

CHAPTER-III

Study of Micellization Properties of Lithium Dodecyl Sulfate in Aqueous Solutions from Conductivity, Density, and Adiabatic Compressibility Measurements

INTRODUCTION

Self-association of hydrophobic molecules generally is of great importance for many physiological molecules, food constituents and drugs. More recently, surfactants have been the subject of intense investigation due to their wide industrial and technological applications. The micellization of surfactants above a critical concentration (called the critical micelle concentration, *cmc*) is an important solution property which needs evaluation to know the existence of micelle in solution and to obtain the thermodynamic parameters associated with the process which are essential for characterization and comparison in the light of spontaneity and stability^{1, 2}. Though, many investigations have been done on sodium dodecylsulfate (SDS)³⁻¹⁰, but much is not known about micellar behavior of lithium dodecylsulfate (LDS) at different temperatures.

The results on conductometric, densitometric, and interferometric measurements on aqueous solutions of lithium dodecylsulfate at different temperatures are reported here. Among these measurements, densitometric and interferometric measurements were never considered in the past for the evaluation of micellar properties of LDS. From the experimental data, the ionization degree of micelle, α , free energy of micellization, ΔG_m° , standard enthalpy of micellization, ΔH_m° , standard entropy of micellization ΔS_m° , apparent molar volume, and apparent molar adiabatic compressibility were calculated. These parameters provide useful information regarding the solution behavior of lithium dodecylsulfate in aqueous solutions.

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EXPERIMENTAL

Materials and Methods

Lithium dodecylsulfate (E. Merck, Germany) was used as received. Doubly distilled water (specific conductance, 2-3 $\mu\text{S cm}^{-1}$) was used in all preparations. Measurements were made at each temperature in a thermostated water-bath maintained within ± 0.01 K.

The conductometric measurements were carried out on a Pye-Unicam PW9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{-1} and having an accuracy of 0.1%. Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities. Corrections were made for the specific conductance of water at all temperatures.

Densities were measured with an Ostwald-Sprengel type pycnometer of about 25 mL capacity and an internal diameter of the capillary of about 1 mm. Uncertainties in the solute concentration and weighing can produce errors in the density values of *ca.* $5 \times 10^{-5} \text{ g cm}^{-3}$.

Sound velocities were measured using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the cell by a circulating pump. The details of these procedures have been described in Chapter II.

RESULTS AND DISCUSSION

Conductivity results:

The variations of the specific conductivity of LDS solutions with the molality of LDS at various temperatures are shown in Fig. 1. An approximate value of the ionization degree of micelles, $\alpha = S_2/S_1$, was determined from the ratio of the mean gradients of the specific conductivity (κ) vs. concentration plots above (S_2) and below (S_1) the *cmc*¹¹⁻¹⁵.

According to the charged phase separation model of micellization, the activity of the monomer remains constant above *cmc*, and the standard free energy of

micellization per mole of monomer, ΔG_m^0 , can be calculated from the following relation¹⁶:

$$\Delta G_m^0 = (2 - \alpha) RT \ln X_{cmc} \quad (1)$$

where X_{cmc} is the value of cmc expressed in mole fraction. The standard enthalpy, ΔH_m^0 , and entropy, ΔS_m^0 , of micellization were obtained, on the assumption that α is practically constant (Table 1). Insertion of Eq. 1 into the Gibbs-Helmholtz equation gives the following relations^{17, 18}:

$$\Delta H_m^0 = -(2 - \alpha) RT^2 \left(\frac{\partial \ln X_{cmc}}{\partial T} \right)_p \quad (2)$$

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (3)$$

The value of $(\partial \ln X_{cmc} / \partial T)_p$ was determined by fitting the $\ln X_{cmc}$ vs. T data with the polynomial function

$$\ln X_{cmc} = a + bT + cT^2 \quad (4)$$

The values of the fitting constants were $a = 4.33464$, $b = -.08681$, and $c = 1.44288 \times 10^{-4}$. The temperature dependent values of cmc obtained from different measurements, α and the thermodynamic parameters at different temperatures are presented in Table 1.

