Micellization behaviour of lithium dodecyl sulphate in aqueous solutions using conductivity, density and adiabatic compressibility measurements

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Temperature effects on micellar behaviour of lithium dodecyl sulphate in aqueous solutions have been measured using conductometric, densiometric, and interferometric techniques. All these methods yield almost identical critical micelle concentration (cmc) for the surfactant system. Conductivity studies, in the range 288.15-318.15 K at 5 K intervals, show a shallow minimum of the cmc values at around 298.42 K. The ionization degree of micelles (\(\alpha\)) has been found to increase whereas the standard free energy of micellization (\(\Delta G_m^\circ\)) decreases upon increase in temperature. Variation in standard enthalpy upon aggregation has been calculated by using Gibbs-Helmholtz equation. From density measurements carried out at 288.15, 298.15 and 308.15 K, the changes of the apparent molar volume upon micellization of the surfactant have been calculated. The apparent adiabatic compressibilities of the surfactant solutions have also been calculated using density and ultrasound velocity measurements and provide information on the solution behaviour of the surfactant in aqueous solution.

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Self-association of hydrophobic molecules generally is of great importance for many physiological molecules, food constituents and drugs. The micellization of surfactants above a critical concentration (called the critical micelle concentrations, cmc) is an important solution property which needs evaluation to know the existence of micelle in solution as well as evaluating the thermodynamics of the process which is essential for characterization and comparison in the light of spontaneity and stability\(^1\). Though, many investigations have been done on sodium dodecyl sulphate (SDS)\(^2-10\), but much is not known about micellar behaviour of lithium dodecyl sulphate (LDS).

The results on conductometric, densiometric, and interferometric measurements at different temperatures of aqueous solutions of LDS are reported here. Among these measurements, densiometric 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, \(\alpha\), free energy of micellization, \(\Delta G_m^\circ\), standard entropy of micellization, \(\Delta S_m^\circ\), standard enthalpy of micellization \(\Delta H_m^\circ\), apparent molar volume, and apparent adiabatic compressibility have been calculated. These parameters provide useful information regarding the solution behaviour of LDS in aqueous solutions.

Materials and Methods

LDS (E.Merck, Germany) was used as received. Doubly distilled water (specific conductance, 2-3 \(\mu\)S cm\(^{-1}\)) was used in all preparations. Measurements were made at various temperatures in a 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 molarities being converted to molaliti es by the use of densities. Corrections were made for the specific conductance of water at all temperatures.

Densities were measured with an Ostwald-Spengler 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 values of density, ca. 5x10\(^{-5}\) gm cm\(^{-3}\).

Sound velocities were measured using single-crystal variable-path ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 4 MHz, which was calibrated with water, methanol and benzene at each
Table 1 — The cmc, α, and thermodynamic parameters of LOS at various temperatures

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>cmc</th>
<th>Cond</th>
<th>Dens</th>
<th>Comp</th>
<th>ΔG\text{m}^m</th>
<th>ΔH\text{m}^m</th>
<th>ΔS\text{m}^m</th>
<th>J K^{-1} mol^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>0.405</td>
<td>9.33</td>
<td>9.11</td>
<td>9.08</td>
<td>-33.21</td>
<td>4.03</td>
<td>129.24</td>
<td></td>
</tr>
<tr>
<td>293.15</td>
<td>0.415</td>
<td>9.09</td>
<td>9.06</td>
<td>8.93</td>
<td>-33.68</td>
<td>2.51</td>
<td>123.45</td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>0.426</td>
<td>8.98</td>
<td>9.28</td>
<td>9.18</td>
<td>-34.06</td>
<td>0.89</td>
<td>117.22</td>
<td></td>
</tr>
<tr>
<td>303.15</td>
<td>0.437</td>
<td>9.06</td>
<td>9.21</td>
<td>9.18</td>
<td>-34.36</td>
<td>-0.80</td>
<td>110.70</td>
<td></td>
</tr>
<tr>
<td>308.15</td>
<td>0.446</td>
<td>9.32</td>
<td>9.06</td>
<td>8.93</td>
<td>-34.92</td>
<td>-4.47</td>
<td>97.23</td>
<td></td>
</tr>
<tr>
<td>313.15</td>
<td>0.457</td>
<td>9.30</td>
<td>9.21</td>
<td>9.18</td>
<td>-35.26</td>
<td>-6.46</td>
<td>90.52</td>
<td></td>
</tr>
<tr>
<td>318.15</td>
<td>0.465</td>
<td>9.39</td>
<td>9.21</td>
<td>9.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The error limits of cmc, ΔG\text{m}^m, ΔH\text{m}^m, and ΔS\text{m}^m are ±5, ±4, ±3, ±4 % respectively.

