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Conductometric Study of the Thermodynamics of Micellization of Sodium dodecylsulfate (SDS) in the Presence of Some Aromatic Ammonium Salts

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The effect of three organic aromatic salts - Phenyltrimethylammonium (PhTMAB), benzyltrimethylammonium (BzTMAB) and benzyltriethylammonium (BzTEAB) bromides - on the micellization of sodium dodecylsulfate has been investigated by conductometric method. The critical micelle concentration (CMC) values were found to decrease with increase in the concentration of the aromatic ammonium salts. Thermodynamic parameters of micellization were obtained from CMC measurement in the presence of 0.001 M of the three quaternary aromatic ammonium salts in the temperature range 293-313 K at 5 K intervals. The Gibbs free energy values were generally negative in the presence of the aromatic salts and slightly varied with temperature. The micellization process was both enthalpy and entropy driven. Enthalpy-entropy compensation was observed for all the system with a constant compensation temperature values around 302 K and negative intrinsic enthalpy of compensation.

Keywords: Micellization, Aromatic ammonium salts, Thermodynamic parameters, Enthalpy-entropy compensation

INTRODUCTION

Aggregate and micelle formation by surfactant involves a complex interplay of different intermolecular forces with contributions from the solvents, molecular structure of the monomer, temperature, pressure and the presence of other co-solutes [1]. Most of the applications of surfactants in such area as detergency, pharmaceutical and cosmetic formulations, enhanced and tertiary oil recovery, agrochemicals, solubilisation, biochemical research, *etc.* require the addition of other substances such as another surfactant, polar organic compounds, and organic salts (also often called hydrotropes) with a view to improving the performance of the surfactants [2-5].

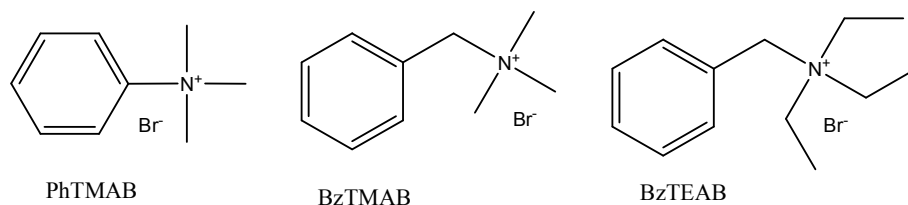
The presence of organic salts in surfactant solutions can significantly affect the micellization process by decreasing the electrostatic repulsion among the head-groups of surfactant molecules and through hydrophobic interactions. These effects lead to a concomitant decrease in the CMC of

the surfactant [6-9].

The micellization of sodium dodecylsulfate (SDS) in the presence of tetraalkylammonium salts ($R_4N^+Br^-$; R = H, CH₃, C₂H₅, C₃H₇, and C₄H₉) has been extensively studied [10-12]. The salts were shown to cause a remarkable decrease in the CMC and enhanced solubilisation of the surfactants. In addition, (C₄H₉)₄N⁺Br⁻ was found to produce cloud point phenomenon in the micellization of lithium dodecylsulfate [13].

Although, the hydrotropic properties of phenyltriethylammonium salts are well documented [14-16], the effect of these salts on the micellar properties of surfactants is scantily reported [16]. In this work, the effects of phenyltrimethylammonium bromide (PhTMAB), benzyltrimethylammonium bromide (BzTMAB) and benzyltriethylammonium bromide (BzTEAB) on the micellar properties of SDS have been studied using conductometric method. The effect of the structural differences in the organic salts on the micellar properties of SDS was also investigated. Thermodynamic properties of the micellization process in the presence of 0.001 mol dm⁻³

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Scheme 1. Structures of the aromatic ammonium salts used in this work

of each of the salts were obtained in the 293-313 K temperature range at 5 K intervals.

EXPERIMENTAL

Materials

PhTMAB, BzTMAB and BzTEAB from Sigma-Aldrich, USA with stated purity > 99% were used as received, SDS was of molecular biology grade also from Sigma-Aldrich, USA. The structures of the organic salts are shown in Scheme 1.

