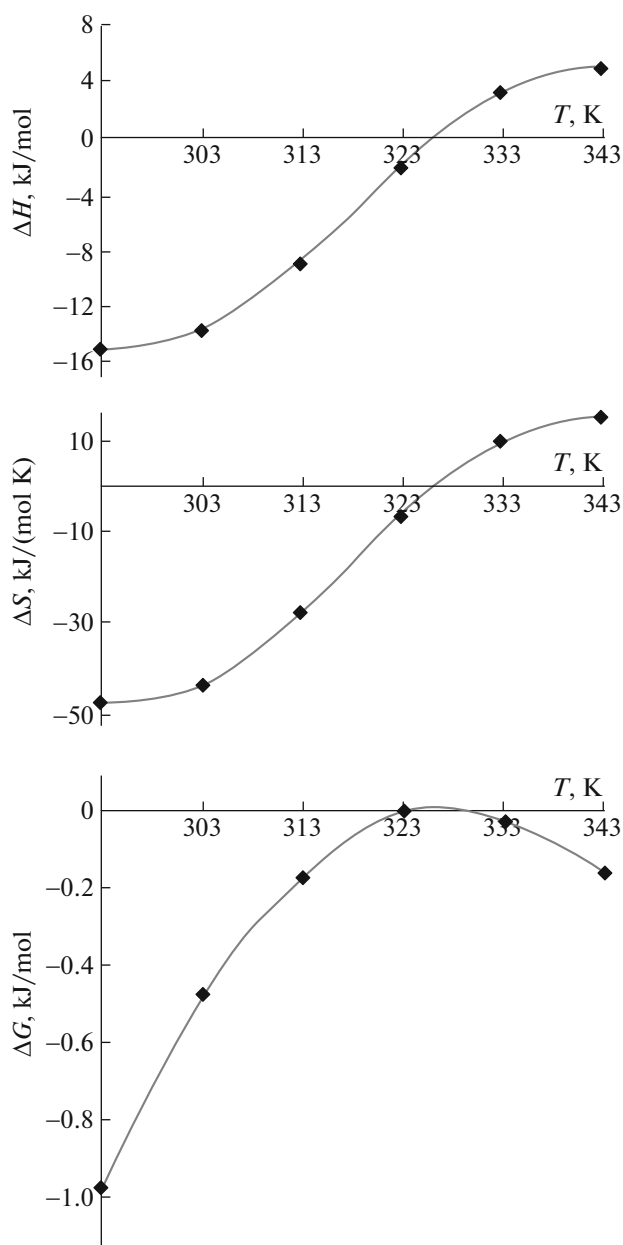


Fig. 3. Temperature dependences of the thermodynamic functions of the intermicellar transition in an SDS solution at $\text{CMC}_3 = 0.33 \text{ mol/kg}$.

ΔG during the second part of the process (323–343 K), and ΔH and ΔS become positively charged ($T\Delta S = 5.26 \text{ kJ/mol}$, $\Delta H = 5.10 \text{ kJ/mol}$ at 343 K). We can see from Figs. 2 and 3 that at equilibrium temperature $T_0 = 323 \text{ K}$, $(\partial\Delta\bar{C}p_2/\partial T)_{p,m} = (\partial^2\Delta H(T)/\partial T^2)_{p,m} = 0$. At this point, there is a kink on isoconcentrate $\Delta H(T)$ (Fig. 3) and $\partial\Delta G(T)/\partial T)_{p,m} = 0$. However, the condition of equilibrium $\Delta S = 0$ that is typical of isolated systems is in this case not met, though the entropy is low:

$\Delta S(323 \text{ K}) \approx -6.5 \text{ J/(mol K)}$. When temperature is varied from 293 to 343 K (using the denotation in formula (6)), the integral thermodynamic functions of transition are $[\Delta H]_{T_f}^{T_i} = -20.094 \text{ kJ/mol}$, $[T\Delta S]_{T_f}^{T_i} = -19.176 \text{ kJ/mol}$, $[\Delta S]_{T_f}^{T_i} = -0.0322 \text{ kJ/(mol K)}$, and $[\Delta G]_{T_f}^{T_i} = -0.918 \text{ kJ/mol}$. In other words, the energy factor is only 5% greater than the decline in the entropy factor.

