

The effect of temperature on the micellization of an anionic surfactant in mixed solvent systems.

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Abstract: The micellization and thermodynamic properties of Sodium dodecyl sulphate (SDS) in ethylene glycol-water mixture has been studied at various mole fractions (X) of the solvent mixture and at different temperatures through conductivity measurements. The critical micelle concentration of SDS decreased as the mole fraction of ethylene glycol (EG) increased at constant temperature and increased with increasing temperature at constant mixture composition. Similarly, the degree of micelle ionization was inversely proportional to mixture composition but directly proportional to temperature. These trends are indicative of the interactions of SDS ionic head groups and the association of SDS molecules with the binary mixed solvents. The properties of the mixtures also indicate spontaneous formation of thermodynamically stable micelles.

I. Introduction

Surfactant solutions play important roles in the manufacture of detergents, paints, biocides (sanitizers), hair conditioners and tooth pastes (Quina and Romsted, 1991; Khan and Ali, 2009). In biology, they are involved in membrane mimetics and enzymatic processes (Al-Wardian *et al.*, 2004; Farn, 2006). In addition, cationic surfactants are known to exhibit excellent antistatic effects (Schramm *et al.*, 2003; Singh and Mitra, 2010).

With respect to micellization and phase behaviour, one of the extensively studied surfactant is SDS (Misra *et al.*, 2010). It is an anionic surfactant with excellent foaming properties and low cost of production. SDS is an essential ingredient in such products as shampoo, toothpaste and detergents. Thus, the use of SDS in several applications reduces overall production cost and environmental impact.

Surfactants are generally used in aqueous medium but are also found useful in applications involving water-free or water-poor media. This has stimulated interest in understanding the behaviour of surfactants in non-aqueous and aqueous/non-aqueous mixed systems. Thus in recent times, investigations are being focused on the influence of polar organic solvents on the aggregation behaviour of surfactants and the structural properties of the aggregates formed (Sar Santosh and Rathod, 2011; Olaseni *et al.*, 2012; Prajapati and Patel, 2012). Solution properties of surfactants in polar organic solvents and aqueous organic mixed systems depict in literature (Ghosh *et al.*, 2008; Kabir-ud-din *et al.*, 2006; Rodriguez *et al.*, 2007; Kolayet *et al.*, 2008). Prajapati and Patel, 2012, have studied the micellization of SDS, cetyltrimethyl ammonium bromide and tweens-80 in ethylene glycol/water and formamide/water mixed solvents at constant temperature using surface tension, viscosity and conductance measurements. The results obtained showed that ethylene glycol, the formamide/water mixed solvent was a better solvent for the surfactants compared with water. However, there is dearth of recorded reports on the systematic study of the influence of ethylene glycol additive on the aggregation behaviour of SDS at different temperatures. In this study, the effect of ethylene glycol and temperature on the formation of SDS micelles and the thermodynamic properties associated with this process in binary mixed aqueous solutions of ethylene glycol have been reported.

II. Materials And Methods

The Pure samples (99%) of sodium dodecyl sulphate (purchased from Lancaster synthesis, England) and Ethylene Glycol (obtained from Sure Chemical Products Ltd, England) were used without further purification. Doubly distilled water was used to prepare binary mixed aqueous-organic mixed systems at 0.1, 0.3, 0.5, 0.7 and 0.9 mole fractions of ethylene glycol (EG). For each mole fraction, stock solutions of SDS were prepared at concentrations approximately ten times the literature value of its CMC. All experiments were carried out using freshly prepared solutions. Conductivity was measured with a digital microprocessor based conductivity meter (model DDS-307A). The conductance of 25 ml of the distilled water was first measured at a specific temperature in thermostated water bath with accuracy of $\pm 0.2^\circ\text{C}$. Subsequently, a precise volume of a stock solution was added into the distilled water using an Eppendorf pipette. After ensuring thorough mixing and temperature equilibration, the specific conductance was measured. The method was repeated twice and a mean value obtained. A plot of specific conductivity versus concentration gave a break point. The point of interception of two straight lines above and below this inflection point gave the CMC value of SDS in the mixture (Jones *et*

al., 2001; Shi *et al.*, 2011; Zhang *et al.*, 2012). The procedure was repeated at different mole fractions and at different temperatures.