Method

Conductometric titration method involving the titration of a known volume of a concentrated surfactant solution prepared in different aromatic organic salt solutions, into a fixed volume of aqueous solutions of the respective organic salts contained in a thermostatted beaker was employed. Surfactant solutions were prepared by dissolving accurately weighed quantities of surfactants in requisite volumes of distilled water. Distilled water (conductivity < 3 $\mu\text{s cm}^{-1}$, at 298 K) was used for all purposes. All measurements were made at 298 K (except for the temperature dependent studies) in a thermostatted water bath Grant Y14 from Grant Instruments (Cambridge) Ltd, England, maintaining the temperature constant within ± 0.1 K.

The conductivity measurements were made as a function of total SDS concentration at 0.0005, 0.001, 0.002, 0.003, 0.004 and 0.005 mol dm^{-3} of the respective aromatic organic salt. All the conductivity plots showed a linear variation in the specific conductivity values as total surfactant concentration increases in both the pre-micellar and post-micellar regions. Measurements were repeated three times for reproducibility. The uncertainties in CMC determination error did not exceed 3%.

RESULTS AND DISCUSSION

Critical Micelle Concentration

The values of the CMC of SDS in the presence of different concentrations of the aromatic ammonium salts in aqueous systems were determined by conductometric method. The plot of the specific conductivity against SDS concentration in pure aqueous system at 298 K is shown in Fig. 1. Typically, the conductometric plots can be linearly correlated to the surfactant concentrations in both the pre-aggregate and the post-aggregate regions with the point of intersection between the two straight lines given the CMC. The degree of counter-ion dissociation, δ , of the micelle in the presence of the organic salts was obtained from the ratio of the slopes in the post-micellar region to that of the pre-micellar region. The CMC of the surfactants was found to decrease in the presence of these salts with the decrease being dependent on the concentration of the organic salts as shown in Fig. 2 for all the three hydrotropic salts. The observed decrease in the CMC of SDS in the presence of these organic ammonium salts can be explained in terms of the electrostatic interaction between the positively charged ammonium ion and the negatively charged ($-\text{OSO}_3^-$) head group of the surfactant. Such interaction will reduce the repulsion between the polar head group of SDS micelles, which in turn will increase the stability of the ionic micelle. In addition, the organic moieties of the organic ammonium salts interact with the alkyl chain in SDS through hydrophobic bonding. These two factors combined to cause a marked reduction in the CMC of the surfactant in the presence of these salts.

The variation of the CMC of SDS with the concentrations of the organic ammonium salts is displayed in Fig. 2 below and the micellization parameters obtained from the conductometric studies are included in Table 1.

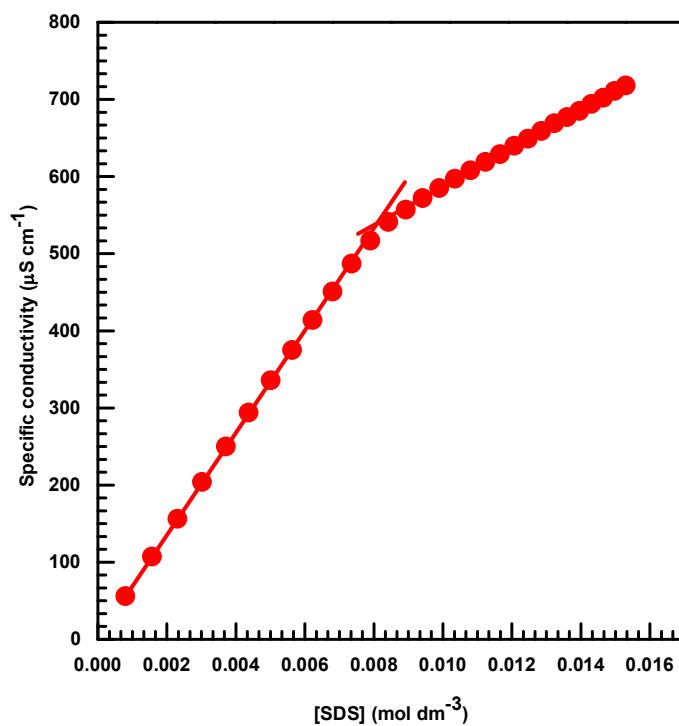


Fig. 1. Variation of specific conductivity with [SDS] in pure aqueous system at 298 K.

