Asian Journal of Chemistry Vol. 18, No. 1 (2006), 165–175

Physico-Chemical and Thermodynamic Studies Associated with Micellization of Sodium Dodecyl Sulfate in *n*-Alkanol/Water Mixtures

A.A. RAFATI* and M. SAFARPOUR†
Department of Chemistry, Faculty of Science
Bu-Ali Sina University, P.O. Box 65174, Hamadan, Iran
Fax: (98)(811)8272404; E-mail: aa_rafati@basu.ac.ir

Conductometric technique has been used to investigate the equilibrium properties of sodium dodecyl sulfate in the presence of a series of aliphatic alcohols. The influence of medium chain alcohols on the micellization behaviour of sodium dodecyl sulfate is investigated and it is shown that the critical micelle concentration and degree of micellar dissociation (α) increase upon addition of alcohols, depending on the chain length of alcohols. The thermodynamic functions for the micellization were calculated at various conditions. The results showed that the presence of alcohols decreases the tendency for micelle formation. The addition of alcohols is considered to affect the micellar stability by changing the composition and dielectric constant of the environment.

Key Words: Electrical conductivity, Surfactant, Micellization, Mixed solvent, Thermodynamic, Sodium dodecyl sulfate.

INTRODUCTION

It is well known that surfactant molecules are associated into micelles above the critical micelle concentration (cmc). The micellization of surfactants has been a topic of considerable interest for many years, with an enormous literature of several thousand papers published year after year in journals of widely differing scopes. The association of surfactant molecules with micellar aggregates in aqueous solutions leads to a reduction of the energetically unfavorable contact between water and the apolar parts of the surfactant molecules while the polar groups are still solvated by the water[1, 2]. The driving force for surfactant aggregation in water is closely related to the low solubility of the hydrocarbon chains of the surfactant in water[3]. It is well known that the micelle formation is affected by a number of environmental factors such as pH, ionic strength, temperature and the presence of various additives[4–10].

Some surfactant molecules are known to self-assemble in polar organic solvents properly like glycol, glycerol and formamide[11–13]. These solvents like water form hydrogen bonds, have relatively high dielectric constants and are immiscible with hydrocarbon solvents. Consequently, these solvents also give rise to a solvophobic interaction that promotes surfactant association. However, it is not completely clear which solvent properties are involved.

In highly non-polar solvents, the polar groups of the amphipathic molecules become solvophobic and, in such media, aggregates form in which the polar groups

---

†Department of Chemistry, School of Science, Persian Gulf University, Booshehr, Iran.

form the core. Such species are often referred to as inverse, reverse or reverted micelles.

From a physico-chemical point of view, one of the most interesting questions concerns the physical parameters of micellization of surfactants in non-aqueous polar solvents. It is also important to investigate the effects of additives on the micelles, *i.e.*, to what extent the solubilizate causes structural changes of micelles or influence the micellar aggregation number. Changes in the critical micelle concentration and the counter-ion association are also of considerable importance.

On the other hand, many published investigations have been aimed at evaluating the changes in thermodynamic variables which accompany micelle formation in mixed solvents, both in order to discover what factors are responsible for the stability of micelles and to test theoretical predictions[14–18]. The most readily measurable thermodynamically interesting property of such solutions is usually the critical micelle concentration (cmc) and it is commonly agreed that the quantity RT ln (cmc) is very nearly equal to the standard free energy of micellization[19].

It becomes possible to describe the variation of the critical micelle concentration (cmc), the degree of micelle dissociation and thermodynamic parameters with variation of the structure and dielectric constant of solvent.

The micellization in dilute aqueous sodium dodecyl sulfate (SDS) solutions has long been studied[20–24] but the study of these phenomena in non-aqueous polar solvent nevertheless is still a matter of discussion. In order to compare the solvophobic effect in mixed solvent with the hydrophobic effect in water-SDS micellization, conductivity measurements have been performed in various mixtures of solvents with different hydrocarbon chain length, different dielectric constant and different number of hydroxyl groups. The purposes of the present study are to measure the thermodynamic parameters of micellization of SDS in mixed solvents, using conductometric technique.

EXPERIMENTAL

Sodium dodecyl sulfate was obtained from Merck (purity > 98%) and used without further purification. Ethanol, *n*-propanol and *n*-butanol were purchased from Merck and used as received.

Specific conductivities of the solutions were measured using Genway conductometer Model 4020 and a dipping cell with platinum electrode (cell constant = 1 cm^{-1}). The conductivity cell was calibrated with KCl solution in the appropriate concentration range. The measuring cell was immersed in a thermostat bath keeping the temperature constant with ±0.1 K.