The dependence of specific conductivity of LOS on molality at various temperatures is shown in Fig. 1. The dependence of specific conductivity on the molality of LOS at various temperatures is shown in Fig. 1. 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 earlier.

Results and Discussion

Conductivity studies

The dependence of the specific conductivity on the molality of LOS at various temperatures is 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 conductivity against concentration plots above \( (S_2) \) and below \( (S_1) \) of the cmc.

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, \( \Delta G_{\text{m}}^m \), can be calculated using:

\[
\Delta G_{\text{m}}^m = (2 - \alpha) RT \ln X_{\text{cmc}}
\]

where \( X_{\text{cmc}} \) is the cmc in mole fraction. The standard enthalpy, \( \Delta H_{\text{m}}^m \), and entropy, \( \Delta S_{\text{m}}^m \), of micellization were obtained assuming that \( \alpha \) is practically constant (Table 1) and by insertion of Eq.(1) into a Gibbs-Helmholtz equation, which gives Eqs (2)-(3):

\[
\Delta H_{\text{m}}^m = -(2 - \alpha) RT \ln X_{\text{cmc}}/\beta T
\]

\[
\Delta S_{\text{m}}^m = \left(\Delta H_{\text{m}}^m - \Delta G_{\text{m}}^m/T\right)
\]

The value of \( \ln X_{\text{cmc}}/\beta T \) was determined by fitting the ln \( X_{\text{cmc}} - \beta T \) with the polynomial function:

\[
\ln X_{\text{cmc}} = a + bT + cT^2
\]

The values of the fitting constants were \( a = 4.33464 \), \( b = -0.8081 \), and \( c = 1.44288 \times 10^{-4} \). The temperature dependent values of cmc as well as \( \alpha \) and different thermodynamic parameters are given in Table 1. The cmc value determined conductometrically at 298.15 K for the surfactant LDS is in good agreement with that reported earlier.

The temperature dependence of cmc for LDS is given in the insert of Fig. 1 which exhibits a shallow minimum at about 298.42 K.

The degree of ionization, \( \alpha \), of micelles of LDS increases with temperature as found earlier for cationic surfactants. The higher values of \( \alpha \) can be explained qualitatively in terms of larger size of the hydrated Li\textsuperscript{+} 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. The mean value of \( \Delta \alpha/\Delta T \) estimated in the temperature range 288.15-318.15 K
amounts to 0.0014 K\(^{-1}\). It is low compared to that found earlier for cationic surfactants dodecyldimethylbenzylammonium chloride (0.0030)\(^{24}\), tetradecyltrimethylammonium bromide (0.0030)\(^{25}\) and tetradecyldimethyl-phenylammonium bromide (0.0029)\(^{26}\).

Analyses of the thermodynamic parameters of micellization indicate that the aggregation of LDS is driven mainly by the positive \(\Delta S_\text{mic}^\circ\). Similar changes from entropic to enthalpic micellization with temperature increase have been noted with many different surfactants\(^{21,27,29}\). The standard free energies of micellization, calculated for LDS decrease linearly with temperature. The low rate of decrease of \(\Delta G_\text{mic}^\circ\) with growth of temperature is typical for aqueous solutions of surfactants and results from an entropy-enthalpy compensation effect\(^{30,34}\). Positive values of \(\Delta H_\text{mic}^\circ\), 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 micelle\(^{35}\). Such hydrophobic interactions become increasingly insignificant with the partial breakdown of the structure of water as the temperature is increased, the negative \(\Delta H_\text{mic}^\circ\) values suggesting the importance of the London-dispersion interactions as an attractive force contribution for micellization\(^{36}\). However, it may be seen from Table 1 that at a certain temperature the enthalpy of micellization vanishes and the process is driven only entropically. This is a direct consequence of Eq.(2) only when the temperature dependence of \(\approx\) is being neglected.

**Density studies**

Density (\(\rho\)) measurements of aqueous solutions of LDS are presented in Fig. 2 in the form of plots of \(\rho - \rho_o\) versus molality of LDS, \(\rho_o\) being the density of water at the appropriate temperature. It is seen that in both pre- and post-micellar range studied, the densities increase linearly with the increase of molality.

