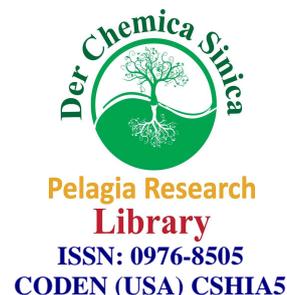




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Der Chemica Sinica, 2012, 3(3):628-635



### A study on solution behaviour of sodiumdodecyl sulphate and cetyltrimethylammonium bromide in water - alcohol mixed media

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#### ABSTRACT

The solution behaviour viz micellization of sodiumdodecyl sulphate (SDS) an anionic surfactant and cetyltrimethylammonium bromide (CTAB) a cationic surfactant in aqueous-rich mixtures of alcohols like methanol (MeOH), ethanol (EtOH), n-Propanol (n-PrOH) and iso-Propanol (i-PrOH) have been investigated between 25°C – 45°C. The critical micelle concentration (CMC) was determined by conductometric method and was further utilized to obtain thermodynamic functions of micellization. Data indicate inhibitory effect of MeOH on micellization of SDS and CTAB; whereas CMC of SDS decreased with alcohols in the order EtOH < i-PrOH < n-PrOH, it remained practically independent of the nature of these solvents in case of CTAB. Thermodynamic parameters of micellization, enthalpy ( $\Delta H_m^\circ$ ), entropy ( $\Delta S_m^\circ$ ) and free energy ( $\Delta G_m^\circ$ ) were determined from temperature dependence of CMC. Constant  $\Delta H_m^\circ$ ,  $\Delta S_m^\circ$  values and  $\Delta H_m^\circ < 0$  is indicative of the stabilization of water structure by MeOH in aqueous solutions of both SDS and CTAB and near constant  $\Delta G_m^\circ$  values is as a consequence of compensation between entropy and enthalpy of micellization. Near constant values of counterion binding ( $\beta$ ) irrespective of nature of head group of SDS and CTAB, is indicative of the fact that size and shape of micelle remain practically constant in the range of composition studied.

**Key Words:** Ionic surfactants, micellization, alcohols, conductance, counterion binding.

#### INTRODUCTION

The ternary alcohol - surfactant - water systems provide vital information about intermolecular interactions and hence have lead to structural, kinetic and thermodynamic studies of such systems [1]. It is quite evident that micellization of surfactants in aqueous- rich mixtures is dependent on various external factors like temperature [2, 3], pressure [4] and presence of solvents etc. The solvent effects have been studied by many investigators [5-10]. Addition of small amount of organic solvents has been found to affect the CMC of ionic surfactants due to their tendency to make or break water structure. The studies of physicochemical properties of surfactants are of both theoretical and practical interest. Thus in pursuance of our interest [11-13] to investigate solution properties of surfactants, in the present work we studied the effect of methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH) and iso-propanol (i-PrOH) on micellization behaviour of sodiumdodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) in aqueous-rich mixtures between 25 – 45°C from conductivity measurements. Results have been discussed in terms of thermodynamic parameters of micellization, which are obtained from the values of CMC.

## MATERIALS AND METHODS

**Materials:** AR grade MeOH obtained from Ranbaxy Laboratory Ltd. was vacuum dried on 3Å molecular sieves [14] and distilled under reduced pressure. The fraction of solvent of conductivity  $(4 - 6) \times 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$  at 25°C was used. EtOH, n-PrOH and i-PrOH (all AR grade and purity >99%) were also procured from Ranbaxy Labs and used as such. CTAB obtained from Fluka was purified further by recrystallizing it twice from 95% EtOH and dried under vacuum at  $\sim 50 - 60^\circ\text{C}$  in presence of  $\text{P}_2\text{O}_5$  for about 45 hours [15]. Extra pure SDS obtained from SRL Pvt Ltd. was further purified by recrystallizing twice in 95% EtOH [16] and final product was dried in vacuum at  $\sim 40 - 50^\circ\text{C}$  for 24 hours. Double distilled water of conductivity,  $(2 - 3) \times 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$  at 25°C was used.