RESULTS AND DISCUSSION

The change in the electrical conductance of aqueous ionic surfactant solutions at the cmc is due to the different degree of surfactant ionization below and above the cmc. The specific conductivity, κ, of surfactant solutions can easily be calculated in terms of the molar ionic conductivities of ions, λ_i. Electrical conductivity below cmc is written as:

$$\kappa = \lambda_{S^-}[S^-]_f + \lambda_{C^+}[C^+]_f \qquad (1)$$

$$[S^-]_f = [C^+]_f = C_t$$

where $[S^-]_f$ and $[C^+]_f$ are the concentrations of free surfactant and its counterion, respectively and λ_{S^-} and λ_{C^+} correspond to molar ionic conductivities. The complete dissociation of ionic surfactant is assumed below the cmc[25]. The slope (S_1) of molar conductivity becomes:

$$S_1 = \kappa/C_t = \lambda_{S^-} + \lambda_{C^+} \tag{2}$$

Above the cmc, the specific conductivity is expressed as:

$$\kappa_m = \lambda_{S^-}[S^-]_f + \lambda_{C^+}[C^+]_f + \lambda_m[C_m] \tag{3}$$

where κ_m, $[C]_m$ and λ_m are the specific conductivity of solution above the cmc, the concentration and ionic molar conductivity of micelle, respectively. Concentration of free counterion, $[C^+]_f$, is expressed as:

$$[C^+]_f = \text{cmc} + \alpha[M]_m \tag{4}$$

where $[M]_m = C_t\text{-cmc}$, and above the cmc, $[S^-]_f$ is assumed to be constant and equal to cmc. Combining Eqs. (3) and (4), one obtains:

$$\kappa_m = (\lambda_{S^-} + \lambda_{C^+})\,\text{cmc} + \lambda_{C^+}\alpha[M]_m + \lambda_m[C]_m \tag{5}$$

Taking into account that $[C]_m = \dfrac{C_t - \text{cmc}}{N_{agg}}$ and assuming that the contribution of the micelle to the conductance is the same as that of an equivalent number of monomeric ions, the sum of whose charges equals the micellar charge, then $\lambda_m = \alpha N_{agg}\lambda_S$ and Eq. (5) becomes:

$$\begin{aligned}\kappa &= (\lambda_{S^-} + \lambda_{C^+})\,\text{cmc}\,(1 - \alpha) + (\lambda_{S^-} + \lambda_{C^+})\,\alpha C_t \\ &= \kappa_0 + S_2 C_t\end{aligned} \tag{6}$$

where S_2 $(= \alpha S_1)$ is the slope of the linear plot of κ *vs.* C_t above the cmc and κ_0 is the corresponding intercept.

Fig. 1 shows the specific conductivity of aqueous SDS solution in water and

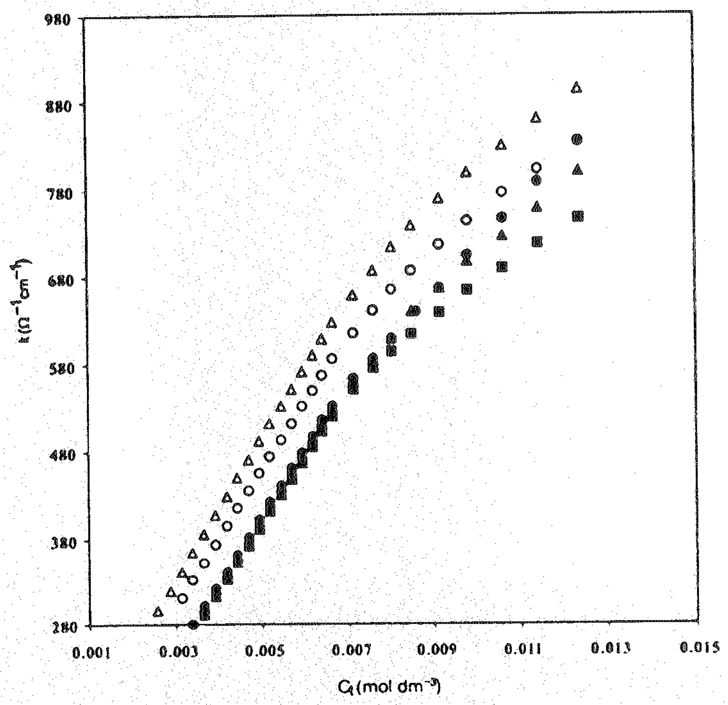

Fig. 1. Specific conductivity (κ) *vs.* total concentration of SDS in different concentrations of ethanol at T = 303 K. (●) 0%; (■) 5%; (▲) 10%; (O) 15%; (Δ) 20% (v/v)