It has been repeatedly shown that in the quasi-chemical approach, a monomolecular reversible reaction can be used to model the rearrangement of micellar structure and shape [5, 11, 12]. When the corresponding standard state and near-unity degree of micellization of a micellar solution are chosen, equilibrium constant K_c depends only on the concentration of surfactant ions in a micelle: $K_c = C_{\text{cyl}}/C_{\text{lam}}$, $C_{\text{cyl}} + C_{\text{lam}} = \text{CMC}_3$.

Since the work done to transfer surfactant ions from micelles with one shape to micelles of a different shape ($P, T = \text{const}$) is described by the isotherm equation, the correlation between the aggregation number n of surfactant ions in a micelle and K_c and ΔG can be established using the equation

$$n = -\ln K_c / (\Delta G / RT). \quad (7)$$

The varying intensity of the transfer of surfactant ions as the temperature rises suggests that the n values in formula (7) differ. As already noted, the transfer of surfactant ions from a cylindrical micelle to a lamellar one (n_1) proceeds mostly at the first stage, while the opposite process occurs during the second stage (n_2). The sum of these two values yields aggregation number n_{lam} for a lamellar micelle; the difference between these values yields aggregation number n_{cyl} for a cylindrical micelle.

Equilibrium constants $K_c(T)$ were calculated in [4], so the mean values of the state function of the micellar systems (the aggregation numbers n) can be determined using Eq. (7) when the ΔG value is known. Analysis of these data shows the linearity of function $\ln K_c((\Delta G/RT))$ is maintained with an error of $\leq 5\%$. It is therefore fair to say that $n_1 = 10$ and $n_2 = 73$. Then $n_{\text{lam}} = 83$ and $n_{\text{cyl}} = 63$.

Changes in Micelle Structure and the Degree of Counterion Bonding

In what follows, we use the familiar droplet model of a direct ionic micelle and the packing equations in [9, 11, 12]. The parameters of the linear hydrocarbon chain of an SDS molecule are well known [13]. Chain length and volume are $l_c = 14.15 \text{ \AA}$ and $V_c = 296.40 \text{ \AA}^3$; the cross-section area of the substituent and its diameter are $a_c = (V_c/l_c) = 20.95 \text{ \AA}^2$ and $d_c = 5.16 \text{ \AA}$, respectively.

Specific (landing) surface area $a = S/n$ (where S is the surface area of the micellar nucleus) is the key parameter in the packing of the head parts of surfactant ions in a micelle. According to the packing equation in [9], $a_{\text{lam}}/a_c = 1$ for a lamellar micelle and $a_{\text{cyl}}/a_c = 2$ for a cylindrical one. The volume of a micelle nucleus is $V_{\text{lam}} = n_{\text{lam}}V_c$, $V_{\text{cyl}} = n_{\text{cyl}}V_c$, $(V_{\text{lam}}/V_{\text{cyl}}) = (n_{\text{lam}}/n_{\text{cyl}}) = 1.32$. The lateral surface area of micelle nuclei depends on the ratio between landing surface area a and cross-section area a_{head} of the head part of a surfactant ion. When $a_{\text{head}} \leq a$, $S = na$; when $a_{\text{head}} > a$, $S = na_{\text{head}}$. Since no data were available, the size of the head part of a surface-active ion of an SDS molecule was assumed to be equal to the size of a sulfate ion with radius $r_{\text{head}} = 2.3 \text{ \AA}$ in solution [14]; $a_{\text{head}} = 16.62 \text{ \AA}^2 < a_c$. The areas of both lamellae of a micelle are then $S_{\text{lam}} = n_{\text{lam}}a_c$, $S_{\text{cyl}} = 2n_{\text{cyl}}a_c$, and $S_{\text{lam}}/S_{\text{cyl}} = n_{\text{lam}}/2n_{\text{cyl}} = 0.66$. It is clear that $V_{\text{lam}}/V_{\text{cyl}} = 2S_{\text{lam}}/S_{\text{cyl}}$.