**Method:** Molar conductances,  $\Lambda_m$  of about 20 different concentrations of SDS in the range  $(10 - 150) \times 10^{-4} \text{ mol dm}^{-3}$  and CTAB in the range  $(3-110) \times 10^{-4} \text{ mol dm}^{-3}$  were determined at 25, 35,  $45 \pm 0.01^\circ\text{C}$  in Shedlovsky type conductance cell using a digital conductance meter ( Model NDC-732, Naina Electronics) working at 1 KHz frequency as described earlier [17]. The cell constant  $0.532 \pm 0.002 \text{ cm}^{-1}$ , of the conductivity cell was determined as described by Fauss *et al* [18]. The CMC values precise to  $\pm 1\%$  were determined from an apparent discontinuity in the plots of molar conductance ( $\Lambda$ ) versus square root of molar concentration of SDS and CTAB. (Fig. 1 a representative plot). These CMC values were however expressed in mole fraction units. Aqueous mixtures of alcohols were prepared by weight precise to  $\pm 0.1\%$ .

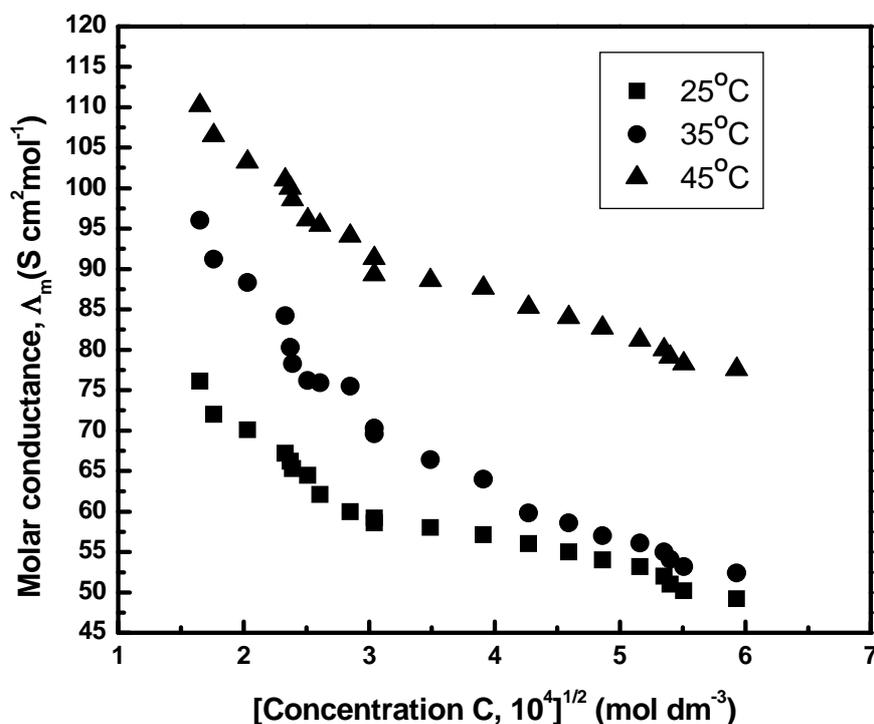


Fig. 1. Representative plot of molar conductance ( $\Lambda_m$ ) versus  $C^{1/2}$ .

All experimental measurements were carried out in a water thermostat precise to  $\pm 0.05^\circ\text{C}$  over the entire temperature range. CMC,  $8.1 \times 10^{-3} \text{ mol dm}^{-3}$  [19] for SDS and  $9.1 \times 10^{-4} \text{ mol dm}^{-3}$  [15] for CTAB were in excellent agreement with the values reported in literature.