in the presence of various concentrations of ethanol. A characteristic shape of the curves can be observed. Once micelles are formed, it undergoes an abrupt change in concentration dependence. The cmc value can then be determined as the cross point of the two straight lines defined by Eqs. (2) and (6). The degree of dissociation of counterion (or degree of micellar ionization), α, can be obtained as the ratio of the slopes of conductance *vs.* C_t above and below the cmc, that is,

$$\alpha = \frac{S_2}{S_1} \tag{7}$$

These plots show how the cmc is affected by a range of ethanol concentrations. The results are reported in Table 1.

The change in cmc with increasing the concentration of ethanol for different temperatures is shown in Fig. 2. All the other alcohols give similar behaviour for cmc increases on increasing its concentration, which can be explained on the following model.

As alcohol is added to a surfactant micellar solution it equilibrates between the micellar and solvent phases, forming mixed micelles with the surfactant. It lowers the dielectric constant of the solvent and degree of structuring. As more alcohol is added, this process continues and the micelles expand; the alcohol molecules at the micelle-solution interface lower repulsions between the SD^- head groups and α (the degree of dissociation of counterion) increases slightly. Fig. 3 shows a typical plot of α *vs.* ethanol percentage at various temperatures. For other alcohols, data are tabulated in Table-2. At a certain concentration of added alcohol, the micelles become saturated with alcohol; the solvent structure has been destroyed to a large extent and the dielectric constant of the solvent lowered. Upon the addition of further alcohol, the two large component micelles fragment.

It is reported in Table 1 that as the concentration of alcohols increases the cmc of SDS increases. The results of previous studies by Shinoda *et al.*[26] indicate a linear relationship between the change of cmc and carbon number of alcohols. As the chain length of the alcohol becomes longer, a larger part of the chain can enter the hydrophobic core. Short chain alcohols are usually known as co-solvents, which are highly miscible with water, while the larger ones are known as co-surfactants, which are soluble in micellar phase.

The decreased solvent structuring allows more contact between the solvent and the hydrocarbon chains of the surfactant molecules and the low dielectric constant of the medium favours smaller aggregates such that the charged head groups can be further apart. These smaller aggregates will probably have a large percentage of alcohol associated with them, oriented at the hydrocarbon-solvent interface. As still more alcohol is added, these tendencies produce smaller and smaller aggregates and hence increase much more rapidly. At a certain alcohol concentration no aggregation is necessary; the solvent structure has been destroyed so effectively that the hydrophobic effect is no longer dominant. Entropy and the need to reduce repulsions between like-charged head groups become more important.

Fig. 4 shows the relative critical micelle concentration as a function of molar concentrations of added ethanol at various temperatures. It is evident that the cmc increases, with increasing concentration of alcohols.

