

## CHAPTER-IV

### **Effect of Tetraalkylammonium Salts on the Micellar Behavior of Lithium Dodecyl Sulfate: A Conductometric and Tensiometric Study**

#### **INTRODUCTION**

The function and properties of surfactant systems depend on their structural type, concentration and composition in addition to other factors, *viz.*, temperature, pressure, *pH*, solvent and additives. Surfactants and their mixtures with additives in aqueous solutions are of interest for their chemical, pharmaceutical, mineral processing, and petroleum engineering applications<sup>1,2</sup>. Micelles with charged surfaces bind counterions selectively, and their solution properties are sensitive to the type and concentration of counterions<sup>3-13</sup>. Recently, studies on the counterion effect of  $R_4N^+$  ions are gaining recognition in micellar systems<sup>4, 14-16</sup>. Due to their hydrophobic nature, quaternary ammonium ions ( $R_4N^+$ ) differ remarkably from the alkali metal cations. Yu and Xu reported an interesting micellar growth behavior of tetrabutylammonium bromide and an anionic surfactant<sup>17, 18</sup>. Since  $R_4N^+$  cations modify the structure of water around them in a similar way as some simple hydrocarbons do, it could be of considerable interest to explore how this kind of interaction would affect the micellar properties of an anionic surfactant.

In the present study, the effect of some quaternary ammonium bromides,  $R_4NBr$  ( $R = H, CH_3, C_2H_5, C_3H_7, \text{ and } C_4H_9$ ) on the micellar properties of lithium dodecylsulfate (LDS) has been studied by the method of conductometry and tensiometry. To derive energetic information of the self-aggregation of the amphiphile, *cmc*s of LDS with solutions of strength 0.001 M of different symmetrical quaternary ammonium salts were determined in the 288.15-318.15 K-temperature range at 10 K intervals conductometrically. Cloud point (CP) phenomenon of this surfactant with tetrabutylammonium bromide ( $Bu_4NBr$ ) has also been investigated.

## EXPERIMENTAL

### *Materials and Methods*

The surfactant lithium dodecylsulfate (E. Merck, Germany) has been used as received. The tetraalkylammonium bromides were of purum or puriss grade (Fluka, Switzerland) and were purified as described in the literature<sup>19, 20</sup>. These salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure maximum purity. The recrystallized salts were dried in vacuo at elevated temperatures for 12 h. Doubly distilled water (specific conductance,  $2-3 \mu\text{S cm}^{-1}$ ) was used in the preparations. Measurements were made at each temperature in a thermostated water-bath maintained within  $\pm 0.01 \text{ K}$ .

In the conductance method, a concentrated surfactant solution, prepared in different aqueous tetraalkylammonium salt solutions, was added in installments with the help of microsyringe to the respective aqueous solutions of tetraalkylammonium salt, placed in a wide-mouth test tube fitted with a dip-type conductivity cell of cell constant  $1.14 \text{ cm}^{-1}$ . After each addition, conductance of the solution was measured (after thorough mixing and temperature equilibration) with a Pye-Unicam PW9509 conductivity meter at a frequency of 2000Hz. The measurements were duplicated. The conductance values were uncertain within the limit of  $\pm 1\%$ .

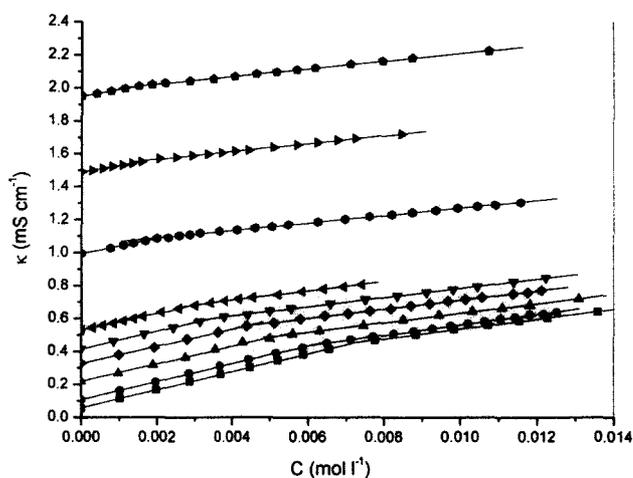
The surface tension of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The measured tensions were corrected according to the procedure of Harkins and Jordon<sup>21</sup>. Here also, the addition of the concentrated surfactant solutions in installments using a Hamilton microsyringe was done and measurements were taken after mixing and temperature equilibration. Duplicate measurements were performed to check the reproducibility. The uncertainty of the measurements was within  $\pm 0.1 \text{ mNm}^{-1}$ .