**Table 1: Values of CMC at different temperatures, counterion binding  $\beta$  and corresponding thermodynamic parameters for CTAB in dilute aqueous solution of methanol, ethanol, n-propanol and i-propanol at 25°C**

Alcohols (Mol%)	10 <sup>4</sup> , CMC (mol fraction)			$\beta$	(-)G <sub>m</sub> <sup>o</sup> (kJ mol <sup>-1</sup> )	(-) $\Delta H_m^o$ (kJ mol <sup>-1</sup> )	$\Delta S_m^o$ (J (mol K) <sup>-1</sup> )
	25°C	35°C	45°C				
<b>Methanol</b>							
0.0	0.17	0.18	0.19	0.74	27.3	4.1	78
0.51	0.18	0.20	0.21	0.73	27.0	4.8	74
1.52	0.20	0.22	0.23	0.73	26.8	5.2	72
2.71	0.21	0.23	0.24	0.72	26.7	5.2	72
5.92	0.22	0.24	0.25	0.72	26.6	5.2	72
9.67	0.22	0.24	0.26	0.72	26.6	5.2	72
<b>Ethanol</b>							
0.0	0.17	0.18	0.19	0.73	27.3	4.1	78
0.51	0.18	0.20	0.22	0.73	27.1	5.5	62
1.52	0.21	0.22	0.24	0.74	26.7	5.4	61
2.71	0.23	0.25	0.27	0.74	26.5	5.9	69
5.92	0.25	0.28	0.30	0.74	26.3	7.0	65
9.67	0.25	0.28	0.30	0.74	26.3	7.0	65
<b>n-Propanol</b>							
0.0	0.17	0.18	0.19	0.73	27.3	4.1	78
0.51	0.20	0.24	0.26	0.74	26.8	9.6	58
1.52	0.21	0.24	0.28	0.73	26.8	10.7	54
2.71	0.21	0.25	0.28	0.73	26.7	10.7	54
5.92	0.23	0.26	0.30	0.73	26.5	10.7	53
9.67	0.23	0.28	0.30	0.72	26.5	10.7	53
<b>i-Propanol</b>							
0.0	0.17	0.18	0.19	0.73	27.3	4.1	78
0.51	0.21	0.24	0.24	0.74	26.9	4.8	74
1.52	0.23	0.26	0.27	0.73	26.5	5.9	69
2.71	0.24	0.26	0.28	0.74	26.3	5.9	68
5.92	0.26	0.28	0.30	0.74	26.2	5.9	68
9.67	0.26	0.29	0.31	0.74	26.2	5.9	68

Estimated uncertainties are  $\pm 0.5 \text{ kJ mol}^{-1}$  in  $\Delta G_m^o$ ,  $\pm 1 \text{ kJ mol}^{-1}$  in  $\Delta H_m^o$  and  $\pm 2 \text{ J (mol K)}^{-1}$  in  $\Delta S_m^o$

## RESULTS AND DISCUSSION

Experimentally determined CMC of CTAB and SDS in aqueous solutions of alcohols at different temperatures and corresponding thermodynamic parameters of micellization such as  $\Delta G_m^o$ ,  $\Delta H_m^o$  and  $\Delta S_m^o$  are reported in Tables 1, 2 respectively. Enthalpy change involved in a micelle formation process is obtained from temperature dependence of CMC through a van't hof type relation

$$\Delta H_m^o = -RT^2 d [\ln \text{CMC}] / dt$$

Free energy of micellization ( $\Delta G_m^o$ ) is estimated from the relation

$$\Delta G_m^o = RT \ln \text{CMC}$$

Entropy of micellization is obtained from the relationship

$$\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o$$

The counterion binding,  $\beta$  for CTAB and SDS – water – alcohol system were obtained at 25°C as suggested by Castedo et. al.[20].

$$\alpha_m = S_2/S_1$$

where  $\alpha_m$  is the counterion dissociation obtained from  $S_2/S_1$ , the ratio of slopes of post and pre micelle regions and subsequently  $\beta$  was calculated as,  $\beta = 1 - \alpha_m$ . The slopes were estimated from the linear plots of conductivity versus concentration of surfactants [21] using least square fitting. At least 7- 8 best possible points were selected in pre and post micellar regions in order to extract the best possible value of slope.  $S_1$  and  $S_2$  values were precise to  $\pm 0.02$ .  $\beta$  values thus obtained from CTAB and SDS are reported in tables 1 & 2 for different alcohols at 25°C.