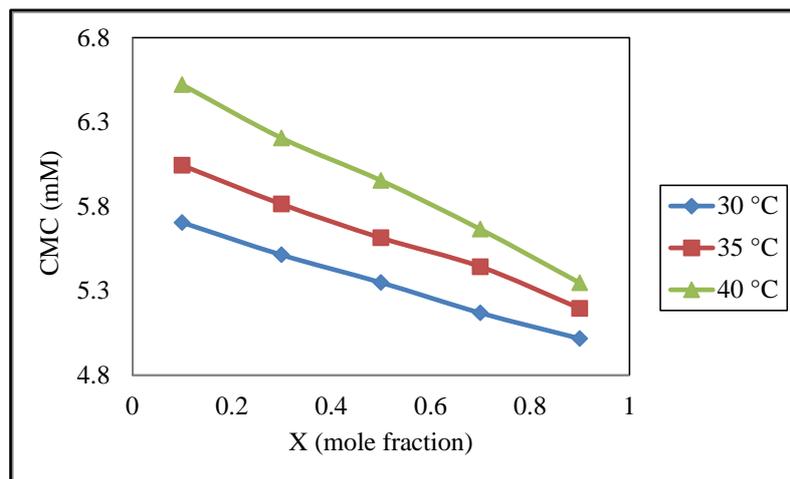


Figure 1: Variation of CMC with mole fraction of ethylene glycol, at different temperatures.

The results (Fig 1) show the dependence of the CMC of SDS on temperature and mole fraction of ethylene glycol in the ethylene glycol-water binary mixture. At a constant temperature, the value of CMC decreases with increase in the mole fraction of ethylene glycol. This trend is in agreement with the studies of Prajapati and Patel, (2012) for SDS solution in the same binary mixed solvents at 30°C. They reported that an increase in the mole fraction of ethylene glycol lowered the CMC value of SDS and attributed it to electrostatic repulsion of SDS ionic head groups, possibly, due to enhanced dielectric constant of water by the addition of ethylene glycol. They further suggested enhanced hydrophobicity as responsible for the inverse relationship between the CMC of SDS and the mole fraction of ethylene glycol. The results obtained in this study are, however, at variance with those of Olaseni *et al.*, (2012). They reported a direct proportionality between the CMC and the mole fraction of EG for solutions of cetyltrimethylammonium bromide (cationic surfactant) in water-ethylene glycol, dimethyl sulfoxide and dimethyl formamide mixed solvents.

In this study, an increase in temperature did not affect the inverse relationship between the CMC and the concentration of EG in the binary mixtures. However, a corresponding increase in CMC was observed with increasing temperature at a given composition. For example, at 0.1 mole fraction of EG, the CMC increased from 5.7mM to 6.7mM as temperature increased from 30°C to 40°C (Fig 1). Earlier studies (Chenet *et al.*, 1998; Ghosh and Deepti, 2009 and Olaseni *et al.*, 2012) have reported similar observations and attributed the increase in CMC with temperature to the breakdown of water structure surrounding the hydrophobic tail of the amphiphile molecules.

Figure 2 represents a plot of the degree of ionization of SDS micelles against the mole fractions of ethylene glycol at different temperatures. The degree of ionization of SDS micelles was determined from the ratio of the slope of conductivity versus concentration curves above and below the inflection point at the different mole fractions and temperatures.

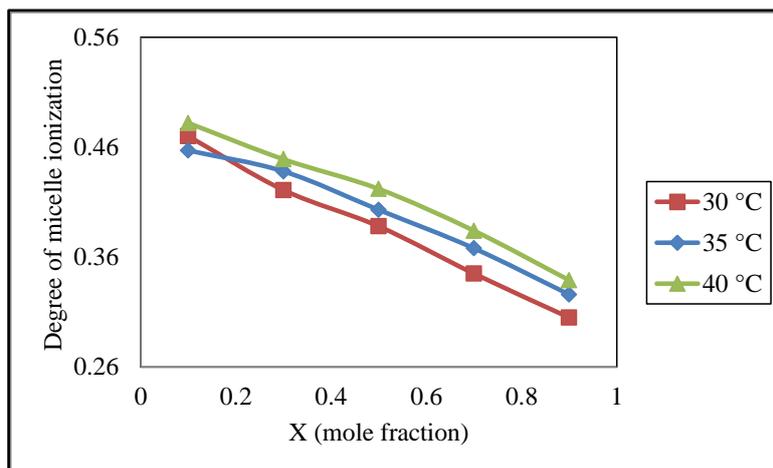


Figure 2: Plot of Degree of Ionization of SDS micelles against mole fractions of ethylene glycol at different temperatures.

