STUDIES OF ANIONIC SURFACTANTS IN THE PRESENCE OF ADDITIVES

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ABSTRACT

Surface tension of anionic surfactants, potassium dodecyl sulphate, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate (KDS, NaDS and NaDBS) in presence of urea (0.5M) in 2.5% alkanol-water systems at different temperature (30-45ºC) were measured using Agla micrometer syringe. The CMC values of anionic surfactants increased with the addition of urea, monohydric alcohols (methanol, propanol and butanol) water systems at different temperature. Various thermodynamic parameters have been reported.

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

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. (1982-83) 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 that effect of urea and monohydric alcohol on the micelle formation of anionic surfactants at different temperature.

Experimental Procedure:

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.

Measurement:

Alcohol-water mixtures (2.5%) of several composition of urea (0.5M) were prepared by mixing requisite quantity of alcohol in water. Stock solution of surfactants was prepared by weighing. The surface tension(γ) 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 γ vs. log C plots. The CMC of the surfactants in the presence of urea, monohydric alcohols in water at different temperature range (30-45ºC).

Results:

The surface tension (γ-values) in the presence of urea (0.5M) in 2.5% alkanol-water systems at different temperatures (30-45°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 (0.5M) in 2.5% alkanol-water systems. The CMC values of KDS, NaDS, NaDBS in pure water are reported in Table (1). The CMC values of KDS, NaDS, NaDBS in the presence of urea (0.5M) in 2.5% alkanol-water systems at different temperatures (30-45°C) are reported in Table (2). The **γ**-values of KDS, NaDS and NaDBS using 0.5M urea in 2.5% butanol-water system at different temperatures (30-45°C) are reported in Table (3-4) respectivily. The **γ**-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 at different temperatures and in different alkanol-water systems studied may be explained as:

1. *Effect of temperature*: Increased kinetic energy tends to overcome net attractive forces of bulk liquid such that cohesive forces between water molecules are decreased which ultimately favours aggregation with increasing surfactants concentration.   The decrease in surface tension with temperature is due to the expansion of surface

2. *Effect of alkanols*: 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.

3. *Effect of urea*: 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 plots of γ vs. log C (Fig 1) for each system suggest the CMC values which are in close agreement with those obtained by conductivity data reported in Tables (1-2). Table 2 reveals that CMC values of KDS, NaDS and NaDBS in the presence of 0.5 M urea in 2.5% butanol-water system increase with increase in temperatures. An increase in temperature would have been expected to increase the CMC value since the kinetic energy of the monomers would have been raised which enables them to overcome the attraction due to aggregation of the hydrocarbon chain.
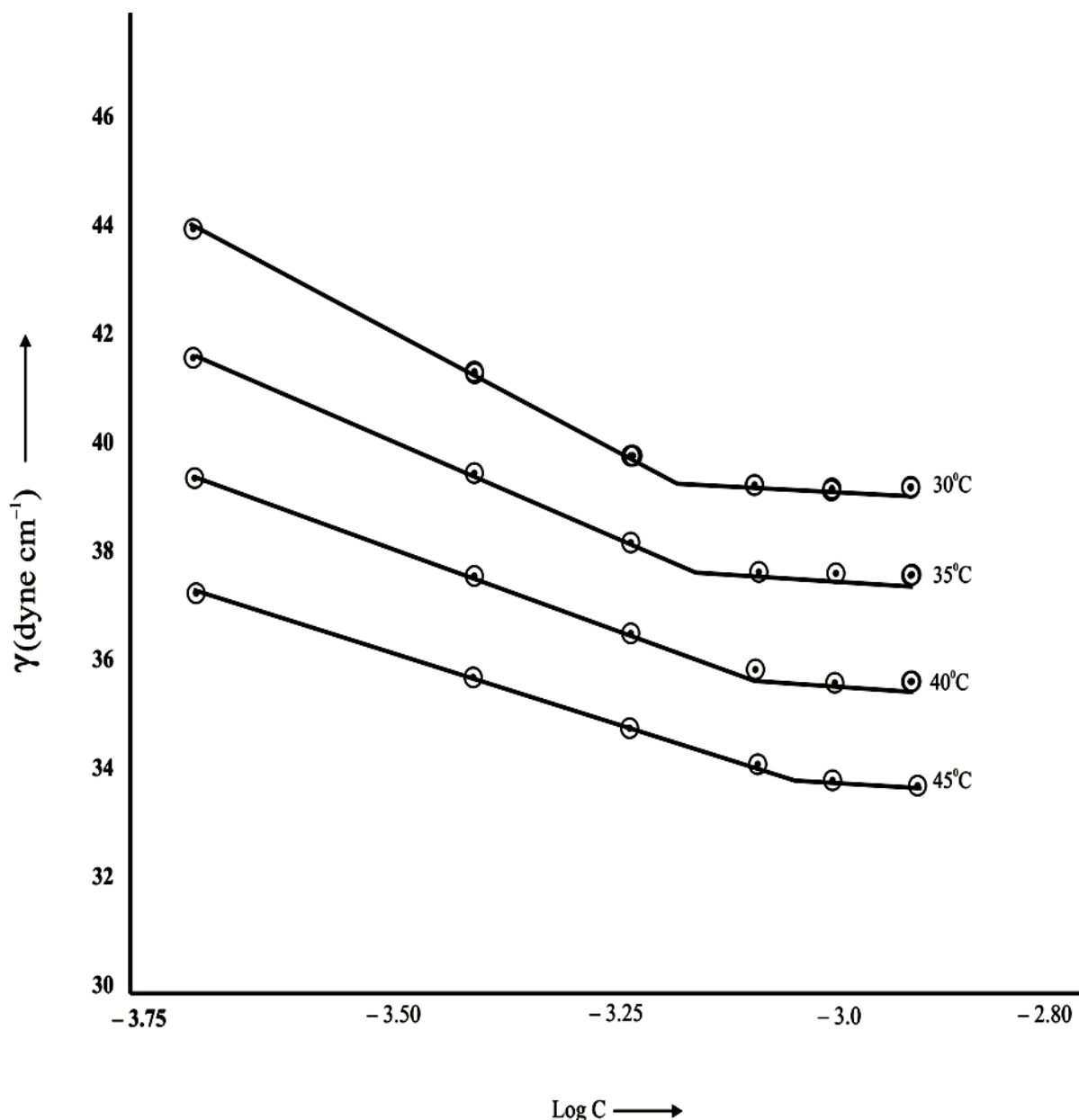
FIGURE 1:   PLOTS OF SURFACE TENSION VS Log C OF NaDBS IN PRESENCE OF