**Table 2: Values of CMC at different temperatures, counter ion binding  $\beta$  and corresponding thermodynamic parameters for SDS in dilute aqueous solution of methanol, ethanol, n-propanol and i-propanol at 25°C**

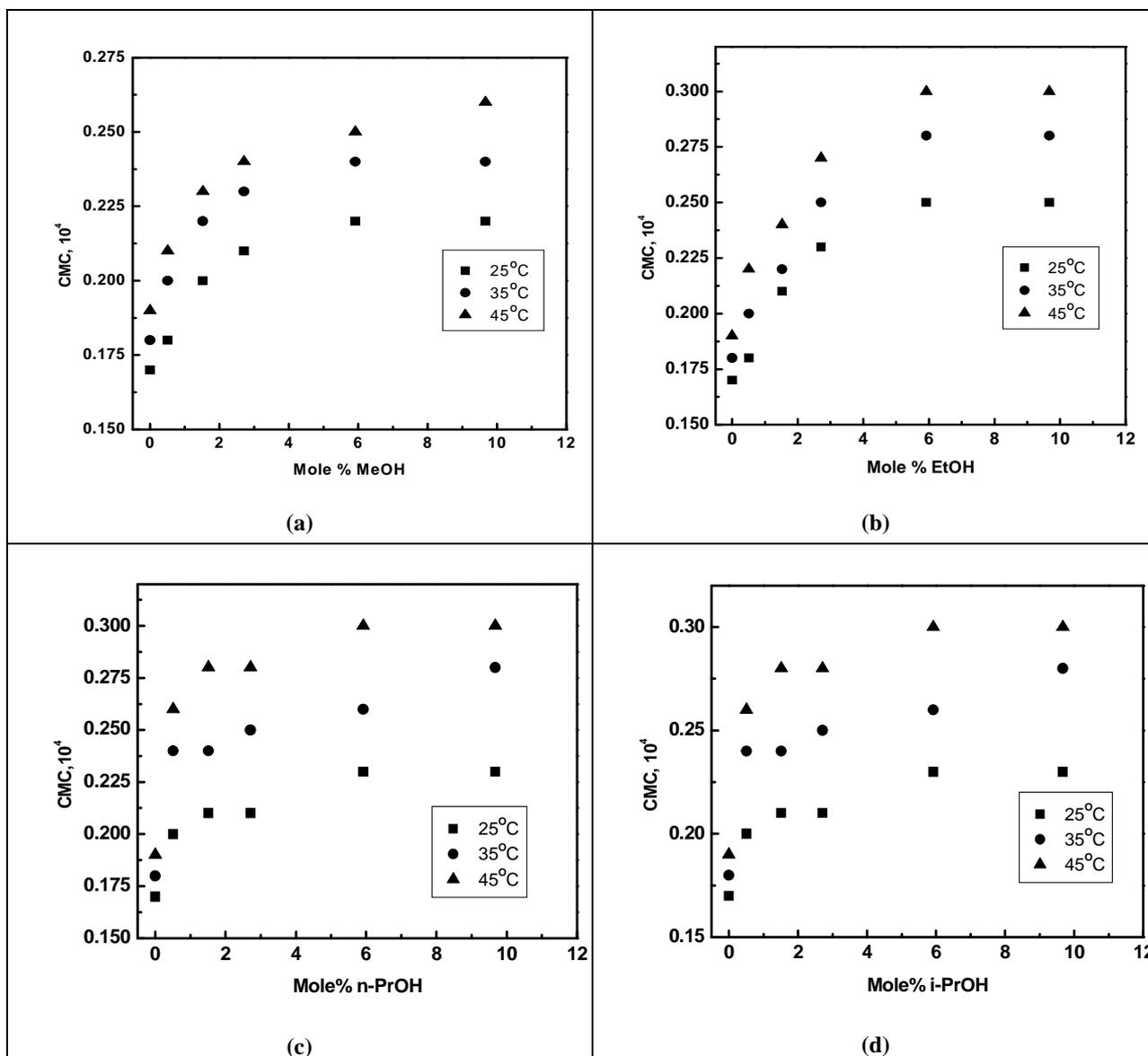
Alcohols (Mol%)	10 <sup>4</sup> , CMC (mol fraction)			$\beta$	(-)G <sub>m</sub> <sup>o</sup> (kJ mol <sup>-1</sup> )	(-) $\Delta H_m^o$ (kJ mol <sup>-1</sup> )	$\Delta S_m^o$ (J (mol K) <sup>-1</sup> )
	25°C	35°C	45°C				
<b>Methanol</b>							
0.0	1.47	1.56	1.62	0.75	21.9	3.3	62
0.51	1.54	1.58	1.67	0.75	21.8	3.0	63
1.52	1.57	1.61	1.71	0.75	21.7	3.3	62
2.71	1.58	1.63	1.73	0.75	21.7	3.3	62
5.92	1.59	1.65	1.74	0.75	21.7	3.3	62
9.67	1.59	1.65	1.74	0.75	21.7	3.3	62
<b>Ethanol</b>							
0.0	1.47	1.56	1.62	0.74	21.9	3.3	62
0.51	1.25	1.39	1.46	0.73	22.3	4.4	60
1.52	1.22	1.39	1.45	0.72	22.3	5.9	55
2.71	1.24	1.41	1.46	0.72	22.3	5.9	55
5.92	1.25	1.42	1.48	0.72	22.3	5.9	55
9.67	1.28	1.43	1.52	0.72	22.2	5.9	55
<b>n-Propanol</b>							
0.0	1.47	1.56	1.62	0.74	21.9	3.3	62
0.51	0.82	0.96	0.99	0.74	23.3	7.2	54
1.52	0.84	1.03	1.05	0.74	23.3	8.2	51
2.71	0.94	1.16	1.21	0.73	23.0	9.3	50
5.92	0.96	1.16	1.24	0.72	22.9	9.4	45
9.67	0.99	1.16	1.25	0.72	22.8	9.6	44
<b>i-Propanol</b>							
0.0	1.47	1.56	1.62	0.74	21.9	3.3	62
0.51	1.12	1.14	1.27	0.75	22.6	4.8	60
1.52	1.13	1.15	1.28	0.74	22.6	4.8	60
2.71	1.22	1.30	1.39	0.73	22.3	5.2	58
5.92	1.27	1.40	1.47	0.73	22.2	5.2	57
9.67	1.27	1.40	1.47	0.73	22.2	5.2	57