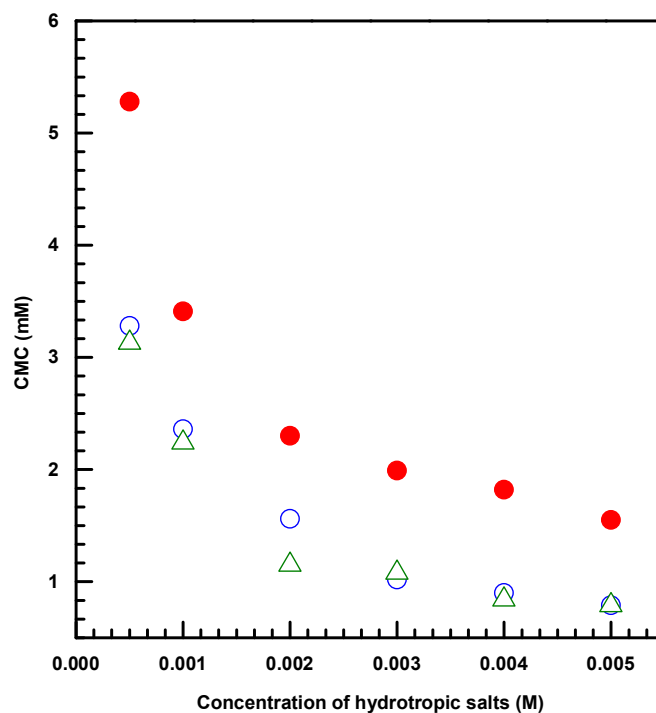


Fig. 2. CMC of SDS as a function of hydrotrope concentrations. (●) PhTMAB, (○) BzTMAB, (Δ) BzTEAB.

Table 1. Critical Micelle Concentration (CMC) and Degree of Counter-ion Dissociation δ , Obtained from Conductometric Study of the Micellization of SDS in Various Concentrations of the Aromatic Ammonium Salts at $298 \pm 0.10 \text{ K}^a$

[Salt] (M)	CMC (mM)	δ
PhTMAB		
0.0000	8.15	0.37
0.0005	5.28	0.37
0.0010	3.41	0.33
0.0020	2.30	0.65
0.0030	1.99	0.62
0.0040	1.82	0.60
0.0050	1.55	0.57
BzTMAB		
0.0005	3.28	0.76
0.0010	2.36	0.70
0.0020	1.56	0.70
0.0030	1.02	0.67
0.0040	0.90	0.55
0.0050	0.79	0.46
BzTEAB		
0.0005	3.13	0.78
0.0010	2.24	0.75
0.0020	1.15	0.72
0.0030	1.08	0.71
0.0040	0.84	0.71
0.0050	0.79	0.67

^aThe standard uncertainties are $u(\text{CMC}) = \pm 0.9\%$; $u(\delta) = \pm 0.075\%$.

The decrease in CMC in the presence of the aromatic ammonium salts is more pronounced with BzTMAB and BzTEAB than in the presence of PhTMAB. This can be attributed to the presence of methylene (CH_2) group in the

former which increases the hydrophobicity of the two salts compared to PhTMAB. This increased in hydrophobicity leads to the marked reduction in CMC of SDS observed. The change in head group from trimethylammonium in