The apparent molar volumes, \(V_\text{app}\) of LDS in function of molalities at the temperatures studied were calculated using Eq.(5)\(^{34}\):

\[
V_\text{app} = \frac{M}{\rho} \frac{10^3(\rho - \rho_o)}{m}\text{ mnp}
\]  

where \(M\) and \(m\) are the molecular mass and the molality of the solute, respectively. The variation of

![Fig. 2 — Density versus molality plot for LDS at 288.15 (■), 298.15 (△), and 308.15 (●) K.](image)

![Fig. 3 — Variation of \(V_\text{app}\) with the reverse of molality for LDS at various temperatures (Symbols as in Fig. 1).](image)

\(V_\text{app}\) with the reverse of molality is given in Fig. 3. It can be seen that the apparent molar volumes remain almost constant in the lower concentration range followed first by a sharp increase in the region close to cmc and then by an approach to a saturation value at the highest concentration studied.

In an ionic surfactant system, below cmc, the dependence of density on concentration can be expressed as\(^{24}\):

\[
(\rho - \rho_o) \times 10^3 = [(M_1 + M_2) - (V_1 + V_2) \rho_o] m
\]  

where \(M_1\), \(V_1\), \(M_2\), \(V_2\) are the molecular masses and the apparent molar volumes of the surfactant ions.
and counterions, respectively. If these apparent molar volumes were negligibly concentration-dependent, then Eq. (6) predicts a linear relation between density and concentration. Indeed, such a behaviour is seen in Fig. 2. Thus, estimated values for \( V_f + V_c \) amount to 229.23±0.26, 235.60±0.24 and 240.44±0.34 cm\(^3\) 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 \( V_f + V_c \) with temperature is related to the relaxation of structured water engaged in the solvation of the hydrocarbon chain, the head group, and the counterion. A similar behaviour can be observed for the data for decylbenzyldimethyl chloride and dodecylbenzylchloride.

Since it is generally accepted that the solutions of surfactants in the premicellar region behave as singly dispersed system, they may be described by:

\[
V_o = V_o^0 + A_v m^{1/2} + B_v m 
\]  
(7)

where \( V_o^0 \) 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 cm\(^3\) kg\(^{-1/2}\) mol\(^{-1}\), respectively. Experimental values of \( V_o \) in the premicellar region were fitted to Eq. (7) and the values of \( V_o^0 \) are listed in Table 2. The \( V_o^0 \) values for LDS increase almost linearly with temperature in conformity with the expected behaviour. Thus, Eq. (7) may be considered as an acceptable approximation of the behaviour of the system. We can assign that the intersection point of the lines above and below \( \text{cmc} \) as the corresponding \( \text{cmc} \). The values, thus obtained, are almost identical with those obtained in conductivity and interferometric techniques at 288.15, 298.15, and 308.15 K, respectively.

Assuming that the rule of additivity for the apparent molar volumes of the ions in the system is valid, we can write:

\[
n_{\text{LDS}} V_o = n_I V_f + n_c V_c + n_m V_m 
\]  
(8)

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

\[
m_I = m_c = m
\]  
(9a)

and above \( \text{cmc} \)^{24}.

\[
m_c = \text{cmc} + \infty (m - \text{cmc})
\]  
(9b)

\[
m_m = \frac{m - \text{cmc}}{N_{agg}}
\]  
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 relations (9), we obtain the following set of equations:

\[
V_o = (V_f + V_c)
\]  
\( m \leq \text{cmc} \) ... (10a)

\[
V_o = (V_m/N_{agg} + \infty V_c) - (V_m/N_{agg} + (\infty - 1) V_c - V_f)
\]  
\( \text{cmc} < m \leq \text{cmc} \) ... (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 \( V_o \) versus \( 1/m \) plot can be expected in the concentration range above \( \text{cmc} \). According to Eq. (10a), the value of \( V_o \) should be constant in the concentration range below \( \text{cmc} \). Such a plot is shown in Fig. 3. It can be seen that the system conforms approximately to the expected behaviour. Thus, Eq. (10) may be considered as an acceptable approximation of the behaviour of the system. We can assign that the intersection point of the lines above and below \( \text{cmc} \) as the corresponding \( \text{cmc} \).

Table 2 — Apparent molar volumes of the surfactant at infinite dilution, \( V_o^0 \), at \( \text{cmc} \), \( V_o^{\text{cmc}} \), and the change upon micellization, \( \Delta V_o^{\text{cmc}} \), for LDS at 288.15, 298.15 and 308.15 K

