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Effect of Temperature on the Micelle Formation of Anionic Surfactants in the Presence of Different Concentrations of Urea

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ABSTRACT: The micellar behaviour of anionic surfactants, potassium dodecyl sulphate, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate (KDS, NaDS and NaDBS) in presence of different concentration of urea (0.5-2.0 M) in 2.5% butanol-water systems at fixed temperature (35°C) has been measured by conductivity measurements. The CMC values of anionic surfactants increased with the addition of urea, butanol- water systems at fixed temperature (35°C). Various thermodynamic parameters have been reported.

Keywords: Potassium dodecyl sulphate (KDS); Sodium dodecyl benzene sulphonate (NaDBS); Sodium dodecyl sulphate (NaDS); Critical micelle concentration (CMC); Conductivity (□).

I. INTRODUCTION

The properties of aqueous solutions of aliphatic monohydric alcohols are of interest in the field of surface chemistry; especially their effect on the phenomenon of micellization of surfactants. Fendler *et. al.* (1975) studied that water-alcohol surfactant systems are so frequently used as media in the studies of chemical equilibria and reaction rate, it is very essential to investigate the nature of the alkyl groups in the alcohol on the CMC of surfactants. Several reviews exist on micellization of surfactants in aqueous media were studied by Linfied *et. al.* (1976). Bahadur *et. al.* (1982, 1983) studied that micelle formation in aqueous solution is well known to be affected by a number of environmental factors such as pH, ionic strength, temperature and the presence of inorganic and organic additives. The micelle formation in an aqueous solution is known to be affected by inorganic additives and there have been many investigations concerning the effects of organic additives on the CMC of anionic surfactants. Bahadur *et. al.* (1998) noticed the effect of organic additives on the micellar behaviour of ionic and non-ionic surfactants in water has been well studies by some authors with the outcome that aliphatic alcohols have been of particular interest.

Enea *et. al.* (1982) studied the use of urea as a denaturant of proteins is well known. Khuarski *et. al.* (1984) observed that the presence of urea and its derivatives modifies the properties of aqueous solutions. Two different mechanisms have been proposed to explain action of urea on aqueous solutions. One is that urea acts as a water structure breaker (indirect mechanism). The other is that urea participates in the solvation of hydrophobic chains in water by replacing some water molecules in the hydration shell of the solute (direct-mechanism). Kabir-ud-din *et. al.* (1996) reported that critical micelle concentrations (CMC) of ionic and non-ionic surfactants significantly increase with the addition of urea in aqueous solutions. Asakawa *et. al.* (1995) studied the action of urea in aqueous solution showed that urea had a negligible influence on the water structure. Bahadur *et. al.* (2003) observed the effect of polymer as additives on sodium dodecyl sulphate. Abdul- Rahem *et. al.* (2009) noticed the physiochemical properties of hydroxyl mixed ether HMEn surfactants and their interaction with sodium dodecyl sulphate. Cohen *et. al.* (2009) studied the effect of calcium ions concentration on the foaming power of anionic surfactants. Parekh *et. al.* (2011) studied that anionic-cationic surfactants systems of sodium dodecyl trioxyethylene sulfate with cationic Gemini surfactants. Patel et. al. (2009) observed that micellization of sodium dodecyl sulfate and polyoxyethylene dodecyl ether in solution. Varade *et. al* (2005) noticed that miceller behaviour of mixture of sodium dodecyl sulfate and dodecyldimethylamine oxide in aquous solution. Bharatiya *et. al* (2009) observed that urea induced demicellazition of pluronic L-64 in water. Kumar *et. al.* (2014) studied the effect of urea and butanol on the micelle formation of anionic surfactants at different temperature.

II. EXPERIMENTAL PROCEDURE

A. Materials

Extra pure sodium dodecyl sulphate (B.D.H.) after recrystallization was used for the preparation of potassium dodecyl sulphate (KDS). Potassium dodecyl sulphate was prepared by direct metathesis. After recrystallization, it was used for physical properties. Sodium dodecyl benzene sulphonate was purchased from Loba Chemie Pvt. Limited, Mumbai, India. Methanol, propanol and butanol were all B.D.H. Laboratory reagent while urea was purchased from Merck (Merck Schuchardt OHG, Germany). Triple distill water obtained from all pyrex glass assembly was used throughout studies.