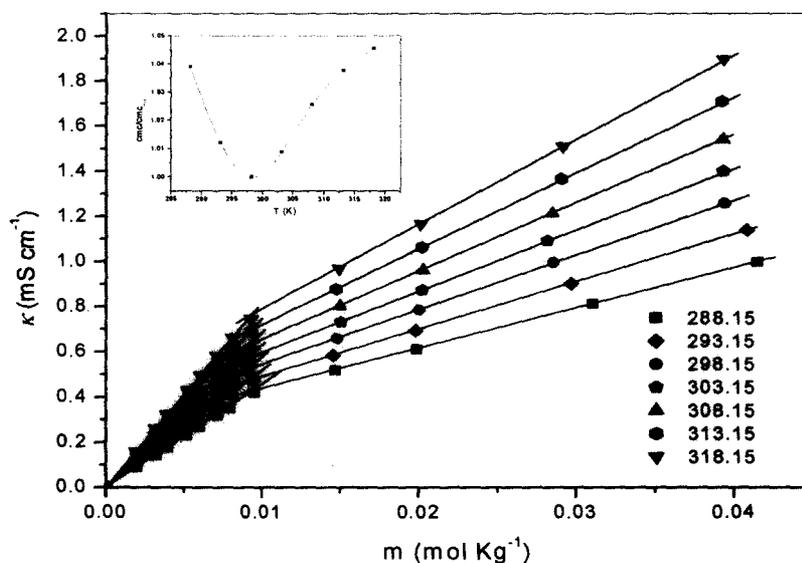


Figure 1. Dependence of specific conductivity of LDS on molality at various temperatures (The plot of dependence of cmc on temperature is displayed in the inset).

The *cmc* value of aqueous LDS at 298.15 K determined conductometrically is in good agreement with that reported earlier⁴. The temperature dependence of *cmc* for LDS is illustrated in the inset of Fig. 1, where a shallow minimum at around 298.42 K is observed.

The values of the degree of ionization, α , of micelles of LDS increases with temperature as found earlier for cationic surfactants^{12, 19}. The higher values of the degree of ionization of LDS can be explained qualitatively in terms of larger size of the hydrated Li^+ ion which cannot approach the highly charged surface of micelle. However, the value obtained at 298.15 K is much higher than those reported earlier^{4, 20}. The mean value of $\Delta\alpha/\Delta T$ estimated in the temperature range 288.15 to 318.15 K amounts to 0.0014 K^{-1} for LDS. This value is low compared with those found earlier for other cationic surfactants: dodecyldimethylbenzylammonium chloride (0.0030)²¹, tetradecyltrimethylammonium bromide (0.0030)²² and tetradecyldimethylphenylammonium bromide (0.0029)²³.

Analysis of the thermodynamic parameters of micellization indicates that the aggregation of LDS is driven mainly by the positive ΔS° . Similar changes from entropic to enthalpic micellization with the rise of temperature have been noted with many different surfactants^{18, 24-26}. The standard free energies of micellization for LDS decrease linearly with temperature. The slow rate of decrease of ΔG_m° with the rise of temperature is typical for aqueous solutions of surfactants and this results from an entropy-enthalpy compensation effect²⁷⁻³¹. Positive values of ΔH_m° , such as those noted at the lowest temperatures, are generally attributed to the release of structural water from the hydration layers around the hydrophobic parts of the micelle³². Such hydrophobic interactions become increasingly insignificant with the partial breakdown of the structure of water as the temperature is increased. The negative ΔH_m° values at the higher temperatures suggest the importance of the London-dispersion interactions as an attractive force contribution for micellization³³. However, it may be seen from Table 1 that at a certain temperature the enthalpy of micellization vanishes and the process is driven solely entropically. This is a direct consequence of Eq. 2 only when the temperature dependence of α is neglected.