Freshly prepared stock solutions of LDS were used to obtain different sample solutions for CP measurements. The solutions were taken in Pyrex glass tubes, which were then immersed in a thermostat and heated with a uniform rate of  $0.1^\circ \text{C}/\text{min}$ . The first appearance of turbidity was taken as the CP.

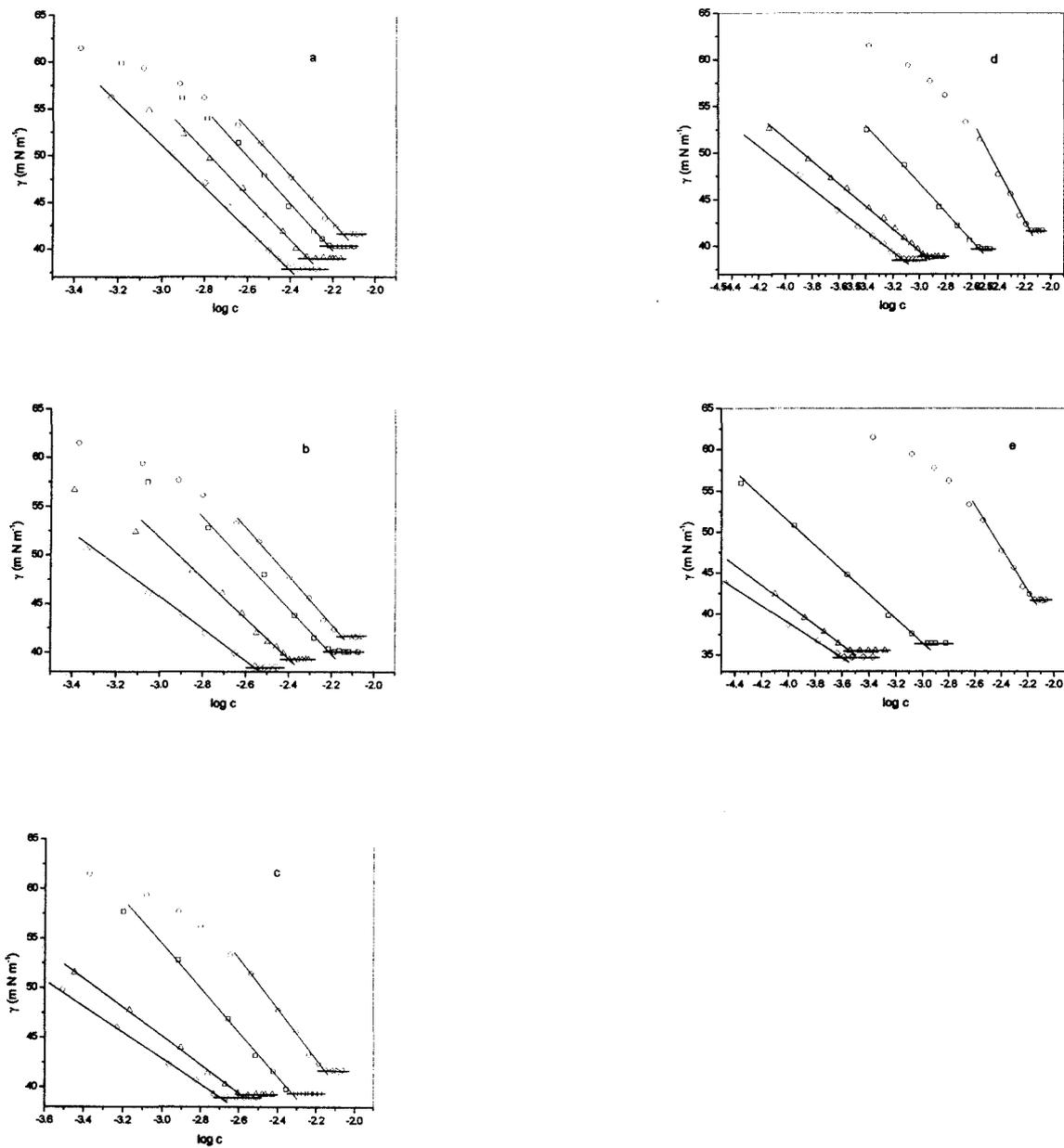
## RESULTS AND DISCUSSION

### *Critical micellar concentration*

The *cmc*s of LDS in presence of different symmetrical quaternary ammonium salts were determined by conductometry and tensiometry. Some selected experimental results are presented in Figs. 1 and 2a-e. Conductometric plots exhibit typical behavior with two linear segments whose intersection is usually treated as corresponding to the *cmc*. In the tensiometric determination of the *cmc*s, we chose the bulk concentration as the *cmc* at which the surface tension reaches the constant equilibrium value in the  $\gamma$ -log  $c$  curves. The *cmc* values realized by the two methods (conductometry and tensiometry) are presented in Table 1. The *cmc* obtained from surface tension measurements were always found to be lower than those obtained from conductance measurements. Similar method dependent *cmc* values are common in the literature<sup>22, 23</sup>.



**Figure 1.** Dependence of specific conductivity of LDS on molarity in presence of 0.0005 (■), 0.001 (●), 0.002 (▲), 0.003 (◆), 0.004 (▼), 0.005 (◄), 0.010 (●), 0.015 (►) and 0.020 (◆) M of Et<sub>4</sub>NBr.



**Figure 2a-e.** Variation of  $\gamma$  with  $\log c$  for LDS in presence of 0.000 ( $\circ$ ), 0.001 ( $\square$ ), 0.005 ( $\Delta$ ), and 0.010 ( $\diamond$ ) M of different tetraalkylammonium salts. (a)  $\text{NH}_4\text{Br}$ ; (b)  $\text{Me}_4\text{NBr}$ ; (c)  $\text{Et}_4\text{NBr}$ ; (d)  $\text{Pr}_4\text{NBr}$ ; and (e)  $\text{Bu}_4\text{NBr}$ .