B. Measurement

Butanol-water mixtures (2.5%) of several composition of urea (0.5-2.0 M) were prepared by mixing requisite quantity of alcohol in water. Stock solution of surfactants was prepared by weighing. The conductance measurements of surfactant solutions were made by Elico conductivity meter (Model CM-180) at a frequency of 1000 Hz using platinized electrode of known cell constant. After measuring the conductivity of solvent, small volume of the stock solution for dilution was added and the conductivity noted after each addition and thorough mixing to a constant reading. The conductivity (κ) was calculated after applying the solvent correction.

The CMC values were determined at the breakpoint of nearly two straight line portion in the conductivity versus concentration plots. The CMC of the surfactants in the presence of urea, butanol in water at fixed temperature (35ºC).

III. RESULTS

The 'κ' values of KDS in pure water at different temperatures (30-45°C) are reported in Table 1. These values were found in close agreement to those reported previously. Also the CMC values obtained from κ vs. C plots in pure water were the same (Table 2) as reported earlier. The 'κ' values of, NaDS using different concentration of urea (0.5-2.0M) in 2.5% butanol-water system at 35°C are reported in Table 3 respectively.

The increase in κ values in presence of urea at fixed temperatures (35ºC) and in butanol-water systems studied may be explained as:

1. Effect of temperature: Increasing ionic mobility with increase in temperature.

2. Effect of alkanols: (a) Change in the nature of the solvent.

(b) Partitioning of alcohol between water and micellar phase, the alcohol form mixed micelles with the surfactant by the incorporation of the hydrocarbon part of the alcohol in micelles.

(c) Increase in the number of the free counter ions from the double layer.

(d) The liberation of surfactant ion from the micelle.

Table 1: Conductivity 'κ' for KDS in pure water at different temperatures (30-45°C).

	Concentration of KDS in Mole litre^{-1}	'κ' x 10^6 (Ohm^{-1} cm^{-1})			
		Temperature °C			
		30ºC	**35ºC**	**40ºC**	45°C
Pure water	0.002	70	100	140	170
	0.004	110	160	200	240
	0.006	165	220	265	310
	0.008	210	270	325	385
	0.010	230	320	375	445
	0.012	270	360	430	490
	0.014	295	395	480	535

Table 2: CMC values for KDS, NaDS and NaDBS in pure water at different temperatures (30-45ºC).

Temperature	CMC x 10^3		CMC x 10^4
	KDS	NaDS	NaDBS
30ºC	8.53	8.35	10.0
35ºC	9.00	8.50	12.5
40ºC	9.25	8.65	13.8
45ºC	9.50	8.80	15.0

3. Effect of urea: The presence of urea and its derivatives modifies the properties of alkanol-water systems. Urea is supposed to act as water structure breaker and its derivatives participate in solvation of hydrophobic chains in water by replacing some water molecules in the hydration shell of the solute. The CMC values for each system were obtained by 'κ' vs. C plots (some representative set of figures are reported in Fig. 1) and all the values so obtained are reported in Table 4.

Table 3: Conductivity 'κ' for NaDS in the presence of different concentration of urea (0.5-2.0M) and 2.5% butanol-water system at 35°C.

	Concentration of NaDS in Mole litre^{-1}	K x 10^6 (Ohm^{-1} cm^{-1})			
		Concentration of urea (M)			
		0.5M	1.0M	1.5M	2.0M
2.5% butanol-water system	0.002	490	610	700	800
	0.004	660	790	900	1000
	0.006	830	690	1100	1125
	0.008	960	1100	1240	1260
	0.010	1100	1230	1300	1395
	0.012	1240	1370	1495	1505