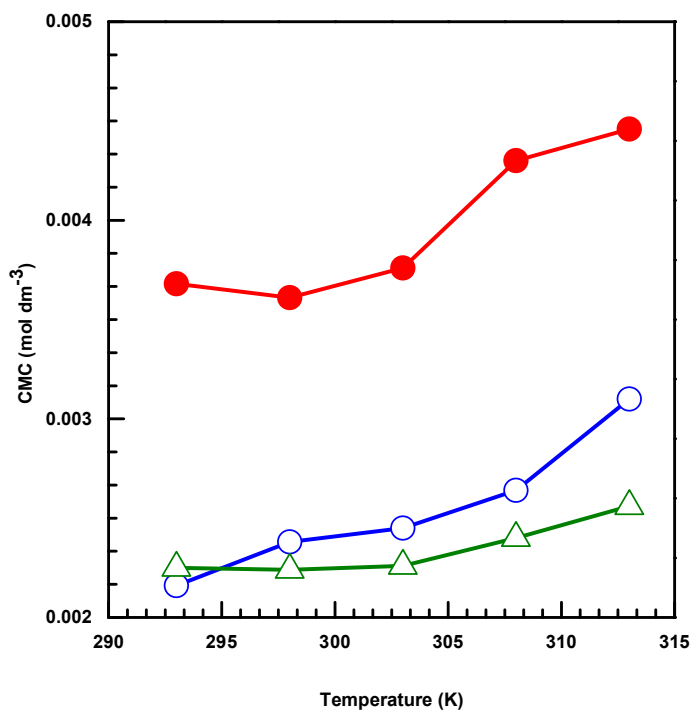


Fig. 3. Temperature dependence of CMC of SDS in the presence of 0.001 M aromatic ammonium salts. (●) PhTMAB, (○) BzTMAB, (Δ) BzTEAB

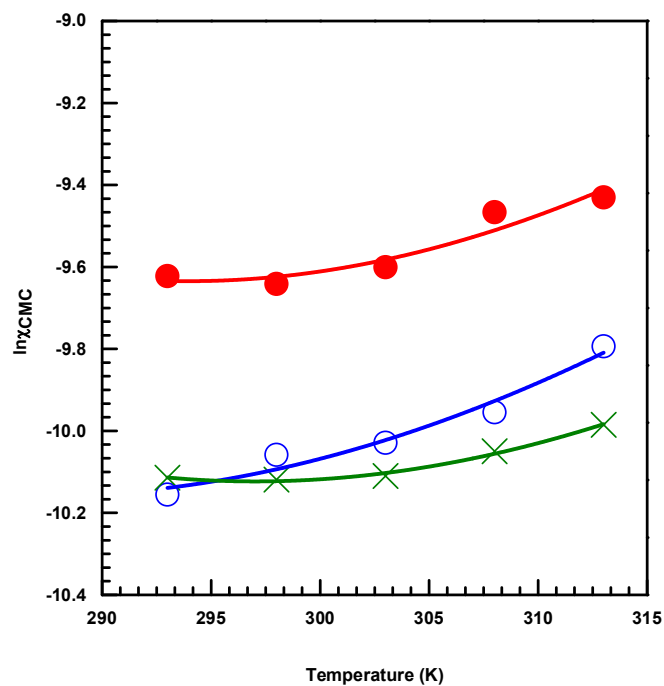


Fig. 4. Variation of $\ln\chi_{CMC}$ with temperature according to the fitting function in Eq. (4). (●) PhTMAB, (○) BzTMAB, (x) BzTEAB.

BzTMAB to triethylammonium in BzTEAB did not result in any significant difference in the effect on CMC by these two salts; this is an indication that the organic cations most probably approached the micellar surface from the phenyl end rather than from the alkylammonium end.

THERMODYNAMICS OF MICELLIZATION

The CMC values of the surfactant in the presence of the organic additives showed a minimum in the plots of the variation of CMC with temperature (Fig. 3). The minimum in these curves is noticed between 298 K and 303 K, which appears to conform to the general finding that the minimum for ionic surfactants with 12 carbon chain lengths is close to room temperature [17,18].