At constant temperature, the degree of micelle ionization decreased with the mole fraction of ethylene glycol. This trend indicates that the presence of ethylene glycol increased the attractive electrostatic interactions of the SDS headgroups. This may be attributed to dilution effect, which weakens the repulsive interactions of the ions. This observation is supported by the decrease in the value of the CMC as the mole fraction of ethylene glycol increased. However, at constant mole fraction, the degree of ionization increased as the temperature increased. Upadhaya and Sharma, (1995) and Olaseni *et al.*, (2012), have attributed increase in the degree of micelle ionization to two major factors; Coulombic and thermal forces. While Coulombic interactions tend to bring the surfactant headgroups together, thermal agitation increases the repulsion between ionic headgroups thereby enhancing separation between surfactant headgroups and the associated counterions. The results obtained in this study indicate that the latter factor dominates the systems as temperature increased.

III. Thermodynamics Of Micelle Formation

Micelle formation is the most significant process in the solution behaviour of surfactants. The understanding of the behaviour of surfactants in solution will help to tune their properties to the desired application. Micellization is characterized by a number of temperature dependent parameters such as Gibbs free energy, enthalpy and entropy. According to Goodwin, 2004, mass-action is one of the widely accepted and frequently used models to interpret the energetics of micelle formation. This model arises from the temperature dependence of the minimum concentration (CMC) above which micelles are formed. Thus, the Gibbs free energy for micelle formation, G_{mic}^0 is usually calculated from the pseudo-phase separation model for ionic surfactants using equation 1 (Deepti *et al.*, 2009, Bell *et al.*, 2003, In and Zana, 2007).

$$\Delta G_{mic}^0 = RT \ln X_{CMC} \quad (1)$$

Where R is gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), T is temperature in degree Kelvin and X_{CMC} is the surfactant CMC in mole fraction range. The corresponding enthalpy (ΔH_{mic}^0) and entropy (ΔS_{mic}^0) of micelle formation were calculated from equations 2 and 3 (Fenta, 2015, Sar Santosh and Rathod, 2011 and Aguiar *et al.*, 2002) respectively.

$$\Delta H_{mic}^0 = -RT^2 \frac{d \ln X_{CMC}}{dT} \quad (2)$$

Equation 2 shows that the enthalpy of micelle formation can be calculated from the slope of $\ln X_{CMC}$ versus temperature curves. With the known values of Gibbs free energy and enthalpy, the entropy of micellization can be deduced at each temperature and mole fraction.

$$\Delta S_{mic}^0 = \frac{\Delta H_{mic}^0 - \Delta G_{mic}^0}{T} \quad (3)$$

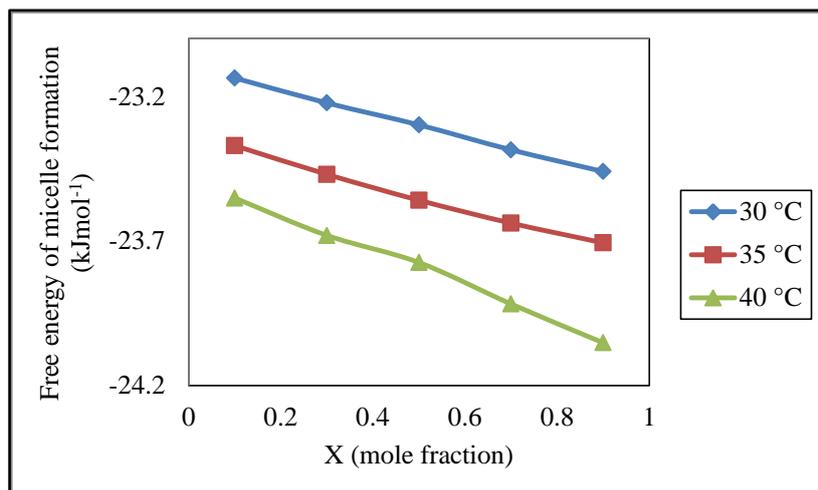


Figure 3: Dependence of free energy of micelle formation on temperature for solutions of SDS in ethylene-water mixture.

The plots of the free energies of micellization of SDS versus mole fractions of ethylene glycol in ethylene glycol-water mixture at the various temperatures studied are shown in Figure 3. The plots illustrate that the values of the free energy of formation of SDS micelles are negative at all mole fractions and different temperatures. They become more negative as both mole fraction and temperature increase. Figure 4 presents the effect of temperature on the free energy of SDS micelle formation at different mole fractions of the ethylene glycol mixed solvent systems.