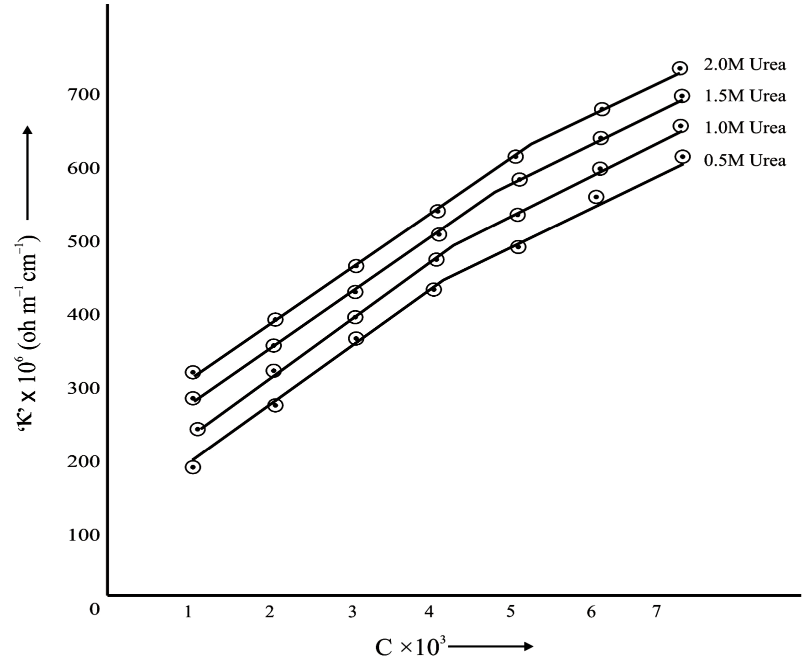

Fig. 1. Plots of Conductivity 'Λ_M' Vs Concentration of KDS in Presence of Different Concentration of Urea and 2.5% Butanol-Water System At 35 °C.

The molar conductance (Λ_M) calculated from the conductivity data of the surfactant solution, decreases with increasing concentration of surfactants (KDS, NaDS and NaDBS). A steep decrease in Λ_M values upto 0.0025 M surfactants concentration (KDS, NaDS) which afterwards decrease slowly with increasing concentration of surfactants. The similar trends were observed in all the systems. However in NaDBS the steep decrease in Λ_M values were noticed at the concentration of 0.00025 M. This may be due to the tendency of the surfactants to form aggregates at higher concentrations. However, the CMC values could not be determined from the plot of Λ_M vs. $\sqrt{C}$ (Fig. 2), which are concave upwards with increasing slopes. The general equation (1) was used to determine the behaviour of surfactant solutions which holds good for all the system as well as at different temperatures.

$$\text{Log}\,\Lambda_M = \text{A} + \text{B}\,\text{logC} \qquad ....(1)$$

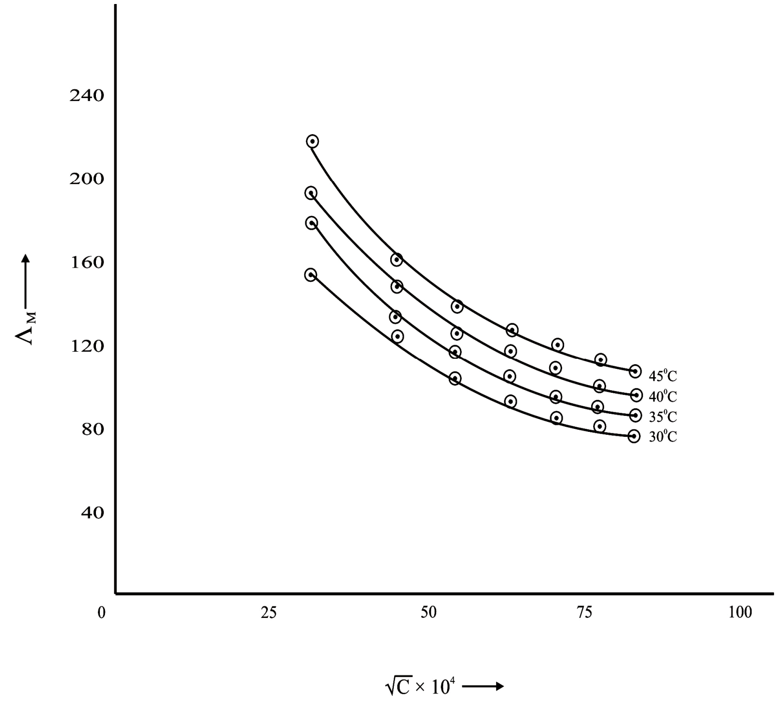

Fig. 2. Plots of Molar Conductance Λ_M vs Square Root of Concentration of KDS in Presence of 0.5 M Urea in 2.5% Butanol-Water System at Different Temperatures.