The relevant thermodynamic parameters, such as ΔG_M^o , ΔH_M^o and ΔS_M^o , of micellization were determined on the basis of the phase separation model [19]. Accordingly

$$\Delta G_M^o = (2 - \delta) RT \ln \chi_{CMC} \quad (1)$$

where χ_{CMC} is the value of CMC expressed on a mole fraction basis, defined as;

$$\chi_{CMC} = \frac{CMC}{CMC + [\text{Salt}] + 55.55} \quad (2)$$

The constant term (55.55) in Eq. (2) is the molar concentration of water in aqueous system. The values of the degree of counter-ion dissociation (δ) did not change appreciably with temperature as can be seen in Table 3; hence, the average values of δ were used in computing the thermodynamic parameters. The enthalpy of micellization

can be obtained from the temperature dependence of the CMC using the Gibbs-Helmholtz Equation.

$$\Delta H_M^o = -T^2 \frac{\partial(\Delta G_M^o/T)}{\partial T} = -(2 - \delta) RT^2 \frac{\partial \ln \chi_{CMC}}{\partial T} \quad (3)$$

The temperature dependence of the $\ln \chi_{CMC}$ was fitted to the

equation derived by Kim and Lim for the temperature dependence of CMC [20];

$$\ln \chi_{CMC} = A + B \ln T + C/T \quad (4)$$

where the A, B and C have been determined by a least-square regression analysis. The fitting of the function in Eq. (4) to the variation of $\ln \chi_{CMC}$ with temperature for the micellization of SDS in the presence of 0.001 mol dm⁻³ of each of the organic salts is shown in Fig. 4. The values of A, B, and C obtained from the regression analysis of equation 4 are listed in Table 2. The ΔS_M^o was then determined by

$$\Delta S_M^o = \frac{1}{T} [\Delta H_M^o - \Delta G_M^o] \quad (5)$$

Various thermodynamic parameters of micellization of SDS in the presence of 0.001 mol dm⁻³ of the obtained from the equations above are listed in Table 3.

The calculated ΔG_M^o values for the micellization of SDS in the presence of the three salts decreases with increase in temperature, albeit at a slow rate. This observation had been attributed to enthalpy-entropy compensation effect. The free energy is negative in the whole temperature range studied for micellization of SDS in the presence of the three organic ammonium salts. The average values being -33.32, -30.67 and 31.17 kJ mol⁻¹ for PhTMAB, BzTMAB and BzTEAB respectively with the slight differences were attributed to the structures of the organic ammonium salts.

It can be seen from Table 3 that the micellization process is both entropic and enthalpic driven with changes from entropic to enthalpic as temperature increases. Similar observations have been reported for different surfactants [13,21-23].

There is a very good correlation between the change in enthalpy and change in entropy of micellization with correlation coefficients close to unity for the micellization of SDS in the presence of the three organic ammonium salts studied with regression equation:

$$\Delta H_M^o = \Delta H^* + T_C \Delta S_M^o \quad (6)$$

The equation above suggests that the enthalpic change consists of two components. The first component ΔH^* is

Table 2. Regression Parameters for the Dependence of $\ln\chi_{\text{CMC}}$ on Temperature According to Eq. (4)^a

Salt	A	B	C	R ²
PhTMAB	-787.08 ± 516.94	116.32 ± 77.00	34197.53 ± 23314.36	0.92
BzTMAB	-666.60 ± 470.23	98.55 ± 70.05	28326.63 ± 21207.81	0.96
BzTEAB	-700.64 ± 95.65	103.16 ± 14.25	30637.80 ± 4313.83	0.99

^aThe uncertainties in the parameters are based on 95% confidence limit.**Table 3.** Thermodynamic Parameters for the Micellization of SDS in the Presence of 0.001 M Aromatic Ammonium salts at Different Temperatures^a