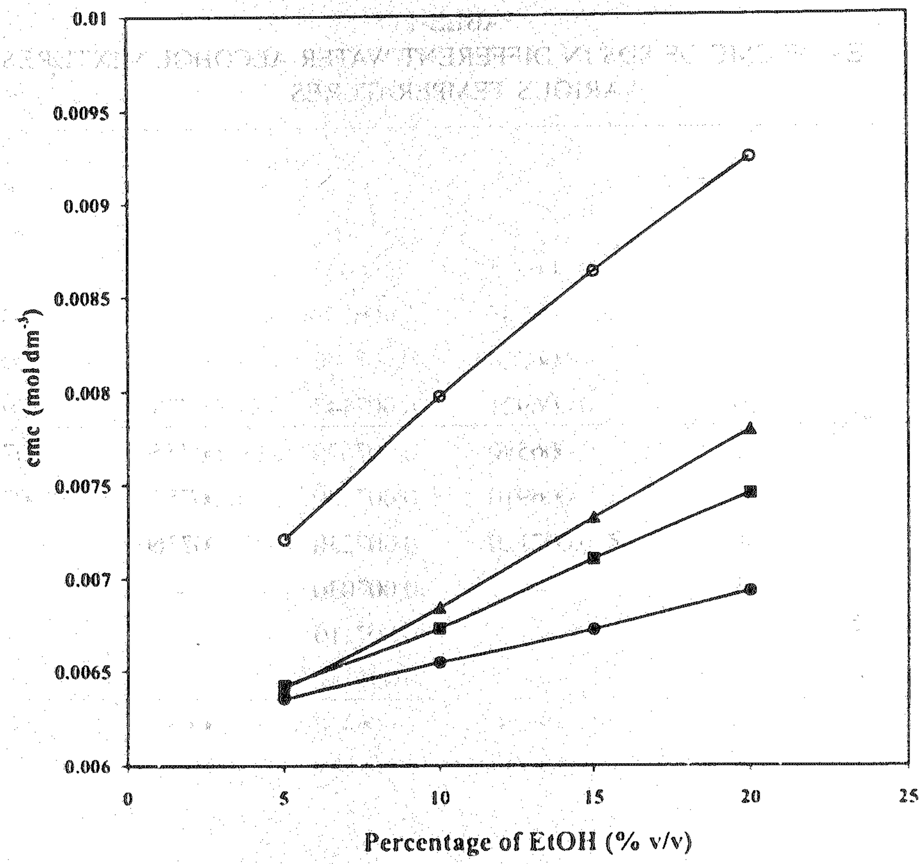

Fig. 2. The cmc of SDS as a function of ethanol percentage (% v/v) at different temperatures: (●) 298 K; (■) 303 K; (▲) 308 K; (O) 313 K

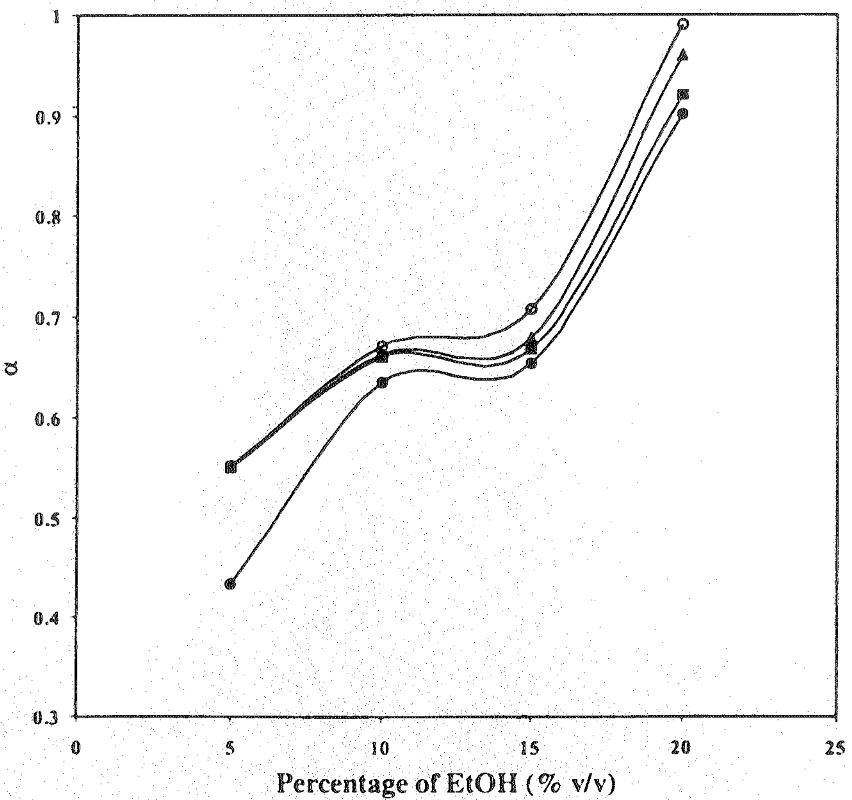

Fig. 3. Degree of dissociation of SDS (α) as a function of ethanol percentage (% v/v) at different temperatures: (●) 298 K; (■) 303 K; (▲) 308 K; (O) 313 K

TABLE-1
THE VALUES OF CMC OF SDS IN DIFFERENT WATER-ALCOHOL MIXTURES AND VARIOUS TEMPERATURES

Alcohol	Percentage (% v/v)	Temperature (K)			
		298	303	308	313
Ethanol	5	0.006355	0.006431	0.006411	0.007206
	10	0.006547	0.006736	0.006838	0.007971
	15	0.006724	0.007100	0.007314	0.008626
	20	0.006921	0.007447	0.007781	0.009243
Propanol	2	0.006580	0.007070	0.007550	0.007910
	3	0.006910	0.007290	0.007520	0.007830
	4	0.007120	0.007230	0.007360	0.007490
	5	—	0.007030	—	—
	10	—	0.007110	—	—
	15	—	0.008730	—	—
Butanol	0.5	0.006300	0.006430	0.006550	0.006660
	3	0.008320	0.008450	0.008580	0.008750
	4	0.008500	0.008650	0.008800	0.008900
	8	0.008070	0.008170	0.008310	0.008420