Table 4: CMC values for KDS, NaDS and NaDBS in presence of different concentration of urea (0.5-2.0M) and 2.5% butanol-water system at 35°C.

Urea concentration (M)	CMC x 10^3		CMC x 10^4
	KDS	NaDS	NaDBS
0.5M	4.10	5.05	7.05
1.0M	4.25	5.32	7.52
1.5M	4.75	5.58	8.00
2.0M	4.95	6.00	8.39

Table 5: Values for constant A (log $\Lambda_{C=1}$) for KDS, NaDS and NaDBS in the presence of different concentration of urea (0.5-2.0M) and 2.5% butanol -water system at 35°C.

Concentration of urea (M)	Surfactants		
	NaDBS	NaDS	KDS
0.5M	47.31	8.91	7.49
1.0M	56.23	10.0	8.41
1.5M	63.09	10.59	8.91
2.0M	79.43	11.88	10.00

The values of A for all the surfactant in different urea-butanol-water systems (Table 5) log Λ_M for zero values of log C (i.e., C = 1) and B (Table 6) were determined by extrapolation of the linear plots of log Λ_M vs. log C. These extrapolated values of a constant A (i.e., log $\Lambda_{C=1}$) signify the limiting molar conductance and are only of theoretical importance, since it was impossible to prepare such concentrated solutions of surfactants due to their low solubility. The standard Gibbs energies of micellization (ΔG^o), in presence of urea (0.5-2.0 M) and 2.5% butanol-water system at 35°C were calculated from equation (2) for KDS, NaDS and NaDBS and are given in Table 7.

$$\Delta G^0 = 2RT \ln CMC_x \qquad ...(2)$$

Table 6: Values for constant B for KDS, NaDS and NaDBS in the presence of different concentration of urea (0.5-2.0M) and 2.5% butanol-water system at 35°C.

Concentration of urea (M)	Surfactants		
	KDS	NaDS	NaDBS
0.5M	0.48	0.57	0.46
1.0M	0.48	0.57	0.46
1.5M	0.48	0.57	0.46
2.0M	0.48	0.57	0.46

Table 7: Thermodynamic parameters for KDS, NaDS and NaDBS in the presence of different concentration of urea (0.5-2.0 M) and 2.5% butanol-water system at 35°C.

(a) Thermodynamic parameter for KDS.

Concentration of urea (M)	KDS		
	$-\Delta G^o$ (kJ/mole)	ΔS^o (kJ/mole)	ΔH^o (kJ/mole)
0.5M	29.47	0.257	14.11
1.0M	28.53	0.139	
1.5M	27.94	0.136	
2.0M	27.63	0.134	

(b) Thermodynamic parameter for NaDS.

Concentration of urea (M)	NaDS		
	$-\Delta G^o$ (kJ/mole)	ΔS^o (kJ/mole)	ΔH^o (kJ/mole)
0.5M	26.99	0.140	16.23
1.0 M	26.76	0.130	
1.5M	26.52	0.129	
2.0M	26.05	0.126	

(c) Thermodynamic parameter for NaDBS.

Concentration of urea (M)	NaDBS		
	$-\Delta G^o$ (kJ/mole)	ΔS^o (kJ/mole)	ΔH^o (kJ/mole)
0.5M	37.12	0.171	16.39
1.0M	36.78	0.179	
1.5M	36.43	0.177	
2.0M	36.19	0.176	

The standard enthalpy change of micellization (ΔH^o) per mole of monomer of KDS, NaDS and NaDBS were calculated from linear plots of log CMC_x vs. 1/T (Fig. 3) using equation (3) and are 14.11, 16.23, 16.39 kJ/mole respectively.

$$\log CMC_x = -\frac{\Delta H^o}{2.303\,RT} + C \quad \text{....(3)}$$

The standard entropies of micellization (ΔS^o), in presence of urea (0.5-2.0 M) and 2.5% butanol-water system at 35°C for KDS, NaDS and NaDBS were calculated from equation (4) and are given in Table 7