0.5 M UREA IN 2.5% BUTANOL-WATER SYSTEM AT DIFFERENT TEMPERATURES.

The standard Gibbs energies of micellization (ΔG^o), in presence of urea (0.5M) and 2.5% butanol-water system at different temperatures (30-45ºC) were calculated from equation (1) for KDS, NaDS and NaDBS and are given in Table (5).

$$\Delta G^0 = 2RT \ln CMC_x \qquad\qquad ....(1)$$

The standard enthalpy change of micellization (ΔH°) per mole of monomer of KDS, NaDS and NaDBS were calculated from linear plots of log CMC$_x$ vs. 1/T (Fig 2) using equation (2) and are 14.11, 16.23, 16.39 kJ/mole respectively.

$$\log \mathrm{CMC}_x = -\frac{\Delta H^{\circ}}{2.303\,RT} + C \qquad \text{....(2)}$$

The standard entropies of micellization (ΔS^{o}), in presence of urea (0.5 M) and 2.5% butanol-water system at different temperatures (30-45ºC) for KDS, NaDS and NaDBS were calculated from equation (3) and are given in Table (6)

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \qquad \text{....(3)}$$
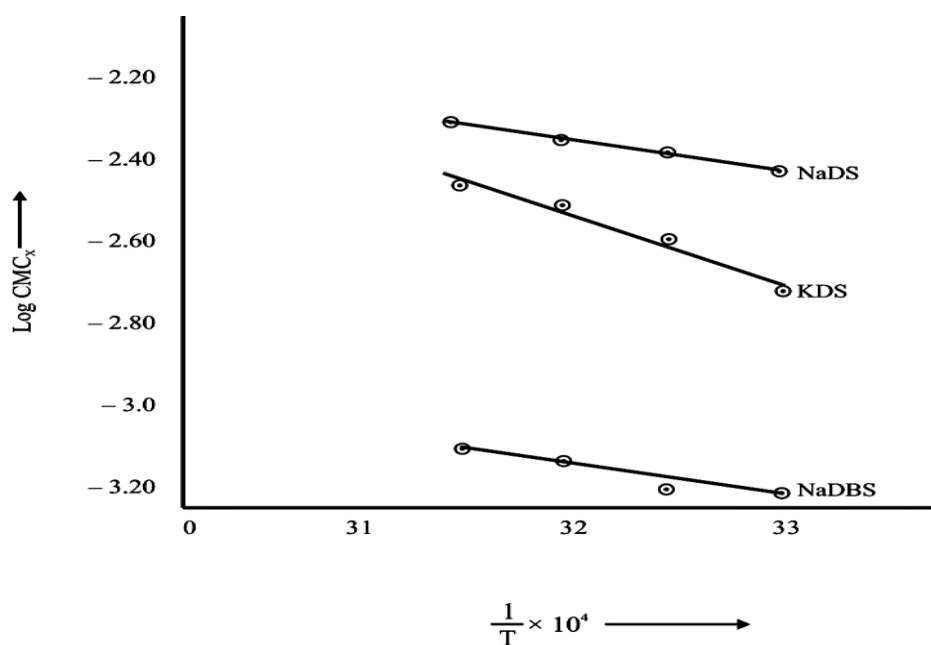
FIGURE 2:   **PLOTS OF Log CMC$_X$ VS $\dfrac{1}{T} \times 10^4$ OF SURFACTANTS IN PRESENCE OF 0.5 M UREA**