Diameter d_{lam} of a lamellar micelle is $\sqrt{2n_{\text{lam}}a_c/\pi} = 33.27 \text{ \AA}$. The maximum thickness of the nucleus of a lamellar micelle is equal to the maximum diameter of the cross section of a cylindrical micelle: $h_{\text{lam max}} = d_{\text{cyl max}} = 2l_c$. Length l_{cyl} of a cylindrical micelle is $V_{\text{cyl}}/\pi l_c^2 = n_{\text{cyl}}a_c/\pi l_c = 29.69 \text{ \AA}$, which is close to the diameter of a lamellar micelle. Note that l_c is the maximum radius of the base of the cylinder. If this radius is equal to $0.9l_c$, then $l_{\text{cyl}} = d_{\text{lam}}$. This is to be expected, according to the generally accepted concept of comparing the two micelle shapes.

In addition to aggregation numbers n and specific surface areas a , degree β of counterion bonding is also a variable of the state of a micellar system. The degree of counterion bonding depends on the concentration, temperature, and permittivity in the surface and diffuse parts of an EDL [15]. However, the maximum value of β for a lamellar micelle can be estimated by assuming that hydrated Na^+ counterions form a dense layer on its surface. We assume the diameter of a hydrated Na^+ ion d_{counter} to be 5.5 \AA [11], and surface a_{counter} of its central cross section to be 23.76 \AA^2 . Number N_{lam} of the counterions is $S_{\text{lam}}/a_{\text{counter}} = n_{\text{lam}}a_c/a_{\text{counter}} = 73$. The degree β_{lam} of counterion bonding is $a_{\text{lam}}/a_{\text{counter}} = a_c/a_{\text{counter}} = N_{\text{lam}}/n_{\text{lam}} = 0.88$. The minimum EDL density on the surface of a single lamella can be written as the sum of the hydrated radii of a counterion and the head part of a surfactant ion: $\delta_{\text{lam}} = r_{\text{counter}} + r_{\text{head}} = 5.05 \text{ \AA}$.

It should be noted that the surface-active head parts on the surface of the nucleus of a lamellar micelle are distributed uniformly but still rather loosely. If $d_{\text{head}} = 2r_{\text{head}} = 4.6 \text{ \AA}$ and $d_c = 5.16 \text{ \AA}$, the average distance between the surface-active heads is $(d_c - d_{\text{head}}) = 0.56 \text{ \AA}$. Of course, neither counterions nor water molecules can penetrate into this void, but nothing prevents the sulfate heads from acquiring additional

degrees of freedom. The free surface of the distorted surface of the nucleus of a cylindrical micelle between sulfate groups ($a_{\text{cyl}} \approx 2a_c$) allows counterions to be partially dragged into these free surface voids, due mainly to hydrophobic interactions. This approach can also be used here to estimate β_{cyl} . Let us assume that C_{counter} is the bulk concentration of counterions in the intermicellar space of a solution and C is the total concentration. At equilibrium concentration CMC_3 , $m = 0.33 = 11.4 \text{ CMC}_1$, degree of micellization α tends to unity and $C_{\text{counter}} = (1 - \beta)C$. It is clear that inequality [11] is a condition of there being no bonding between ion–micelle pairs in a solution of I–I surfactant electrolyte:

$$(1 - \beta)ne^2 / (4\pi\epsilon_0\epsilon\bar{r}kT) \leq 1 \quad \text{and at the limit} \quad (8)$$

$$(1 - \beta) \approx 4\pi\epsilon_0\epsilon\bar{r}kT / ne^2,$$

where ϵ_0 is the vacuum permittivity; ϵ is the static permittivity of the solution; $\bar{r} = (C_{\text{counter}} + C_m)^{-1/3}$ is the average distance between ions, including micelles; and $C_m = C/n$ is the bulk concentration of micelles. When $\text{CMC}_3 = \text{const}$, the \bar{r} value remains virtually the same. If $T_{\text{melt}} = 293 \text{ K}$ and $T_{\text{cyl}} = 343 \text{ K}$, allowance should also be made for function $\epsilon(T)$.

Formula (8) is, of course, not used for calculations, but the relation

$$\frac{1 - \beta_{\text{lam}}}{1 - \beta_{\text{cyl}}} \approx \frac{T_{\text{lam}}\epsilon_{\text{lam}}n_{\text{cyl}}}{T_{\text{cyl}}\epsilon_{\text{cyl}}n_{\text{lam}}} \quad (9)$$

should yield a reliable estimate.