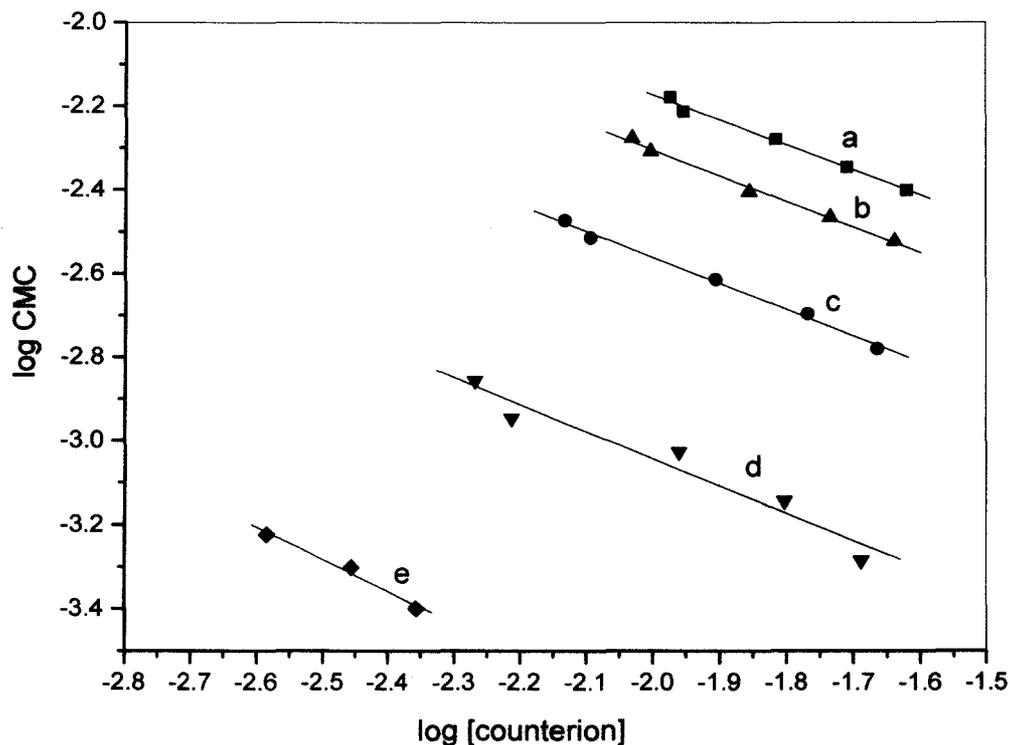
The *cmc* of the surfactant has been found to decrease in presence of  $R_4NBr$ , the decreases being dependent upon the concentration of  $R_4NBr$ . Due to the neutralization of the effective head group charge of the ionic surfactant in presence of simple salts, the electrical atmosphere in the aqueous surfactant solution is altered; this results in a reduced electrostatic repulsion between the polar head groups and hence the micelles are formed at much lower concentration as compared to the situation in pure water. The marked reduction in the *cmcs* with the size of the alkyl group in the quaternaries may be attributed to the hydrophobic interaction of the hydrocarbon part of the quaternary ammonium ions with the hydrocarbon core of the micelle overriding the electrostatic contribution.

### *Counterion binding of micelle*

It is clear, on one hand, that ionic micelles are charged and have counterions and on the other, not all counterions are free in the sense of having the same activity or mobility as those of a simple electrolyte. Yet there is at present no unambiguous method of measuring this degree of freedom or of binding of the counterions. The principal experimental measurements used in these interpretations are conductance slopes, light scattering, and *cmc* determination as a function of counterion concentration. The conductance slope method for the determination of counterion binding was not used here because of its insensitivity in presence of moderate salt concentration. We have employed the method of *cmc* determination as a function of counterion concentration for determining the counterion binding using the Corrin-Harkins equation<sup>24, 25</sup>

$$\log cmc = \text{CONSTANT} - \beta \log [\text{counterion}] \quad (1)$$

The plots of  $\log cmc$  vs.  $\log [\text{counterion}]$  show a linear dependence of  $\log cmc$  on  $\log [\text{counterion}]$  in the range  $[\text{counterion}] > 0.001$  M for  $Bu_4NBr$  and  $> 0.003$  M for other salts. However, a deviation from linearity occurs in the lower concentration region. Considering only the linear part of the plots shown in Fig. 3, counterion binding has been calculated and presented in Table 2. The result shows that counterion binding,  $\beta$ , increases with the increasing size of alkyl chain length of tetraalkylammonium salts.



**Figure 3.** Plot of  $\log [\text{counterion}]$  vs.  $\log \text{cmc}$  of different tetraalkylammonium salts (a)  $\text{NH}_4\text{Br}$ ; (b)  $\text{Me}_4\text{NBr}$ ; (c)  $\text{Et}_4\text{NBr}$ ; (d)  $\text{Pr}_4\text{NBr}$ ; and (e)  $\text{Bu}_4\text{NBr}$ .

Again the hydrophobic interaction of the tetraalkylammonium ions with the hydrocarbon core of the micelle may be the origin of the above observation. It may be mentioned that in the Corrin-Harkins<sup>24, 25</sup> relation the counterion binding has been considered to be independent of salt concentration. The effect of changed aggregation number in the salt environment on the counterion condensation has also been ignored.