Density studies:

Density (ρ) measurements of aqueous solutions of LDS are presented in Fig. 2 in the form of plots of $(\rho - \rho_0)$ vs. the molality of LDS, ρ_0 being the density of water at the appropriate temperature. It is seen that in both pre- and postmicellar regions studied, the densities increase linearly with the increase of molality.

The apparent molar volumes, V_ϕ of LDS as a function of molality at the temperatures studied were obtained using the following Eq. 5³¹ :

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \quad (5)$$

where M and m are the molecular mass and the molality of the solute, respectively. The variation of V_ϕ with reciprocal molality is illustrated in Fig. 3. It can be seen that the apparent molar volumes remain almost constant in the lower concentration region followed by a sharp increase beyond cmc .

For an ionic surfactant system below cmc , the dependence of density on concentration can be expressed as²¹

$$(\rho - \rho_0)10^3 = [(M_f + M_c) - (V_f + V_c)\rho_0]m \quad (6)$$

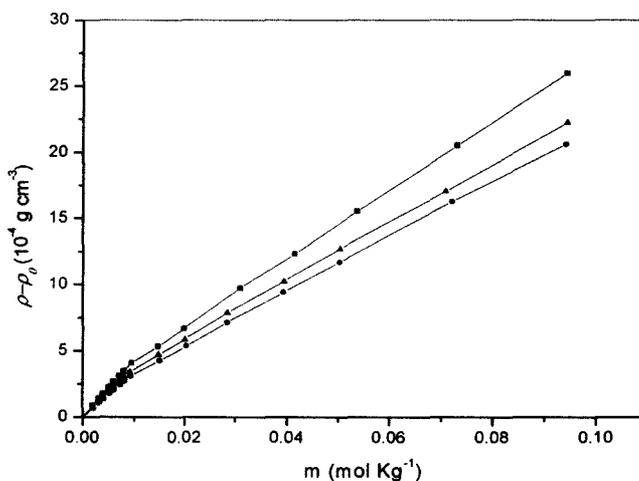


Figure 2. Density vs. molality plot for LDS at 288.15(■), 298.15(▲), and 308.15 (●) K.

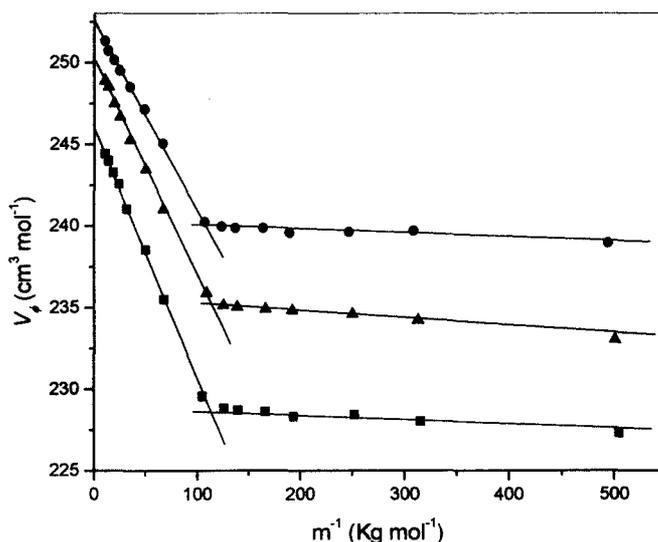


Figure 3. Variation of V_ϕ with reciprocal molality for LDS at various temperatures (Symbols as in Figure 1).