TABLE-2
DEGREE OF DISSOCIATION OF SDS MICELLES IN DIFFERENT WATER-ALCOHOL MIXTURES AND VARIOUS TEMPERATURES

Alcohol	Percentage (% v/v)	Temperature (K)			
		298	303	308	313
Ethanol	5	0.434	0.550	0.551	0.552
	10	0.635	0.661	0.664	0.671
	15	0.655	0.668	0.680	0.708
	20	0.901	0.920	0.960	0.990
Propanol	2	0.513	0.604	0.648	0.559
	3	0.664	0.674	0.610	0.658
	4	0.733	0.736	0.744	0.785
	5	—	0.741	—	—
	10	—	0.830	—	—
	15	—	0.886	—	—
Butanol	0.5	0.453	0.468	0.531	0.532
	3	0.628	0.680	0.787	0.790
	4	0.818	0.825	0.862	0.883
	8	0.861	0.885	0.888	0.986

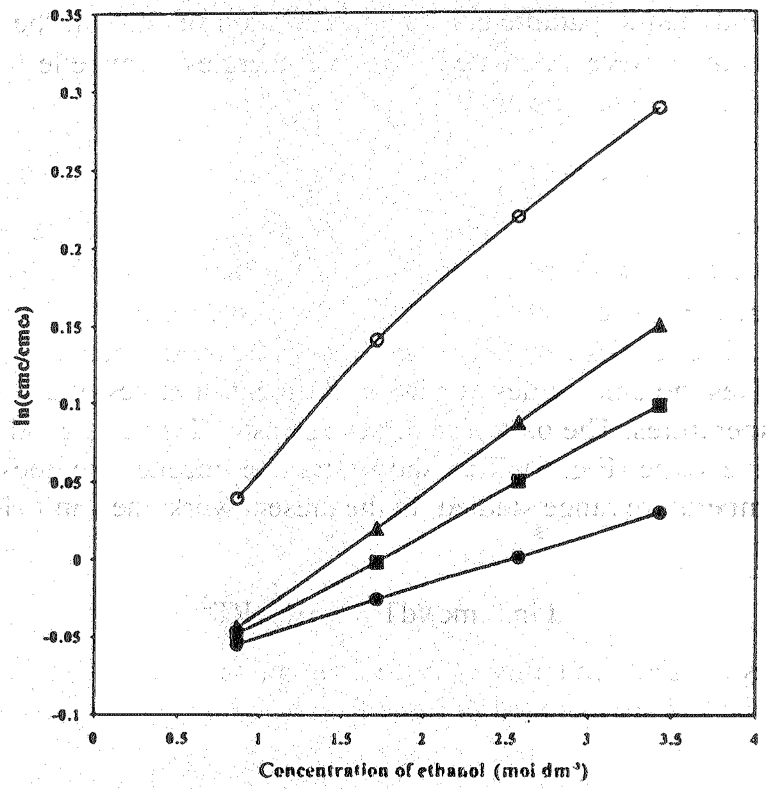

Fig. 4. The ratio of cmc of SDS [ln (cmc/cmc_0)] in the various concentrations of ethanol at different temperatures: (●) 298 K; (■) 303 K; (▲) 308 K; (O) 313 K