For aqueous solutions, we use the familiar empirical equation [16]

$$\epsilon(t) = 78.803[1 - 4.54 \times 10^{-3}(t - 25) + 9.0 \times 10^{-6}(t - 25)^2], \quad (10)$$

which yields $\epsilon_{\text{lam}}(293 \text{ K}) = 80.08$, $\epsilon_{\text{cyl}}(343 \text{ K}) = 62.31$. Assuming $(1 - \beta_{\text{lam}}) = 0.12$, we find that $(1 - \beta_{\text{cyl}}) = 0.15$ and $\beta_{\text{cyl}} = 0.85$, while $N_{\text{cyl}} = \beta_{\text{cyl}}n_{\text{cyl}} \approx 54$.

Let us estimate the density of ionic packing in the EDL on the surface of a cylindrical micelle. In the average parameters of the structure, the distances between the heads ($2d_c - d_{\text{head}}$) are greater than d_{counter} by only 0.2 \AA , and free surface area $(2a_c - a_{\text{head}})n_{\text{cyl}}/N = (2a_c - a_{\text{head}})/\beta_{\text{cyl}}$ of the nucleus per counterion (the void surface area) is greater than a_{counter} by 6 \AA^2 . Void volume $(2a_c - a_{\text{head}})d_{\text{head}}/\beta_{\text{cyl}}$ is greater than V_{counter} by 50 \AA^3 , but $d_{\text{counter}} > d_{\text{head}}$, so the hydrated Na^+ counterion is only partially dragged into the void with the calculated surface area, volume, and height d_{head} . Simple calculations show that the surface layer of a cylindrical micelle is most densely packed with polar heads, counterions, and water molecules if each void contains four water molecules and is filled by 89% of the volume of a hydrated Na^+ ion. Segments of the Na^+ ion's

sphere $\sim 1.1 \text{ \AA}$ high will lie below the layer of the head parts of surface-active ions and at least the diameter of water molecule will be added to the thickness of the EDL: $\delta_{\text{cyl}} = r_{\text{counter}} - r_{\text{head}} + d_{\text{H}_2\text{O}} = 3.5 \text{ \AA}$.

Components of the Gibbs Free Energy of an Intermicellar Transition

The electrostatic energies of the EDL on the surface of a micelle with two different shapes can be compared (when β is near unity) using models of planar and cylindrical capacitors. Suitable models must be compared: only one EDL of a planar bilayer micelle whose diameter is equal to the length of a cylindrical micelle ($d_{\text{lam}} \approx l_{\text{cyl}}$) should be used. The β_{lam} and β_{cyl} values are not equal to unity, so the half-sums of the energies of interaction generated by charges from each lamella must be added to determine the capacitor energy (when calculating the capacitor energy, we must use product $q_1 q_2 = n^2 e^2 \beta$ instead of squared charge) [17]. The expression for determining the energy of ions in a planar capacitor is well known [17]; for a lamellar micelle, it can be written as

$$\begin{aligned} W_{\text{lam}} &\approx e^2 (n_{\text{lam}}/2)^2 \beta_{\text{lam}} \delta_{\text{lam}} / 2 \epsilon_0 \epsilon'_{\text{lam}} S_{\text{lam}} \\ &= -e^2 n_{\text{lam}}^2 \beta_{\text{lam}} \delta_{\text{lam}} / 2 \epsilon_0 \epsilon'_{\text{lam}} S_{\text{lam}} \quad (11) \\ &= e^2 n_{\text{lam}}^2 \beta_{\text{lam}} \delta_{\text{lam}} / 2 \epsilon_0 \epsilon'_{\text{lam}} \pi l'_{\text{cyl}}. \end{aligned}$$

In light of the relations presented above, the capacity and energy of a cylindrical capacitor are

$$\begin{aligned} C_{\text{cyl}} &= 2\pi \epsilon_0 \epsilon'_{\text{cyl}} l_{\text{cyl}} / \ln(l_1/l_2), \quad (12) \\ W_{\text{cyl}} &= e^2 n_{\text{cyl}}^2 \beta_{\text{cyl}} \ln(l_1/l_2) / 4\pi \epsilon_0 \epsilon'_{\text{cyl}} l_{\text{cyl}}. \end{aligned}$$