Estimated uncertainties are  $\pm 0.5 \text{ kJ mol}^{-1}$  in  $\Delta G_m^o$ ,  $\pm 1 \text{ kJ mol}^{-1}$  in  $\Delta H_m^o$  and  $\pm 2 \text{ J (mol K)}^{-1}$  in  $\Delta S_m^o$

First observation to make from table 1 & 2 and also from figures 2 & 3 is that micellization of CTAB and SDS are hindered with rise in temperature from 25 – 45°C over entire solvent composition range of water – alcohol system studied. Figs 3b, 3c, 3d show reduction of CMC on addition of alcohol to aqueous solution of SDS (except MeOH, Fig. 3a). On the other hand addition of alcohol to aqueous solution of CTAB increase the CMC as depicted in the figs.2. Further it is observed that alcohol reduces the CMC of SDS in the order n-PrOH > i-PrOH > EtOH, where as the increase in CMC of CTAB has been observed to be independent of nature of these solvents.

Most noticeable feature in this study of effect of alcohols on CMC is appearance of a minimum in case of SDS between ~ 0.5 – 1.5 mol% of n-PrOH and i-PrOH, which in the order n-PrOH > i-PrOH, as is evident from figs. 3c & 3d. There appears to be no such minima for EtOH (fig 3b), whereas the effect is all together contrary in case of

MeOH i.e inhibitory (fig. 3a). However, at higher concentration of alcohols the CMC of both SDS and CTAB become practically constant.



