



Original Article

Studies of Surface Tension of Anionic Surfactants in the Presence of Urea Derivatives and Butanol at 35°C

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A B S T R A C T

Micellization of anionic surfactants, potassium dodecyl sulphate, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate (KDS, NaDS and NaDBS) in presence urea derivatives (2.0 M) in 2.5% alkanol-water systems at constant temperature (35°C) were measured using Agla micrometer syringe. The CMC values of anionic surfactants decreased with the increase in methyl group in urea derivatives, monohydric alcohols (butanol) water systems at constant temperature.

Keywords: Potassium dodecyl sulphate (KDS); Sodium dodecyl benzene sulphonate (NaDBS); Sodium dodecyl sulphate (NaDS); Critical micelle concentration (CMC); Surface Tension (γ).

1. INTRODUCTION

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.^{1, 2} noticed the effect of organic additives on the micellar behaviour of ionic and non-ionic surfactants in water has been well studied by some authors with the outcome that aliphatic alcohols have been of particular interest. Enea et. al.³ studied the use of urea as a denaturant of proteins is well known. Khurski et. al.⁴ observed that the presence of urea and its derivatives modifies the properties of

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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. ⁵ 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. ⁶ studied the action of urea in aqueous solution showed that urea had a negligible influence on the water structure. Bahadur et. al. ⁷ observed the effect of polymer as additives on sodium dodecyl sulphate. Abdul- Rahem et. al. ⁸ noticed the physiochemical properties of hydroxyl mixed ether HME_n surfactants and their interaction with sodium dodecyl sulphate. Cohen et. al. ⁹ studied the effect of calcium ions concentration on the foaming power of anionic surfactants. Parekh et. al. ¹⁰ studied that anionic-cationic surfactants systems of sodium dodecyl trioxyethylene sulfate with cationic Gemini surfactants. Patel et. al. ¹¹ observed that micellization of sodium dodecyl sulfate and polyoxyethylene dodecyl ether in solution. Varade et. al ¹² noticed that miceller behaviour of mixture of sodium dodecyl sulfate and dodecyl dimethylamine oxide in aqueous solution. Bharatiya et. al ¹³ observed that urea induced demicellization of pluronic L-64 in water. Kumar et. al ^{14, 16} studied that effect of urea, urea derivatives and monohydric alcohol on the micelle formation of anionic surfactants at different temperature as well as constant temperature .

2. EXPERIMENTAL PROCEDURE

2.1 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.

2.2 Measurement: Alcohol-water mixtures (2.5%) of several compositions of urea derivatives (2.0 M) were prepared by mixing requisite quantity of alcohol in water. Stock solution of surfactants was prepared by weighing. The surface tension () measurements of surfactant solutions were made by Agla micrometer syringe (Burroughs Wellcome Co. Ltd. England). The CMC values were determined at the breakpoint of nearly two straight line portion in the vs. log C plots. The CMC of the surfactants in the presence of urea derivatives, monohydric alcohols in water at constant temperature range (35°C).

3. RESULTS

The surface tension (-values) in the presence of urea derivatives (2.0M) in 2.5% alkanol-water systems at constant temperature 35°C were measured using Agla micrometer syringe (Burroughs Wellcome Co. Ltd. England) . Studies however could not be made for higher concentrations of alkanols due to their low solubility of KDS, NaDS and NaDBS in the presence of urea derivatives (2.0M) in 2.5% alkanol-water systems. The CMC values of KDS, NaDS, NaDBS in pure water as well as at constant temperature are reported in Table (1-2). The -values of KDS, NaDS and NaDBS using concentration of urea derivatives (2.0M) in 2.5% butanol-water system at constant temperature 35°C are reported in Table (3-5) respectively. The -values in all the systems decrease with increasing surfactants concentration which may be

due to increasing tendency to form aggregates with increasing surfactants concentration.

The decrease in γ -values in presence of urea derivatives and in butanol-water systems studied may be explained as:

1. Effect of butanols: The addition of alcohols show a decrease in surface tension for a given surfactant concentration which may be due to increase in size of the micelle as alcohol is also incorporated in to the micelle. These observations are in close agreement with literature.