In formulas (11) and (12), ϵ'_{lam} and ϵ'_{cyl} are the permittivities in the respective EDLs. It is known that in the first (dense) layer of the hydration shell of an ion, where dielectric saturation is achieved, the value of $\epsilon' \approx 2$ and virtually independent of concentration and temperature [18]; $l_1 = l_c + r_{\text{head}}$ and $l_2 = l_1 + \delta_{\text{cyl}}$ are the radii of the inner (l_1) and outer (l_2) cylinders of the capacitor. The formula

$$W_{\text{lam}}/W_{\text{cyl}} = 2n_{\text{lam}}^2 \beta_{\text{lam}} \delta_{\text{lam}} / (n_{\text{cyl}}^2 \beta_{\text{cyl}} l_{\text{cyl}} \ln(l_1/l_2)) \quad (13)$$

gives the ratio between the potentials in the EDLs of the corresponding micelles. This ratio is 3.02. When recalculated per mole of SDS in both micelles, the ratio is 1.74. When $\epsilon'_{\text{lam}} \approx \epsilon'_{\text{cyl}} \approx 2$, formulas (11) and (12), recalculated per mole of SDS and in reduced form, yield $W'_{\text{lam}} = 6.86 \text{ kJ/mol} = 2.56RT_0$ and $W'_{\text{cyl}} = 3.94 \text{ kJ/mol} = 1.47RT_0$. The electrostatic component of the Gibbs free energy thus falls by 174% and by $\Delta W' = W'_{\text{cyl}} - W'_{\text{lam}} = -2.92 \text{ kJ/mol} = -1.09RT_0$.

Specific adsorption forces of the interaction between counterions and a micellar nucleus contribute substan-

tially to the formation of EDLs on the surfaces of ionic micelles. Us'yarov [15] obtained an expression for adsorption potential ϕ_{ad} , normalized to the Boltzmann factor and related to electrostatic potential ϕ_{el} of an EDL: $\phi_{\text{ad}} = -\phi_{\text{el}} - \ln(\beta/V_0 C_{\text{counter}}(1-\beta))$, where V_0 is the molar volume of the solvent, and C_{counter} is the molar concentration of counterions in the solution. The expression for changes ΔA in the potential energy of adsorption during the lamella–cylinder intermicellar transition is easily derived using the formula

$$\Delta A/RT_0 = -\Delta W'/RT_0 + \ln(\beta_{\text{lam}}(1-\beta_{\text{cyl}})/\beta_{\text{cyl}}(1-\beta_{\text{lam}})). \quad (14)$$

Calculations yield $\Delta A/RT_0 = -0.82 \text{ kJ/mol}$, where $\Delta A = -2.21 \text{ kJ/mol}$.

If the changes in potential energy related to variation in the number of water molecules in an EDL are considered hydrophobic interactions, then $\Delta G_0(323 \text{ K}) = 0 = \Delta W' + \Delta A + \Delta E$ at the equilibrium point of the transition, where ΔE is the change in the hydrophobic component of the Gibbs free energy of the transition. It follows that $\Delta E/RT_0 = 1.91$ and $\Delta E = 5.13 \text{ kJ/mol}$. The $\Delta E : \Delta W' : \Delta A$ ratio between changes in the hydrophobic, electrostatic, and adsorption components of the Gibbs free energy of the transition is 50 : 28.3 : 21.7%. The electrostatic and adsorption components of the Gibbs free energy diminish, while the hydrophobic component grows when the polymorphic transition is viewed in the context of increasing temperature.

CONCLUSIONS

The thermodynamic functions, the components of Gibbs free energy, and the micellar parameters and structural changes that occur in micelles during intermicellar polymorphic transition corresponding to $\text{CMC}_3 = m = 0.33$ in aqueous SDS solutions were determined. Under conditions where the temperature is increased (293–343 K) with equilibrium temperature $T_0 = 323 \text{ K}$, this lamella–cylinder transition is characterized by denser packing of the surface of a cylindrical micelle, due to the incorporation of counterions; a drop in the β and n values; enhancement of hydrophobic bonding; and reduction of the electrostatic and adsorption energies in the EDL. These results are based on experimental thermodynamic studies (particularly high-precision scanning calorimetry).

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