#### ***Thermodynamics of micellization***

According to the charge phase separation model of micellization, the activity of the monomer remains constant above  $\text{cmcs}$  and the standard free energy of micellization per mole of monomer,  $\Delta G_m^0$  can be calculated from the following relation<sup>26</sup>:

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{\text{cmc}} \quad (2)$$

where  $X_{cmc}$  is the value of  $cmc$  expressed in mole fraction. The standard enthalpy of micellization,  $\Delta H_m^0$ , was calculated from the following equation<sup>27, 28</sup>:

$$\Delta H_m^0 = (1 + \beta)RT^2 (\partial \ln X_{cmc} / \partial T)_p \quad (3)$$

obtained by inserting Eq. (2) into Gibbs-Helmholtz equation based upon the assumption that  $\beta$  is practically temperature-independent.

The values of  $\partial \ln X_{cmc} / \partial T$  was determined by fitting  $\ln X_{cmc} - T$  with the polynomial function

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

where  $a$ ,  $b$  and  $c$  are temperature-independent constants. Then,

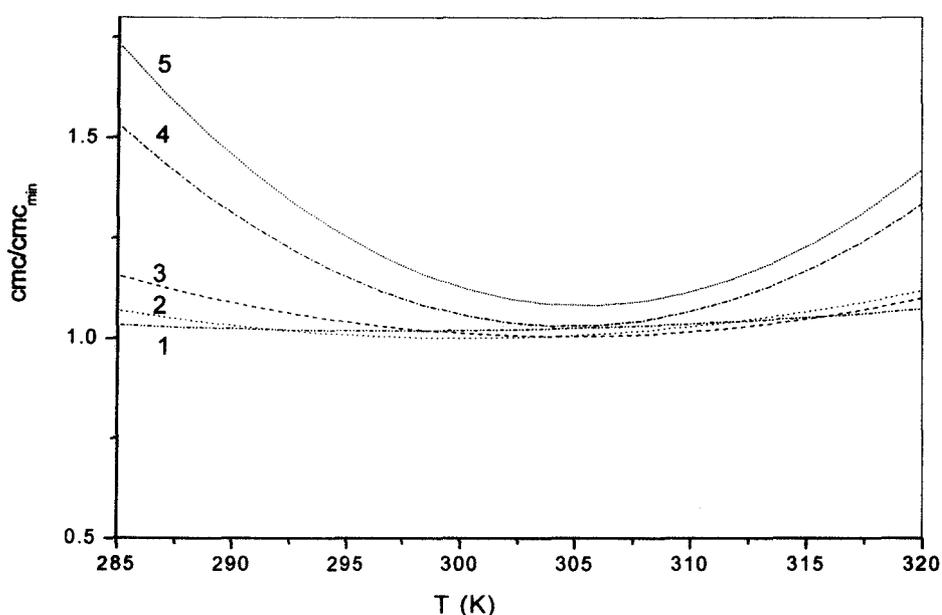
$$\ln X_{cmc} / \partial T = b + 2cT \quad (5)$$

The change in the standard entropy of micellization can then be obtained from

$$\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0 \quad (6)$$

The temperature dependence of the relative  $cmc$  values for LDS in presence of 0.001 M of various tetraalkylammonium salts is illustrated in Fig. 4. The minima in these curves occur typically between 300 to 305 K for all the additives. An initial decrease in the relative  $cmc$  values with temperature may be ascribed to the dehydration of the monomers, while further temperature increase causes disruption of the structured water around the hydrophobic groups which opposes micellization. The  $cmcs$  and the different thermodynamic parameters in presence of 0.001 M of various tetraalkylammonium salts are presented in Table 2. Analysis of the thermodynamic parameters of micellization indicates that the aggregation of LDS is driven mainly by the positive  $\Delta S_m^0$ . Similar changes from entropic to enthalpic micellization with temperature increase have also been observed with some other surfactants<sup>29-31</sup>. The standard free energies of micellization for LDS in presence of various quaternary ammonium salts, decreases linearly with temperature. The slow decrease of  $\Delta G_m^0$  with the growth of temperature is typical for aqueous solutions of surfactants and this results from entropy-enthalpy compensation effect<sup>32-34</sup>. Decreasing values of  $\Delta G_m^0$  with increasing chain length of the alkyl substituent of the added salts indicate that the micellization of LDS becomes more favorable as the hydrophobicity of quaternaries increases. Positive values of  $\Delta H_m^0$  such as those noted at the lowest temperatures are generally attributed to the release of structural waters molecules from the hydration