IN 2.5% BUTANOL-WATER SYSTEM AT DIFFERENT TEMPERATURES.

Discussion:

The highly structured tetrahedral arrangement of water molecules in the liquid state would have to be disrupted by the addition of any solute. When alcohols are added into water, some hydrogen bonds must be broken and new hydrogen bond between water and alcohols would be formed. But the hydrogen bonds formation between water and alcohol does not seem very tangible because in liquid alcohol the tendency for O⬚H---O bond formation is likely to be as strong as in water, though such hydrogen bonds cannot comprise an isotropic net work filling the entire solvent space due the presence of alkyl side chains.

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 weaking 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 (30-45ºC).

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

Table 2: Values of CMC for KDS, NaDS and NaDBS in presence of urea (0.5 M) and 2.5% butanol-water system at different temperatures (30-45ºC) obtained by **γ** vs. log C plots.

Temperature	CMC $\times$ 10^3		CMC $\times$ 10^4
	KDS	NaDS	NaDBS
30ºC	3.75	4.66	6.79
35ºC	4.10	5.05	7.05
40ºC	4.50	5.52	8.53
45ºC	5.00	6.40	8.72

Table 3: Values of surface tension (γ) for KDS in the presence of urea (0.5 M) and 2.5% butanol-water system at different temperatures (30-45°C).

2.5% butanol-water system	Concentration of KDS in Mole litre^{-1}	Temperature °C			
		30°C	35°C	40°C	45°C
		γ (dyne cm^{-1})	γ (dyne cm^{-1})	γ (dyne cm^{-1})	γ (dyne cm^{-1})
	0.001	36.5	41.5	45.0	47.5
	0.002	28.0	34.5	37.0	39.5
	0.003	25.5	31.5	34.5	37.0
	0.004	24.0	28.0	31.5	34.5
	0.005	23.0	27.0	30.0	32.5
	0.006	22.0	26.5	29.5	31.0
	0.007	21.5	26.0	28.5	30.5

Table 4: Values of surface tension (γ) for NaDS in the presence of urea(0.5 M) and 2.5% butanol-water system at different temperatures (30-45°C).

2.5% butanol-water system	Concentration of NaDS in Mole litre^{-1}	Temperature °C			
		30°C	35°C	40°C	45°C
		γ (dyne cm^{-1})	γ (dyne cm^{-1})	γ (dyne cm^{-1})	γ (dyne cm^{-1})
	0.002	43.7	43.3	41.00	39.70
	0.004	40.6	40.2	38.9	38.20
	0.006	40.1	39.3	38.2	37.40
	0.008	40.0	39.2	38.00	37.20
	0.010	39.8	39.2	37.9	37.00
	0.012	39.7	39.1	37.8	36.90

Table 5: Thermodynamic parameters for KDS, NaDS and NaDBS in the presence of urea (0.5 M) and 2.5% butanol-water system at different temperatures (30-45°C).

Temperature (ºC)	Surfactants		
	KDS	NaDS	NaDBS
	$-\Delta G^o$ (kJ/mole)	$-\Delta G^o$ (kJ/mole)	$-\Delta G^o$ (kJ/mole)
30	30.97	27.0	36.75
35	29.47	26.99	37.12
40	28.47	26.95	36.77
45	28.96	26.65	37.11

Table 6: Thermodynamic parameters for KDS, NaDS and NaDBS in the presence of urea (0.5M) and 2.5% butanol-water system at different temperatures (30-45°C).

Temperature (ºC)	Surfactants		
	KDS	NaDS	NaDBS
	ΔS^o (kJ/mole)	ΔS^o (kJ/mole)	ΔS^o (kJ/mole)
30	0.266	0.143	0.175
35	0.257	0.140	0.173
40	0.251	0.137	0.169
45	0.247	0.134	0.168

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