where M_f , V_f and M_c , V_c are the molecular masses and the apparent molar volumes of the surfactant ions and counter ions, respectively. If these apparent molar volumes were negligibly concentration-dependent, then Eq. 6 predicts a linear relationship between density and concentration. Indeed, such a behavior is seen in Fig. 2. The values for $(V_f + V_c)$ thus estimated amount to 229.23 ± 0.26 , 235.60 ± 0.24 and 240.44 ± 0.34 $\text{cm}^3 \text{mol}^{-1}$ at 288.15, 298.15 and 308.15 K, respectively. These values can be taken as zero-order approximation of the accurate values as it is well known that the apparent molar volumes are, in general, concentration-dependent. The observed increase in $(V_f + V_c)$ term with temperature is related to the relaxation of structured water engaged in the solvation of the hydrocarbon chain, the head group, and the counter ion. A similar behavior has also been reported for decylbenzylidimethyl chloride³⁴ and dodecylbenzylidimethyl chloride solutions²¹.

Since it is generally accepted that the solutions of surfactants in the premicellar region behave as singly dispersed system, the V_ϕ values may be described by³⁵

$$V_\phi = V_\phi^0 + A_v m^{1/2} + B_v m \quad (7)$$

where V_ϕ^0 is the value of apparent molar volume at infinite dilution, A_v is the Debye Hückel limiting slope and B_v is an adjustable parameter, which measures the

deviations from the limiting law. For 1:1 electrolytes at 288.15, 298.15 and 308.15 K, the values of A_v are 1.696, 1.865 and 2.04 $\text{cm}^3\text{kg}^{1/2}\text{mol}^{-3/2}$, respectively. Experimental values of V_ϕ in the premicellar region were fitted to Eq. 7 and the values of V_ϕ° obtained are listed in Table 2. The V_ϕ° values for LDS increase almost linearly with temperature in conformity with the observations for other surfactant systems^{21 36}

Assuming the rule of additivity for the apparent molar volumes of the ions in the system to be valid, we can write

$$n_{\text{LDS}} V_\phi = n_f V_f + n_c V_c + n_m V_m \quad (8)$$

where V_m is the apparent molar volume of the micelles in the system and n_{LDS} the total number of moles of the surfactant, whereas n_f , n_c and n_m are the number of moles of free monomers, free counterions, and micelles, respectively. Since LDS is a 1:1 electrolyte, then, according to the pseudo-phase separation model below cmc :

$$m_f = m_c = m \quad (9a)$$

and above cmc ²⁴ :

$$m_f = cmc$$

$$m_c = cmc + \alpha(m - cmc) \quad (9b)$$

$$m_m = \frac{m - cmc}{N_{\text{agg}}}$$

where N_{agg} is the aggregation number of the micelle. Dividing Eq. 8 by the mass of the solvent (in kg) and taking into account the relations in Eq. 9, we obtain the following set of equations²¹

$$V_\phi = (V_f + V_c) \quad m \leq cmc \quad (10a)$$

$$V_\phi = (V_m/N_{\text{agg}} + \alpha V_c) - [V_m/N_{\text{agg}} + (\alpha - 1) V_c - V_f] cmc/m \quad m \geq cmc \quad (10b)$$

If we assume that the molar volumes of the ionic species are not concentration-dependent, then, from the last equation a linear decrease of V_ϕ versus $1/m$ plot can be expected in the concentration range above cmc . According to Eq. 10a, the value of V_ϕ should be constant in the concentration range below cmc . Such a plot is shown in Fig.3. It can be seen that the system conforms approximately to the expected behavior. Thus, Eq. 10 may be considered as an acceptable approximation of the behavior of the system. We can assign the intersection of the lines above and below cmc as the corresponding cmc . The values obtained at 288.15, 298.15, and 308.15 K from conductometry and interferrometry, agree very well (*cf.* Table 1).