layers around hydrophobic parts of the micelle. The high positive value of  $\Delta H_m^0$  in the presence of  $\text{Bu}_4\text{NBr}$  indicates an increased hydrophobicity of the micelle due to the penetration of the alkyl chains of  $\text{Bu}_4\text{NBr}$  with a large hydrophobic volume into the micellar core. Geometric restriction makes it infeasible for all four chains to penetrate. Hence, two chains are located at the micellar surface layer in contact with water thus forming an iceberg structure around the chains<sup>35</sup>. Such hydrophobic interactions become increasingly insignificant with the partial breakdown of the structure of water as temperature is increased, the negative  $\Delta H_m^0$  values suggesting the importance of the London-dispersion interactions as an alternative force contribution for micellization.<sup>3</sup>



**Figure 4.** Temperature dependence of relative  $cmc$  values for LDS in presence of 0.001 M of different tetraalkylammonium salts (1)  $\text{NH}_4\text{Br}$ ; (2)  $\text{Me}_4\text{NBr}$ ; (3)  $\text{Et}_4\text{NBr}$ ; (4)  $\text{Pr}_4\text{NBr}$ ; and (5)  $\text{Bu}_4\text{NBr}$ .

### ***Interfacial adsorption***

The variation of surface tension as a function concentration of aqueous solution of LDS in the absence and presence of various quaternary ammonium salts is

shown in Fig. 2 The *cmcs* have been determined from bulk property corresponding to the surfactant concentration at which surface tension reaches the constant equilibrium value.

The maximum interfacial adsorption,  $\Gamma_{\max}$ , of LDS in presence of different tetraalkyl salts has been evaluated according to a suitable form of the Gibbs adsorption equation<sup>26, 28</sup>.

$$\Gamma_{\max} = -\frac{1}{4.606RT} \left( \frac{d\gamma}{d \log c} \right) \quad (7)$$

The slope of the linear portion of the  $\gamma$  vs.  $\log c$  curve below the *cmc* was determined by the method of least squares.

The minimum surface area per surfactant head group at the aqueous solution-air interface,  $A_{\min}$ , nm<sup>2</sup> / molecule, is then calculated from the equation<sup>37</sup>

$$A_{\min} = 10^{18} / N_A \Gamma_{\max} \quad (8)$$

where  $N_A$  is the Avogadro's number.

Interfacial properties of LDS in presence of various tetraalkylammonium salts are presented in Table 1. The *cmc* of LDS in water is found to be 8.98 mM at 298.15 K in agreement with those reported in the literature<sup>12, 38</sup>. The  $\gamma_{cmc}$  in the  $\gamma$  vs.  $\log c$  profile of LDS decreases with increasing concentration of R<sub>4</sub>NBr salts as well as with increasing chain length of the alkyl groups of the additives. The factor 4.606 in the denominator of Eq. 7 depends on the charge of the adsorbed amphiphile at the air/liquid interface. In presence of excess salts, the amphiphile ions behave like neutral species and the factor reaches its limiting value of 2.303. In presence of added R<sub>4</sub>NBr at a concentration of 0.005 to 0.01 mol dm<sup>-3</sup>, the factor 2.303 is realistic. The values of  $\Gamma_{\max}$  and  $A_{\min}$  obtained on such a basis are listed in Table 1. The results, in general, indicate lower interfacial adsorption at *cmc* ( $\Gamma_{\max}$ ) in presence of the salts as additives in solution. The variation of  $A_{\min}$  with the concentration of a given additive follows an opposite trend to that of the  $\Gamma_{\max}$  values. The observed trends in the measured parameters in the studied salt environments are considered to be inherently controlled by interfacial charge neutralization in presence of R<sub>4</sub>NBr. For quantification of the observations on a firm basis, further study in this direction is worthwhile.