2. Effect of urea and its derivatives: The lowering in γ -values with increasing concentration of urea may be explained in terms of strengths of cohesive forces. Stronger hydrophobic interactions produces higher cohesive forces for urea due to effective caging of bulk water around them. Hence it develops higher integrated molecular forces among urea with stronger adhesion with glass.

The CMC values shifts toward lower values (Table 2) with increasing number of methylene groups in the urea derivatives. It may therefore be proposed that increasing number of methylene groups in urea derivatives showing hydrophobic effect associated with the hydrophobic moieties of the surfactant as well as the alkanols. This gives rise to increase in HLB scale and there by showing reduction in CMC.

4. DISCUSSION

In fact the lowering of CMC 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 urea (polar third component) and the temperature.

The inclusion of alcohol molecules into the surfactant micelle is clearly reflected from the decrease in slopes above the CMC. It is also clear that the inclusion effect is stronger for alcohols with larger alkyl chain which brings about the reduction of the surface- charge density on the micelle.

The presence of urea in the soap solutions breaks the hydrogen- hydrogen bonds, thereby weakening the cohesive forces existing between the water molecules. The 'pushing out' tendency for the hydrophobic portion is thus lessened with the result that larger proportion of single soap molecule can remain in solution. Micelle formation would, therefore take place at higher soap concentration.

Table 1: CMC values for KDS, NaDS and NaDBS in pure water at different temperatures (30-45°C).

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

Table 2: Values of CMC for KDS, NaDS and NaDBS in presence of urea and its derivatives (2.0 M) and 2.5% butanol-water system at 35°C obtained by vs. log C plots

2.5% butanol-water system	CMC × 10 ³		CMC × 10 ⁴
	KDS	NaDS	NaDBS
Urea	4.95	6.00	8.39
N-methyl urea	4.20	4.93	7.65
N, N ¹ dimethyl urea	3.40	4.66	6.60
Tetramethyl urea	2.50	4.39	6.00

Table 3: Values of surface tension () for KDS in the presence of urea derivatives (2.0 M) and 2.5% butanol-water system at 35°C.

2.5% butanol-water system	Concentration of KDS in Mole litre ⁻¹	Concentration of urea derivatives (2.0 M)		
		N-methyl urea	N, N ¹ dimethyl urea	Tetramethyl urea
		(dyne cm ⁻¹)	(dyne cm ⁻¹)	(dyne cm ⁻¹)
	0.001	24.0	20.5	18.0
	0.002	17.5	16.0	14.8
	0.003	15.0	13.3	11.8
	0.004	14.0	12.3	10.8
	0.005	13.5	11.8	10.0
	0.006	13.0	11.5	9.5
	0.007	12.3	11.3	8.8

Table 4: Values of surface tension () for NaDBS in the presence of urea derivatives (2.0 M) and 2.5% butanol-water system at 35°C.

2.5% butanol-water system	Concentration of NaDBS in Mole litre ⁻¹	Concentration of urea derivatives (2.0 M)		
		N-methyl urea	N, N ¹ dimethyl urea	Tetramethyl urea
		(dyne cm ⁻¹)	(dyne cm ⁻¹)	(dyne cm ⁻¹)
	0.0002	39.3	37.5	35.7
	0.0004	38.3	34.6	33.2
	0.0006	37.9	33.8	32.7
	0.0008	36.8	33.7	32.5
	0.0010	34.7	33.6	32.4
	0.0012	34.5	33.4	32.2

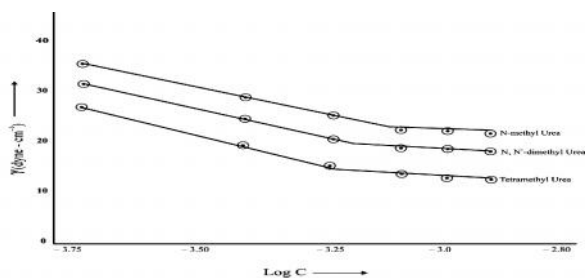


Fig 1: plots of surface tension vs log c of nadbs in presence of 2.0 m urea derivatives in 2.5% butanol-water system at 35 °c.

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