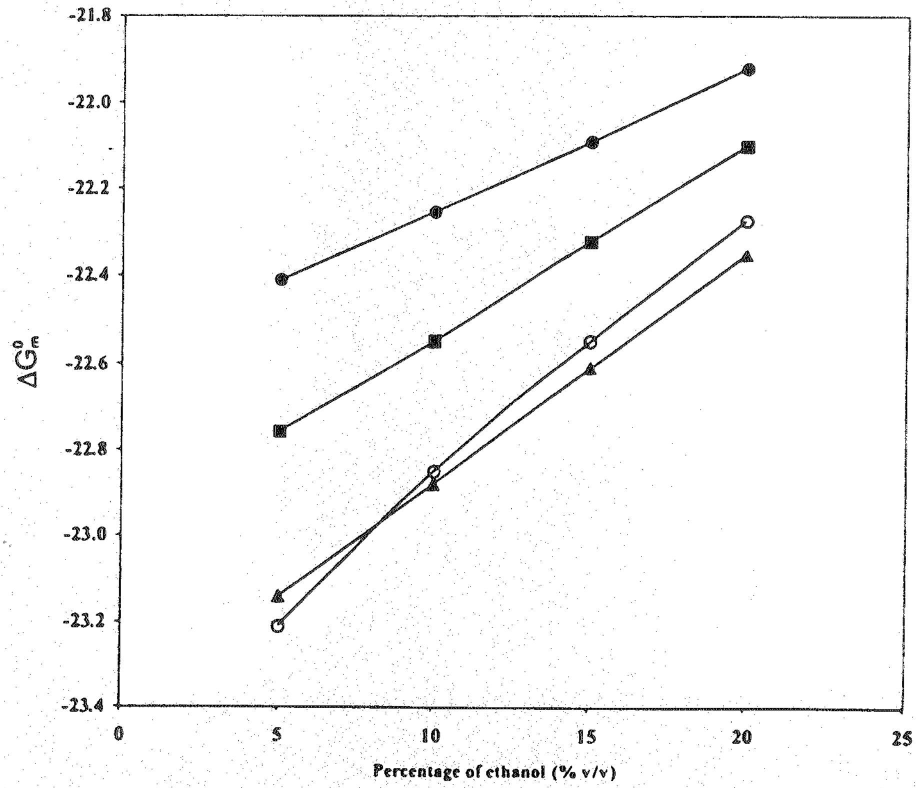

Fig. 5. Plot of ΔG^{o}_{m} as a function of ethanol percentage (% v/v) at different temperatures: (●) 298 K; (■) 303 K; (▲) 308 K; (O) 313K

The thermodynamic parameters for micellization of SDS in the presence of different *n*-alkanols were calculated. The free energies of micelle formation are calculated using the relationship:

$$\Delta G^\circ_m = RT \ln X_{cmc} = RT \ln cmc - RT \ln \omega \qquad (8)$$

where R, T, ΔG°_m, X_{cmc} and ω are gas constant, absolute temperature, Gibbs free energy of micellization, mole fraction of SDS at cmc and molar concentration of solvent, respectively. Fig. 5 shows plot of ΔG°_m *vs.* percentage of ethanol at various temperatures. The results for various conditions are mentioned in Table-3.

Table-1 gives the cmc values of SDS in different mixtures of alcohol-water at different temperatures. The plot of ln (cmc) against 1/T gives a good straight line with a negative slope (Fig. 6). This shows that the micelle size does not change within the temperature range studied. In the present work, the van't Hoff equation is applicable:

$$d \ln (cmc)/dT = -\Delta H^\circ_m/RT^2 \qquad (9)$$

The values of ΔH°_m, enthalpy of micellization, have been calculated from the slope of the line and are included in Table-3.

These values are in the range of the hydrogen bond energy. Water molecules have a strong tendency to form hydrogen bonding. The standard entropies of micellization, ΔS°_m were calculated from the values of ΔH°_m and ΔG°_m using $\Delta G^\circ_m = \Delta H^\circ_m - T\,\Delta S^\circ_m$ and are also listed in Table-3.

TABLE-3
THERMODYNAMIC PARAMETERS OF MICELLIZATION OF SDS IN DIFFERENT ALCOHOL/WATER MIXTURES

Alcohol	Percentage (% v/v)	Temperature (K)	ΔG^0_m (kJ/mol)	ΔH^0_m (kJ/mol)	ΔS^0_m (J/mol)
EtOH	5	298	–22.41	–5.75	55.88
		303	–22.76		56.11
		308	–23.14		56.44
		313	–23.21		55.76
	10	298	–22.25	–9.34	43.30
		303	–22.55		43.58
		308	–22.88		43.94
		313	–22.85		43.14
	15	298	–22.09	–12.01	33.81
		303	–22.32		34.01
		308	–22.61		34.40
		313	–22.55		33.66
	20	298	–21.92	–14.10	26.23
		303	–22.10		26.39
		308	–22.35		26.77
		313	–22.27		26.09