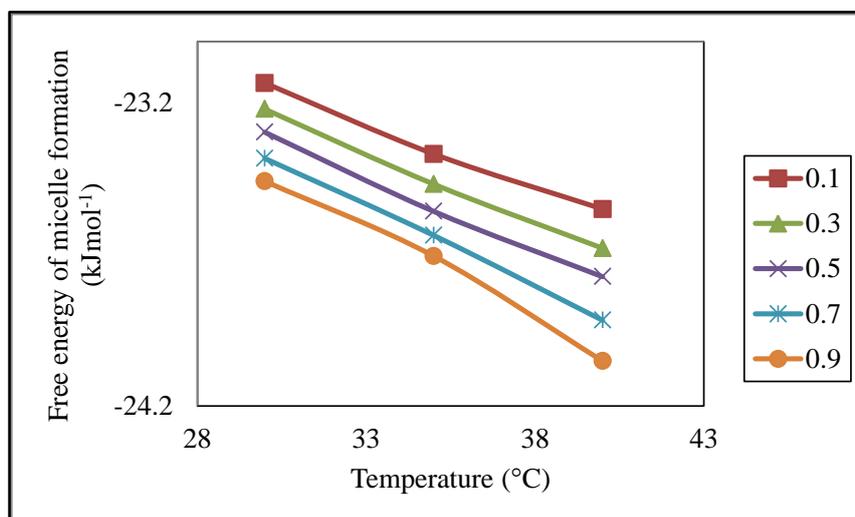


Figure 4: The dependence of free energy of micelle formation on mole fraction of ethylene glycol at different temperatures.

Fundamentally, free energies signify the ease with which micelles are formed. The more negative the value of free energy is, the more spontaneous and feasible will micellization be. This result is in agreement with that of Ghosh and Deepti, 2009 in their study of micellization behaviour of $[C_{16-4}-C_{16}]_2Br$ gemini surfactants in binary aqueous-solvent mixtures through conductivity measurements. The decreasing value of ΔG_{mic}^0 was attributed to the tendency to drive equilibrium towards hydrophobic bonding as temperature increased. It is important to note that the decreasing value of the CMC with mole fraction of ethylene glycol is in agreement with the increasing negative values of the free energy as mole fraction increases.

The values of the change in standard enthalpy of micelle formation are negative at all mole fractions and at the different temperatures (Table 1). However, ΔH_{mic}^0 becomes more negative with increasing temperature but increases as the mole fraction of ethylene glycol increases. The negative values of the enthalpy suggest that the process of micelle formation of SDS in the binary mixed solvents is exothermic. The entropies of the systems are positive at all mole fractions and at the different temperatures, indicating entropy driven

micellization which increases with increasing mole fraction of ethylene glycol but decreases as the temperature increases though not significantly. The trend thus implies that addition of the organic solvent increased the level of disorder in the binary mixed system. This behaviour might be attributed to strong intermolecular interactions between water and ethylene glycol through hydrogen bonding which might lead to distortion in water structure (Homendra and Devi, 2006).

Table 1: Thermodynamic properties of the micellization of SDS in aqueous solutions of ethylene glycol at different temperatures and mole fractions of ethylene glycol.

X	T(K)	$-\Delta G_{mic}^0 / \text{kJmol}^{-1}$	$-\Delta H_{mic}^0 / \text{kJmol}^{-1}$	$\Delta S_{mic}^0 / \text{kJmol}^{-1} \text{K}^{-1}$
0.1	303	23.14	10.23	0.043
	308	23.37	10.57	0.042
	313	23.57	10.91	0.041
0.3	303	23.22	9.01	0.047
	308	23.47	9.31	0.046
	313	23.68	9.61	0.045
0.5	303	23.30	8.63	0.049
	308	23.56	8.91	0.048
	313	23.77	9.20	0.047
0.7	303	23.38	7.02	0.054
	308	23.64	7.26	0.053
	313	23.92	7.49	0.052
0.9	303	23.46	3.15	0.067
	308	23.71	3.26	0.066
	313	24.05	3.36	0.065

IV. Conclusions

The effect of ethylene glycol and temperature on the aggregation behaviour of aqueous solutions of SDS has been investigated through conductivity measurements. Plots of conductivity versus mole fraction of ethylene glycol were used to determine the CMC and degree of ionization of SDS micelles at the different temperatures. The thermodynamic parameters of micelle formation were calculated from the data obtained. The CMC of SDS in the binary mixtures decreased with increasing mole fraction of ethylene glycol but increased with increase in temperature. The degree of micelle ionization was found to decrease with increasing mole fraction of the organic solvent but increased as temperature increased. The values of the change in Gibbs free energy and enthalpy showed that increase in temperature resulted in more spontaneous micellization process of SDS in the aqueous-organic mixed solutions while addition of ethylene glycol made it less spontaneous. The process was entropy driven that proceeded through exothermic process.

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