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad \text{....(4)}$$

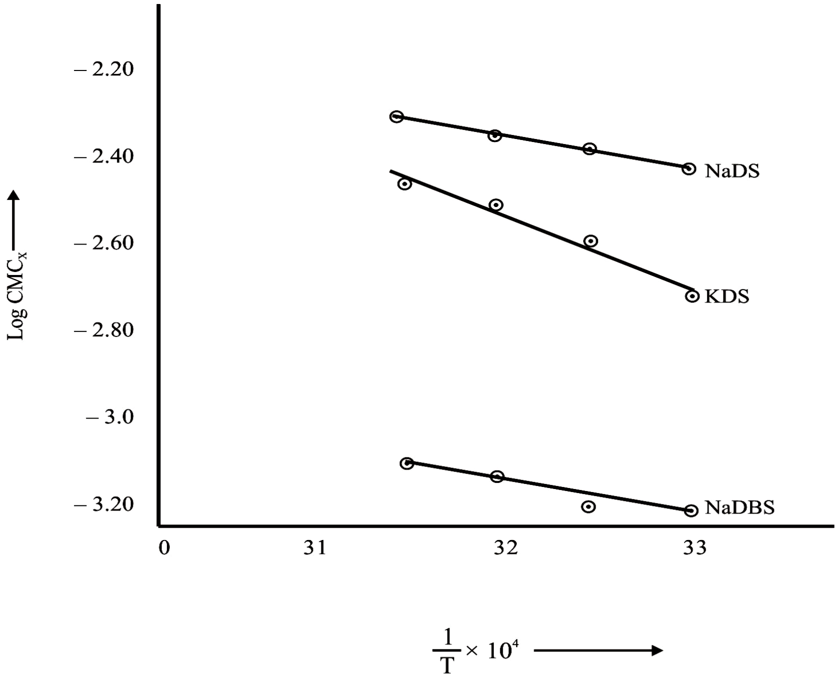

Fig. 3. Plots of Log CMC$_x$ Vs $\frac{1}{T}\times 10^4$ of Surfactants in Presence of 0.5 M Urea in 2.5% Butanol-Water System at Different Temperatures.

IV. DISCUSSION

Micelle formation is assumed to occur when the energy released as a result of aggregation of hydrocarbon chain of the monomers is sufficient to overcome the electric repulsions between ionic head groups and to balance the decrease in entropy accompanying aggregation. It has also been noticed (Table 4) that CMC values of KDS, NaDS and NaDBS in the presence of 0.5-2.0M urea in 2.5% butanol-water system at 35°C shows a continuous increase with increase in concentration of urea. The addition of urea to the micellar solution is well known to increase the CMC and is related to the free energy of transfer of an alcohol molecule from the water to micellar phase.

It may be suggested that in the presence of these butanol, the polar groups at the micelles surface would lead to reduction of the effect due to repulsion of the charged polar head groups and hence the CMC decreases. The hydrophobic effect associated with the hydrophobic moiety of the alkanol molecules also favours micellization and will increase as the length of hydrocarbon chain of the alkanol increases. This explains the decreased lowering of the CMC as the number of methylene group increases in alkanol series. Table 5 reveals that the values of A increase with increasing the concentration of urea (0.5-2.0M) in 2.5% butanol-water system. The values of constant B were obtained from the slopes of plots of log Λ_M vs. logC for KDS, NaDS and NaDBS in all the systems, and are reported in Table 6. The values of B were also found independent of concentration of urea (Table 6) in 2.5% butanol-water system at 35°C for all the surfactants.

V. CONCLUSION

In fact the CMC lowering of surfactants by the small addition of alcohols may be due to their direct action on water structure and the subsequent addition may cause secondary effects such as their solubilization in micelle and decrease of hydrophobic effect. This further supports the view that the formation of the cavity of more ordered water molecules is favored by the long hydrocarbon chain of the alcohols. In the presence of such a cavity, a decrease in CMC is not unexpected. The role of water cavity in the micelles formation has been further verified by studying the effect of urea on CMC. Urea is a strong water structure breaker in presence of alcohols it may destroy the cavity of ordered water structure. It is, therefore, expected that the CMC should increase with the increase in the concentration of urea.

These results indicate that the addition of urea results in the breaking of water structure even at the concentration of alcohols where it is expected to be more ordered. This partition of additive between the solution and the micelles may be sensitive to the structure of the polar third component and the temperature.

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