Linear fitting of the points in the $cmc/m \leq 1$ region allows us to obtain the value of the apparent molar volume, V_ϕ^{cmc} , (intercept + slope) of the surfactant at cmc , and the change in the apparent molar volume upon micellization, ΔV_ϕ^{cmc} (slope). The results are shown in Table 2. The deviation of about 0.25 to $0.35 \text{ cm}^3 \text{ mol}^{-1}$ between the values of V_ϕ^{cmc} obtained by applying Eq. 10b (for data above cmc) with corresponding values of $(V_f + V_c)$ obtained via Eq. 6 (for data below cmc) can be taken as a measure of the error in the results. The values of V_ϕ^{cmc} for LDS are found to be positive. A similar observation was also reported earlier for other surfactant system.^{34,37} It is generally accepted that this effect is mainly due to the release of structured water in the hydration shell of the monomers when the micelles are formed.

According to Eq. 10b, the slope of V_ϕ vs. cmc/m plot, ΔV_ϕ^{cmc} , shows a positive dependence on the degree of ionization. The last magnitude, as pointed out above, grows with temperature. Thus, an increase in ΔV_ϕ^{cmc} values should be expected when the temperature is raised. This effect might be interpreted as being due to growth in the electrostatic repulsion between the ionic head groups at the surface of the micelles. Results in Table 2 show, however, a reverse behavior, *i.e.*, ΔV_ϕ^{cmc} decreases with temperature. Again, the structured water surrounding the hydrocarbon chain of the monomers might be the origin of this phenomenon. At higher temperatures, the water sheath is less structured, and thus its contribution to ΔV_ϕ^{cmc} due to the release of water molecules is much lower. This effect is mainly responsible to compensate the growth in ΔV_ϕ^{cmc} due to the increase of the electrostatic repulsion that occurs when the degree of ionization rises.²¹

Adiabatic compressibility studies:

The concentration dependence of the ultrasound velocity in aqueous solutions of LDS at temperatures 288.15, 298.15 and 308.15 K is shown in Fig. 4. Each plot can be divided into two linear segments, which correspond to the monomeric and micellar forms of the surfactant in aqueous solution.

The change in adiabatic compressibility, β_s of the aqueous solutions of LDS with the surfactant concentration at different temperatures has been depicted in Fig. 5. The β_s values can be calculated from the relation $u^2 = 1/(\rho\beta_s)$, where u is the ultrasound velocity, expressed in m s^{-1} , and ρ is the density, expressed in kg m^{-3} of the aqueous surfactant solution. Again each plot can be divided into two line segments

corresponding to monomeric and micellar forms of the surfactant. The signs of the slopes of the plots for the monomeric forms are always negative, while the sign of the slopes above *cmc* depends on the temperature and it increases with increased temperature. A similar behaviour was also observed by Zielinski *et al*³⁷ for aqueous solutions of dodecyltrimethylammonium bromide.

For surfactant system of sufficiently low concentration, the dependence of the adiabatic compressibility, β_s , on molality, (below and above *cmc*), can be expressed by two approximation equations²⁴ of the exact equations used by Zielinski *et al*³⁷:

$$\frac{1000(\beta_s - \beta_{s_0})}{\rho_0} = (\bar{\beta}_{s_1} - \beta_{s_0}) V_{\phi_1} m \quad m < cmc \quad (11a)$$

$$\frac{1000(\beta_s - \beta_{s_0})}{\rho_0} = (\bar{\beta}_{s_m} - \beta_{s_0}) V_{\phi_m} (m - cmc) \quad m > cmc \quad (11b)$$