Alcohol	Percentage (% v/v)	Temperature (K)	ΔG_m^0 (kJ/mol)	ΔH_m^0 (kJ/mol)	ΔS_m^0 (J/mol)
PrOH	2	298	–22.37	–9.61	42.80
		303	–22.57		42.75
		308	–22.77		42.71
		313	–23.14		43.21
	3	298	–22.12	–6.31	53.03
		303	–22.45		53.24
		308	–22.83		53.61
		313	–23.30		54.26
	4	298	–22.11	–2.64	65.30
		303	–22.47		65.41
		308	–22.84		65.55
		313	–23.10		65.34
	5	298	—	—	—
		303	22.52		
		308	—		
		313	—		
	10	298	—	—	—
		303	22.39		
		308	—		
		313	—		
	15	298	—	—	—
		303	–21.77		
		308	—		
		313	—		
BuOH	0.5	298	–22.47	–2.88	65.72
		303	–22.84		65.85
		308	–23.16		65.82
		313	–23.50		65.86
	3	298	–21.77	–2.58	64.36
		303	–22.06		64.25
		308	–22.42		64.38
		313	–22.76		64.44
	4	298	–21.73	–2.41	64.80
		303	–22.02		64.68
		308	–22.66		65.71
		313	–22.29		63.48
	8	298	–21.74	–2.24	65.40
		303	–22.09		65.48
		308	–22.40		65.42
		313	–21.10		60.23

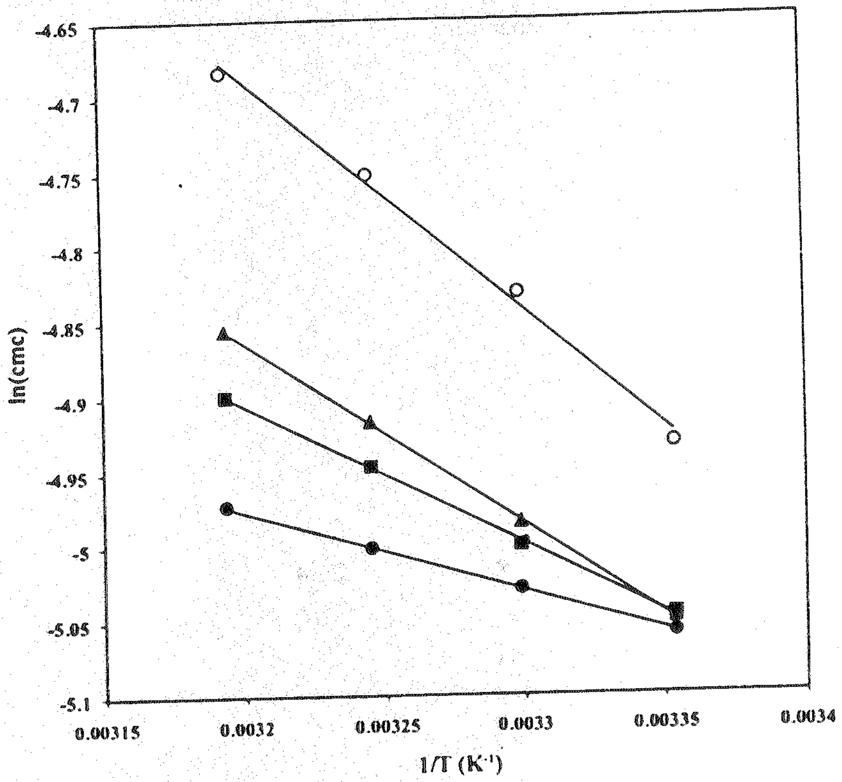

Fig. 6. Plot of ln (cmc) against T^{-1} for SDS in different percentages of ethanol: (●) 5; (■) 10; (▲) 15; (○) 20% (v/v).

It is evident from Table-3 that in all cases micellization is exothermic. This may be interpreted as a consequence of decrease in energy required to break up the iceberg structure surrounding the hydrocarbon chains of the monomeric surfactant. It was also observed that in presence of higher concentration of alcohols, the enthalpy is more negative and entropy is less positive. Similar behaviour of more negative enthalpy in presence of organic additives has been observed[27–29].

As mentioned earlier, the dielectric constant of water is higher than the dielectric constant of alcohols. It seems that dielectric constant plays a more dominant role in cmc formation than dipole moment. The ionization of the surfactant in water is higher than in alcohol-water mixtures because water has a higher dielectric constant. Therefore, there is tendency of forming micelle at a higher concentration.

On the other hand, alcohol molecules intercalated between the head groups of the surfactant molecules will screen the electrostatic repulsion of the head groups less than the water molecules they replace. This leads to an increase of the electric field of the charged head groups of the ionic micelle[30, 31]. This larger repulsion will lead to an increased area per head group and decrease in this way the charge density at the micellar surface. Even if this decrease of the charge density at the micellar surface is obtained by a decrease of the aggregation number, it will not necessarily lead to a decrease of the total volume of the micelle. This effect, which counteracts the previous one, will also lead to a decreased electrostatic attraction of counterions.