**Fig. 2. Critical micelle concentration (CMC) of CTAB as a function of mole % MeOH (a), mole%EtOH (b), mole% n-PrOH (c) and mole% i-PrOH (d) in aqueous solutions at different temperatures.**

According to Kozo Shinoda [22] solubility of paraffin chain alcohol in water is very small so that large entropy of solution is expected. Yet enthalpy and entropy of solutions of these solutes at room temperature are small or negative. This abnormality has been explained by taking in to account 'iceberg' formation of water molecules surrounding the solute molecules. MeOH with its  $-OH$  group [23] interact preferentially with water molecules forming an 'iceberg' at hydrocarbon - water interface. Thus small MeOH additions to aqueous solutions of SDS stabilizes the water structure explaining constant  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  values reported in tables 1, 2 respectively. However,  $\Delta H_m^\circ < 0$  takes in to account the slight greater energy of water - MeOH hydrogen bond [22]. Moreover relatively small  $\Delta H_m^\circ$  in mixtures indicate the disruption of chain and cyclic polymeric structure [24, 25] of MeOH

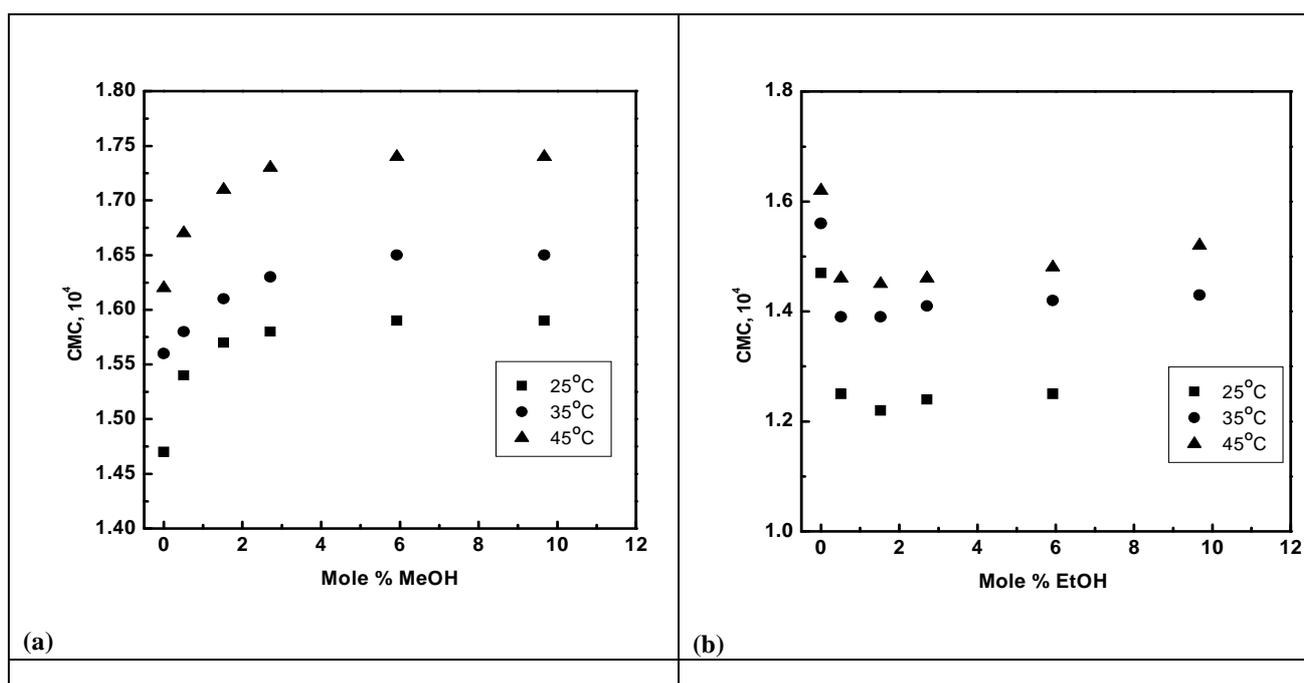
and formation of hydrogen bonds with water. Similar interpretations must hold good in respect of  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  values for MeOH addition to CTAB reported in table 1