### ***CP Phenomenon***

It is well known that  $\text{Bu}_4\text{NBr}$  is one of the most effective additives in producing CP phenomenon in anionic surfactants<sup>35, 39</sup>. In this study, we have also measured the CP of 0.025, 0.05 and 0.1 M LDS in the presence of different amounts of  $\text{Bu}_4\text{NBr}$ . From the data in Table 4, it is clear that CP decreases with increasing salt concentration, while an increase is observed with an increase in the surfactant concentration. Clouding behavior has been attributed to the dehydration of the hydrophobic group of the surfactant with the increase in temperature<sup>39</sup>. Large amount of added salt screens the electrostatic repulsion and this is believed to be responsible for the ionic micellar system exhibiting CPs. The butyl chain of  $\text{Bu}_4\text{NBr}$  may penetrate into the micellar interior due to hydrophobic interaction<sup>35, 39</sup>. Van der Waals attraction and the penetration effect will help attract two micelles together, while the electrical repulsion will prevent the micellar contact. Dehydration of the ionic heads of the surfactant monomers takes place on increasing the temperature, which increases the interaction between the anionic heads and  $\text{Bu}_4\text{N}^+$ . At the CP the micelles would collapse and this results in the formation of two phases. An increase in the concentration of  $\text{Bu}_4\text{NBr}$  will produce more structured water and the phase separation is expected to appear at a lower temperature since the LDS concentration is constant. This is clearly reflected in Table 3.

## CONCLUSIONS

The above measurements show that the *cmc* of lithium dodecylsulfate is dependent upon the concentration and the alkyl chain length of the added tetraalkylammonium bromide salts. The marked reduction in *cmc* with the increase in the size of the alkyl chain of the quaternaries may be attributed to the hydrophobic bonding of these salts with the hydrophobic core of the micelles. The weak temperature dependence of the standard Gibbs energy of micellization reflects an enthalpy-entropy compensation effect. The decreasing values of  $\Delta G_m^0$  with increasing chain length of the alkyl substituents of the added salts indicates that micellization of LDS becomes more favorable as the hydrophobicity of the quaternaries increases. The occurrence of the cloud point phenomenon for this anionic surfactant in presence of  $\text{Bu}_4\text{NBr}$  is accounted for in terms of the penetration of the butyl chains of the  $\text{Bu}_4\text{N}^+$  ions into the hydrophobic cores of two neighboring micelles due to the hydrophobic effect.

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TABLE-1

Critical Micellar Concentration and Interfacial Properties of LDS in Presence of Different Quaternary Ammonium Salts at 298.15 K

[salt] (mol dm <sup>-3</sup> )	cmc / mM		$\gamma_0$ (mN / m)	$\gamma_{cmc}$ (mN / m)	$10^6 \Gamma_{max}$ (mol m <sup>-2</sup> )	$10^2 A_{min}$ (n m <sup>2</sup> )
	Cond	s.t.				
			<b>NH<sub>4</sub>Br</b>			
0.0000	8.98	7.12	72.2	41.8	2.01	82.52
0.0005	8.63	-				
0.001	8.24	5.86	72.1	40.3	2.06	80.64
0.002	7.72	-				
0.003	6.97	-				
0.004	6.63	-				
0.005	6.13	4.80	72.0	38.9	1.89 (3.78)	87.66 (175.32)
0.01	5.27	3.82	71.9	37.9	1.87 (3.74)	88.54 (177.08)
0.015	4.51	-				
0.02	3.97	-				
			<b>Me<sub>4</sub>NBr</b>			
0.0005	8.31	-				
0.001	7.62	6.33	71.8	40.1	1.81	91.68
0.002	6.90	-				
0.003	5.90	-				
0.004	5.30	-				
0.005	4.93	4.02	71.7	39.3	1.55 (3.10)	107.05 (214.10)
0.01	3.94	2.80	71.6	38.5	1.33 (2.66)	124.74 (249.48)
0.015	3.43	-				
0.02	3.00	-				
			<b>Et<sub>4</sub>NBr</b>			
0.0005	7.12	-				
0.001	6.25	4.69	71.7	39.4	1.86	
0.002	5.17	-				
0.003	4.47	-				
0.004	3.37	-				
0.005	3.06	2.51	71.6	39.3	1.25 (2.50)	133.25 (266.50)
0.01	2.43	1.94	71.4	39.0	1.15 (2.30)	145.00 (290.00)
0.015	2.00	-				
0.02	1.66	-				
			<b>Pr<sub>4</sub>NBr</b>			
0.0005	4.00	-				
0.001	3.34	2.86	71.6	39.7	1.33	125.31
0.002	2.41	-				
0.003	1.96	-				
0.004	1.39	-				
0.005	1.13	1.15	71.3	38.9	1.02 (2.04)	162.93 (325.86)
0.01	0.94	0.73	70.8	38.6	1.01 (2.02)	163.41 (326.82)
0.015	0.72	-				
0.02	0.52	-				
			<b>Bu<sub>4</sub>NBr</b>			
0.0005	1.55	-				
0.001	1.24	0.98	69.1	36.4	1.26	131.66
0.002	0.63	-				
0.003	0.47	-				
0.004	0.37	-				
0.005	-	0.29	67.0	35.5	1.06 (2.12)	157.22 (314.44)
0.01	-	0.26	65.9	34.7	0.90 (1.80)	184.48 (368.96)