REFERENCES

1. J.M. Rosen, Surfactant and Interfacial Phenomena, 2nd Edn., Wiley, New York (1989).
2. G.S. Kresheck, in: F. Franks (Ed.), Surfactants in Water: A Comprehensive Treatise, Vol. 4, Plenum, New York (1975).
3. M. Sjöberg, R. Silveston and B. Kronberg, *Langmuir*, **9**, 973 (1993).
4. T. Cserháti, E. Forgacs and G. Oros, *J. Biochem. Biophys. Methods*, **1**, 38 (1999).
5. V. Monticone and C. Treiner, *Colloids and Surfaces A*, **104**, 2 (1995).
6. C.-M. Chen, C.-H. Chang, Y.-M. Yang and J.-R. Maa, *Colloids and Surfaces A*, **174**, 357 (2000).
7. S.S. Shah, N.U. Jamroz and Q.M. Sharif, *Colloids and Surfaces A*, **1**, 178 (2001).
8. G. Briganti and A. Bonincontro, *J. Non-Crystalline Solids*, **235**, 704 (1998).
9. H. Gharibi, B.M. Razavizadeh and A.A. Rafati, *Colloids and Surfaces A*, **136**, 123 (1998).
10. A.A. Rafati, H. Gharibi and H. Iloukhani, *Phys. Chem. Liq.*, **39**, 521 (2001).
11. A. Martino and E.W. Kaler, *Colloids and Surfaces A*, **99**, 91 (1995).
12. H. Okuyama, Y. Ikeda, S. Kasai, K. Imamori, K. Takayama and T. Nagai, *Int. J. Pharm.*, **186**, 141 (1999).
13. M.S. Akhter and S.M. Alawi, *Colloids and Surfaces A*, **173**, 95 (2000).
14. K. Shirahama, J. Liu, I. Aoyama and N. Takisawa, *Colloids and Surfaces A*, **147**, 133 (1999).
15. J.-B. Huang, M. Mao and B.-Y. Zhu, *Colloids and Surfaces A*, **155**, 339 (1999).
16. S. Bracko and J. Špan, *Dyes and Pigments*, **50**, 77 (2001).
17. N. Marquez, B. Bravo, G. Chavez, F. Ysambertt and J.L. Salager, *Anal. Chim. Acta*, **405**, 267 (2000).
18. M.A. Safarpour, A.A. Rafati, H. Gharibi and M.R. Sameti, *J. Chin. Chem. Soc.*, **46**, 1 (1999).
19. P. Molyneux, C.T. Rhodes and J. Swarbrick, *Trans. Faraday Soc.*, **61**, 1043 (1980).
20. C. Tanford, The Hydrophobic Effect, Formation of Micelles and Biological Membranes, Wiley, New York (1980).
21. P.L.O. Volpe and E.A.S. Filho, *Thermochim. Acta*, **257**, 59 (1995).
22. S.S. Shah, A. Saeed and Q.M. Sharif, *Colloids and Surfaces A*, **155**, 405 (1999).
23. S.S. Shah, N.U. Jamroz and Q.M. Sharif, *Colloids and Surfaces A*, **178**, 199 (2001).
24. C.-E. Lin, M.-J. Chen, H.-C. Huang and H.-W. Chen, *J. Chromatogr. A*, **924**, 83 (2001).
25. T. Sasaki, M. Hattori, J. Sasaki and K. Nukina, *Bull. Chem. Soc. (Japan)*, **48**, 1397 (1975).
26. K. Shinoda and H. Hutchinson, *J. Phys. Chem.*, **66**, 577 (1962).
27. S. Miyagishi, *Bull. Chem. Soc. (Japan)*, **47**, 2972 (1974).
28. ———, *Bull. Chem. Soc. (Japan)*, **48**, 2349 (1975).
29. K.T. Parekh, G.M. Malik, P.H. Kothwala and P. Bahadur, *Fat. Sci. Technol.*, **10**, 395 (1988).
30. M. Almgren and S. Swarup, *J. Colloid Interface Sci.*, **91**, 256 (1983).
31. ———, *J. Phys. Chem.*, **86**, 4212 (1980).

(*Received*: 13 December 2004; *Accepted*: 17 September 2005) AJC-4379