<table>
<thead>
<tr>
<th>T, K</th>
<th>( V_o^0 ), cm(^3) mol(^{-1})</th>
<th>( V_o^{\text{cmc}} ), cm(^3) mol(^{-1})</th>
<th>( \Delta V_o^{\text{cmc}} ), cm(^3) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>227.16 ±0.24</td>
<td>229.04 ±0.28</td>
<td>17.17 ±0.19</td>
</tr>
<tr>
<td>298.15</td>
<td>232.99 ±0.38</td>
<td>235.28 ±0.34</td>
<td>14.88 ±0.23</td>
</tr>
<tr>
<td>308.15</td>
<td>238.92 ±0.21</td>
<td>240.06 ±0.26</td>
<td>12.37 ±0.18</td>
</tr>
</tbody>
</table>
assumed 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 $V_o$ versus $cmc/m$ plot, $\Delta V_o^{cmc}$, shows a positive dependence on the degree of ionization. The last magnitude, as pointed out above, grows with temperature. Thus, an increase in $\Delta V_o^{cmc}$ 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. Table 2 shows, however, a reverse behaviour, i.e., $\Delta V_o^{cmc}$ decreases with growth of temperature. Again, the structured water surrounding the hydrocarbon chain of the monomers is the origin of this phenomenon. At high temperatures, the water sheath is less structured, and thus the contribution to $\Delta V_o^{cmc}$ due to the release of water molecules is much lower and this effect is mainly responsible to compensate the growth in $\Delta V_o^{cmc}$ due to the increase of the electrostatic repulsion that occurs when the degree of ionization rises.

Adiabatic compressibility studies

Figure 4 is representative example of the changes in the ultrasound velocity in aqueous solutions of LDS with the surfactant concentration at temperatures 288.15-308.15 K. Each plot can be divided into two straight-line segments, which correspond to the monomeric and micellar forms of the surfactant in aqueous solution.

The change in adiabatic compressibility, $\beta_s$, of the aqueous solutions of LDS with the surfactant concentration at different temperatures is depicted in Fig. 5. The $\beta_s$ can be calculated from the relation

$$\alpha^2 = \frac{1}{\rho \beta_s}$$

where $\alpha$ is the ultrasound velocity, expressed in ms$^{-1}$, and $\rho$ 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. Slopes of the plots for the monomeric forms are negative while the sign of the slopes above $cmc$ depends on the temperature and it increases with temperature. A similar increase is observed on the plots of adiabatic compressibility in aqueous solutions of dodecyltrimethylammonium bromide with temperature as shown by Zielinski et al.

For surfactant system of sufficiently low concentration, the dependence of the adiabatic compressibility, $\beta_s$, on molality (below and above $cmc$), can be expressed by two-approximation equations of the exact equations used by Zielinski et al.:

$$\frac{1000(\beta_s - \beta_{so})}{\rho_o} = (\beta_{s1} - \beta_{so}) V_{o1} \ m < cmc \ldots \ (11a)$$

$$\frac{1000(\beta_s - \beta_{so})}{\rho_o} = (\beta_{sm} - \beta_{so}) V_{ocm} (m - cmc) \ m > cmc \ldots \ (11b)$$
where \( V_{0i} \) and \( V_{0m} \) are the apparent molar volumes of the system below and above cmc, \( \rho_0 \) is the density of pure water (in gm cm\(^{-3}\)), \( \beta_{0i} \), \( \beta_{s} \), and \( \beta_{sm} \) are the adiabatic compressibilities of pure water and apparent adiabatic compressibilities of surfactant in the monomeric and micellar states, defined respectively by:

\[
\beta_{sm} = -\frac{1}{V_{0m}} \left( \frac{\partial V_{0m}}{\partial P} \right)_T; \quad \beta_{s} = -\frac{1}{V_{0}} \left( \frac{\partial V_{0}}{\partial P} \right)_T; \quad \beta_{0i} = -\frac{1}{V_{0i}} \left( \frac{\partial V_{0i}}{\partial P} \right)_T
\]

Figure 5 shows that the dependence of \( \beta_s \) on molality is well represented by two straight lines of different slopes in the pre- and post-micellar concentration range. From the value of the slope above cmc, the value of \( \beta_{sm} \) can be estimated by applying Eq.(11b). The results are shown in Fig. 6. The value of \( \beta_{sm} \) increases asymptotically at all experimental temperature to a limiting value, which compares well with the behaviour for other surfactant systems.\(^{1,40-42}\) The limiting values obtained for \( \beta_{sm} \) are \( 3.87 \times 10^{-10}, 3.99 \times 10^{-10}, \) and \( 4.20 \times 10^{-10} \) Pa\(^{-1}\) at 288.15, 298.15, and 308.15 K, respectively.

Conclusions

The present investigations show that cmc of LDS in aqueous medium is temperature dependent and exhibits a shallow minimum at around 298.42 K. 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, \( \Delta V_m^{\text{app}} \) is due to several processes, an important contribution coming probably from the dehydration of the counterions bound to the micelle and also due to the release of structured water in the hydration shell of monomers, which occurs upon micellization.

Acknowledgement

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References