T (K)	CMC (mM)	δ	ΔG_M^0 (kJ mol ⁻¹)	ΔH_M^0 (kJ mol ⁻¹)	ΔS_M^0 (kJ mol ⁻¹)
PhTMAB					
293	3.68	0.63	-32.42	+3.75	123.47
298	3.61	0.63	-33.04	-4.78	94.82
303	3.76	0.65	-33.45	-13.32	66.44
308	4.30	0.54	-33.53	-21.86	37.89
313	4.46	0.63	-33.94	-30.40	11.32
BzTMAB					
293	2.16	0.75	-30.13	-5.56	83.86
298	2.38	0.78	-30.35	-10.53	66.46
303	2.45	0.78	-30.77	-15.54	50.29
308	2.64	0.79	-31.05	-20.52	34.17
313	3.10	0.79	-31.04	-25.51	17.67
BzTEAB					
293	2.25	0.78	-30.13	+4.22	117.65
298	2.24	0.75	-30.53	-1.05	99.77
303	2.26	0.76	-30.77	-6.32	82.35
308	2.40	0.78	-31.05	-11.59	64.96
313	2.56	0.78	-31.04	-16.86	48.07

^aThe standard uncertainties are u (CMC) = ±0.9%; u (δ) = ±0.075%; u (ΔG_M^0) = ±0.5%; u (ΔH_M^0) = 0.5%; u (ΔS_M^0) = 0.71%.

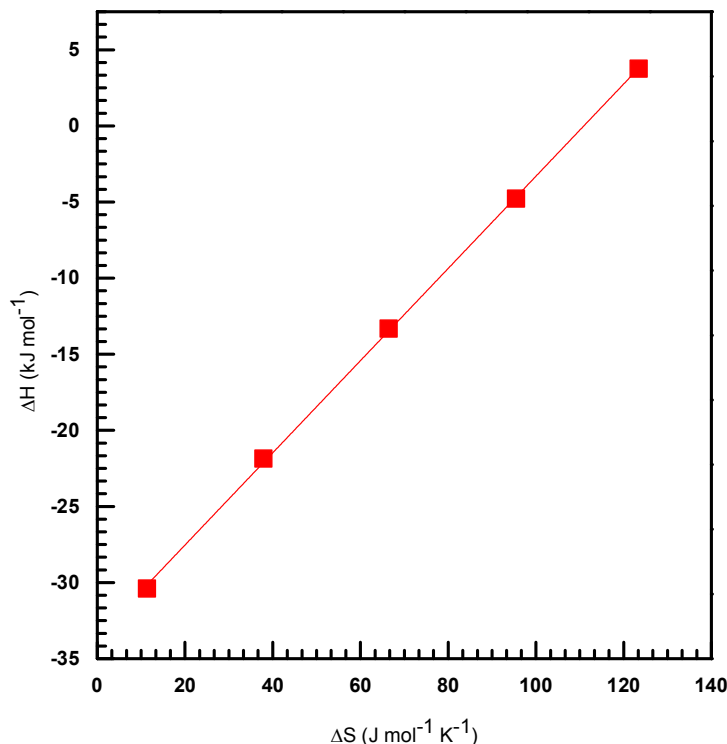


Fig. 5. Typical enthalpy-entropy plot for the micellization of SDS in the presence of 0.001 M PhTMAB.

independent of the entropy change and the second one $T_c \Delta S_M^o$ is proportional to it. The slope T_c is known as the compensation temperature and interpreted as a measure of the desolvation process of micellization. The values obtained was essentially the same (303.54 ± 2.46 , 302.91 ± 2.52 and 302.90 ± 1.74 K) for the micellization process in the presence of the three organic salts studied which implies that the slight structural differences in the organic additives has no effect on the desolvation part of the micellization process. The values of the intrinsic enthalpy gain, ΔH^* , were -33.59 ± 0.19 , -30.83 ± 0.14 and -31.33 ± 0.15 kJ mol^{-1} , respectively, in the presence of PhTMAB, BzTMAB and BzTEAB. The negative values of this intrinsic enthalpy gain indicate that the micellization process is favoured with or without any entropic contribution. A typical enthalpy-entropy compensation plot is shown in Fig. 5.

CONCLUSIONS

This study shows that the micellization of SDS is significantly affected by the aromatic ammonium salts by causing a marked reduction in the CMC of the surfactants. The decrease in CMC was found to be dependent on the concentration of the salts. The presence of methylene group in two of the salts also contributed to the observed reduction in CMC. However, head group modification of the salts appeared not to impact significantly on the reduction in CMC of the surfactant.

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