The uncertainty limit of *cmc* is  $\pm 3\%$

TABLE-2

Critical Micellar Concentrations and Thermodynamic Parameters of LDS in Presence of 0.001 M of Various Quaternary Ammonium Salts at Different Temperatures

Temp/ K	cmc/mM	$\beta$	$\Delta G_m^0/ \text{kJ mol}^{-1}$	$\Delta H_m^0/ \text{kJ mol}^{-1}$	$T\Delta S_m^0/ \text{kJ mol}^{-1}$
<b>NH<sub>4</sub>Br</b>					
288.15	8.41		-33.71	0.29	34.00
298.15	8.24		-34.75	-1.35	33.40
308.15	8.55	0.60	-35.98	-3.21	32.77
318.15	8.61		-37.12	-5.34	31.78
<b>Me<sub>4</sub>NBr</b>					
288.15	7.96		-34.14	-1.20	32.94
298.15	7.62		-35.44	-8.42	27.02
308.15	7.78	0.61	-36.05	-16.61	19.94
318.15	8.35		-37.43	-25.83	11.60
<b>Et<sub>4</sub>NBr</b>					
288.15	6.99		-35.06	-1.40	33.66
298.15	6.25		-36.74	-13.55	23.19
308.15	6.44	0.63	-37.85	-27.35	10.50
318.15	6.96		-38.73	-42.88	-4.15
<b>Pr<sub>4</sub>NBr</b>					
288.15	4.71		-37.06	28.86	65.92
298.15	3.33		-39.77	4.00	43.77
308.15	3.77	0.65	-40.57	-24.46	16.11
318.15	4.11		-41.52	-56.70	-15.18
<b>Bu<sub>4</sub>NBr</b>					
288.15	1.99		-43.16	71.27	114.42
298.15	1.24		-46.73	45.07	91.80
308.15	1.56	0.76	-47.23	14.78	62.01
318.15	1.59		-48.70	-19.79	28.91

The uncertainties of the  $\Delta G_m^0$ ,  $\Delta H_m^0$  and  $\Delta S_m^0$  are  $\pm 4$ ,  $\pm 3$  and  $\pm 4$  % respectively.

TABLE-3

Cloud Point Data on LDS + Tetrabutylammonium Bromide System

[Bu <sub>4</sub> NBr] (mol dm <sup>-3</sup> )	CP <sup>a</sup> (°C)		
	[LDS] = 0.025 M M	[LDS] = 0.050 M	[LDS] = 0.100
0.30	22.4	22.8	24.4
0.25	23.4	24.2	25.9
0.20	24.6	25.5	28.4
0.15	26.1	27.7	31.6
0.10	28.1	31.6	40.7
0.05	34.8	46.5	>100
0.04	37.8	59.2	>100
0.03	43.6	>100	>100
0.02	60.3	>100	>100
0.01	>100	>100	>100

<sup>a</sup>Reproducibility: ± 0.1 °C