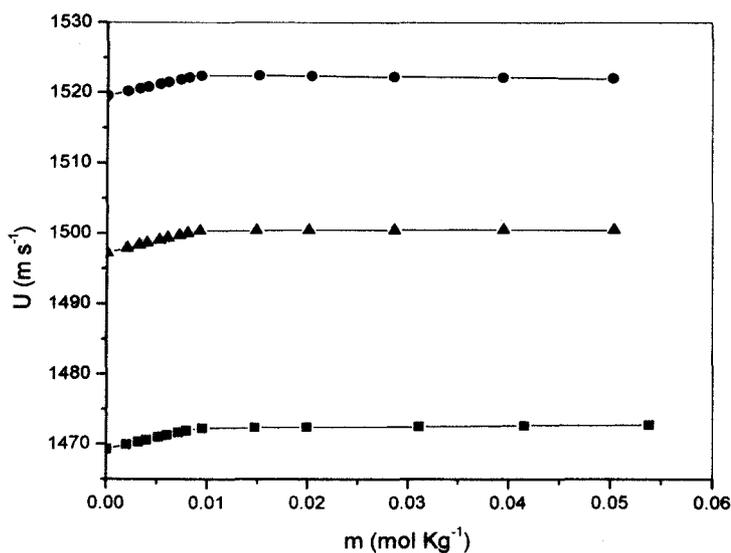


Figure 4. Effect of LDS molality on ultrasound velocity, u , in aqueous solutions at three different temperatures (Symbols as in figure 1).

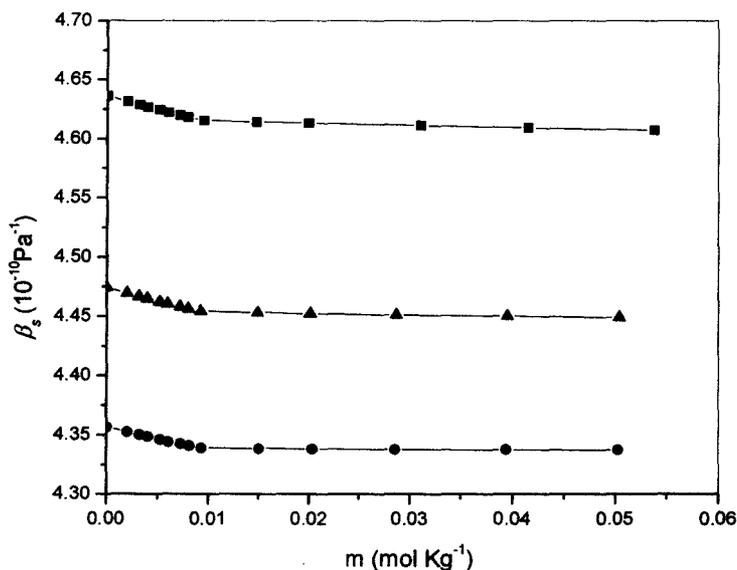


Figure 5. Dependence of adiabatic compressibility, β_s , of LDS on molality in aqueous solutions at 288.15(■), 298.15(▲), and 308.15 (●) K.

where V_{ϕ_1} and V_{ϕ_m} are the apparent molar volumes of the system below and above the *cmc*, respectively, ρ_0 is the density of pure water (in g cm⁻³), β_{s_0} , β_{s_1} and $\bar{\beta}_{s_m}$ are the adiabatic compressibility of pure water and apparent adiabatic compressibilities of surfactant in the monomeric and micellar states, defined respectively by

$$\beta_{s_0} = -1/V_0 (\partial V_0 / \partial P)_s, \quad \bar{\beta}_{s_1} = -1/V_{\phi_1} (\partial V_{\phi_1} / \partial P)_s, \quad \bar{\beta}_{s_m} = -1/V_{\phi_m} (\partial V_{\phi_m} / \partial P)_s$$

Figure 5 shows that the dependence of β_s on molality is well represented by two straight lines of different slopes in the pre- and postmicellar regions. From the value of the slope above *cmc*, the value of $\bar{\beta}_{s_m}$ can be estimated by applying Eq 11b. The results obtained are shown in Fig. 6. The value of $\bar{\beta}_{s_m}$ increases asymptotically at all experimental temperatures to a limiting value, which compares well with the behavior for other surfactant systems^{1, 37-39}. The limiting values obtained for $\bar{\beta}_{s_m}$ are 3.87×10^{-10} , 3.99×10^{-10} , and 4.20×10^{-10} Pa⁻¹ at 288.15, 298.15, and 308.15K respectively.

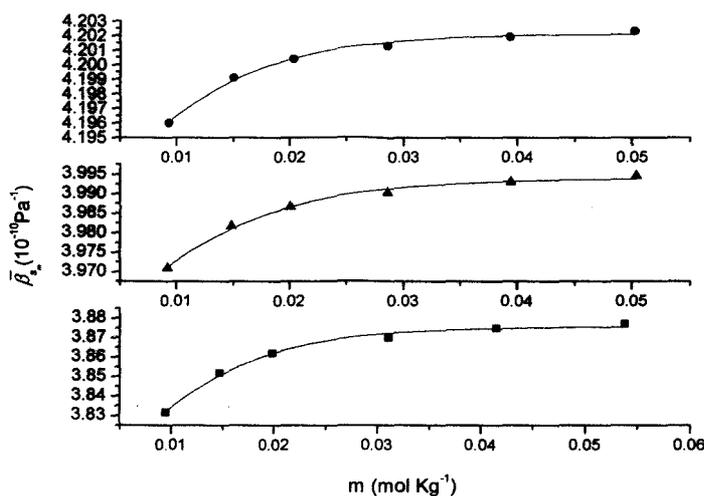


Figure 6. Molality dependence of the apparent adiabatic compressibility of LDS at 288.15(■), 298.15(▲) and 308.15 (●) K.

CONCLUSIONS

This investigation shows that the *cmc* of lithium dodecylsulfate in aqueous medium is temperature dependent and exhibit a shallow minimum at around 298.42K. Moreover, different experimental techniques exhibit almost the same *cmc* values for the surfactant. The high degree of ionization for the surfactant system is due to larger size of hydrated Li^+ ion. The weak temperature dependence of the standard Gibbs energy of micellization reflects an enthalpy-entropy compensation effect. The apparent molar volume change upon micellization, ΔV_ϕ^m may be attributed to several processes, an important contribution coming probably from the dehydration of the counter-ions bound to the micelle.

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TABLE-1

cmc, α , and Thermodynamic Parameters of LDS at Various Temperatures^a

Temp/K	α	<i>cmc</i> /mM			$\Delta G_m^\circ/\text{kJ mol}^{-1}$	$\Delta H_m^\circ/\text{kJ mol}^{-1}$	$\Delta S_m^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
		cond	dens	comp			
288.15	0.405	9.33	9.11	9.08	-33.21	4.03	129.24
293.15	0.415	9.09			-33.68	2.51	123.45
298.15	0.426	8.98	8.96	8.93	-34.06	0.89	117.22
303.15	0.437	9.06			-34.36	-0.80	110.70
308.15	0.446	9.21	9.28	9.18	-34.66	-2.59	104.07
313.15	0.457	9.32			-34.92	-4.47	97.23
318.15	0.465	9.39			-35.26	-6.46	90.52

^aThe uncertainties of α , *cmc*, ΔG_m° , ΔH_m° and ΔS_m° are ± 5 , ± 4 , ± 3 , ± 4 and ± 4 % respectively.

TABLE-2

Apparent Molar Volumes at Infinite Dilution, V_{ϕ}° , those at cmc , V_{ϕ}^{cmc} , and their Changes upon Micellization, ΔV_{ϕ}^{cmc} for LDS at 288.15, 298.15 and 308.15 K

$T(K)$	$V_{\phi}^{\circ}(\text{cm}^3 \text{ mol}^{-1})$	$V_{\phi}^{cmc} (\text{cm}^3 \text{ mol}^{-1})$	$\Delta V_{\phi}^{cmc} (\text{cm}^3 \text{ mol}^{-1})$
288.15	227.16 \pm 0.24	229.04 \pm 0.28	17.17 \pm 0.19
298.15	232.99 \pm 0.38	235.28 \pm 0.34	14.88 \pm 0.23
308.15	238.92 \pm 0.21	240.06 \pm 0.26	12.37 \pm 0.18