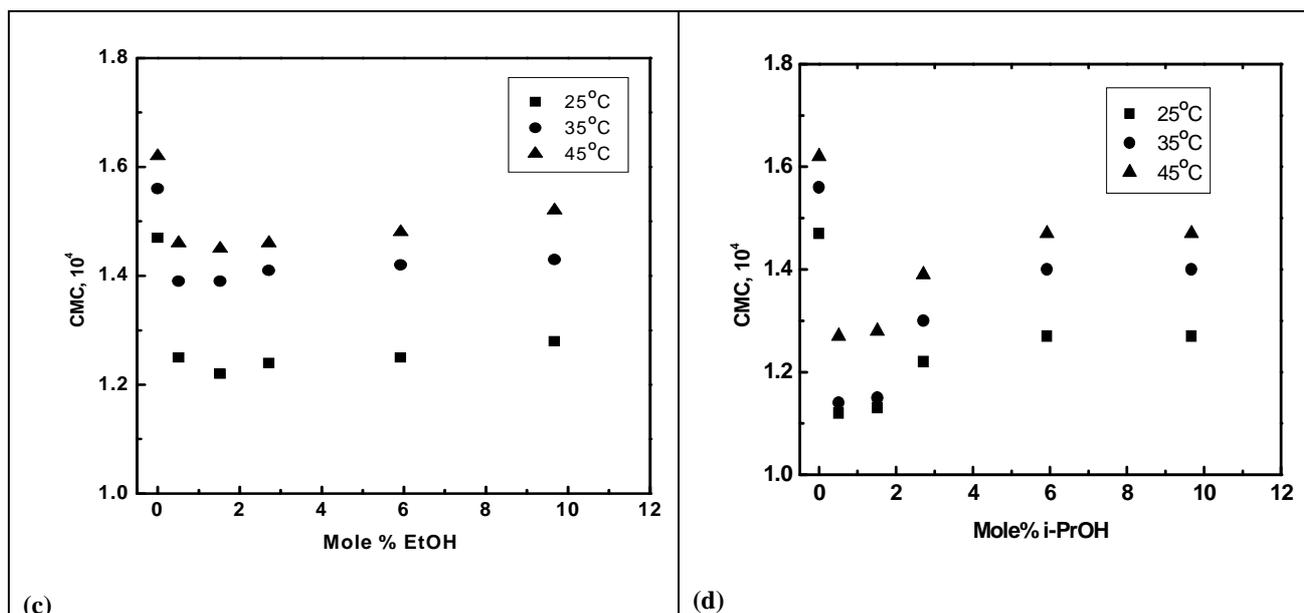
As the hydrocarbon chain of alcohol lengthens, better situations exist for its penetration in to the micelle interior and hence alcohols with larger hydrocarbon tail are comicellized and favour the CMC reduction. On the other hand a less penetrating solvent like MeOH increases the CMC by enhancing its solubility [20].

Apparently conflicting effects of EtOH, n-PrOH and i-PrOH on micellization of CTAB and SDS reflected in CMC versus solvent compositions (figs 2b – 2d & 3b – 3d) suggest the possibility of contribution due to the polar head groups of these surfactants. This seems to be convincing in view of the trends of  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  values for CTAB-water-alcohols and SDS-water-alcohols systems as reported in Tables 1 and 2.

It is further observed from table 1 and 2 that  $\Delta G_m^\circ < 0$ , remains practically constant over the entire solvent composition range studied, which is believed to be due the different arrangement of water molecules at the hydrocarbon interface as well as at polar head group of these various alcohols such that both  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  changes in a mutually compensating manner, so that  $\Delta G_m^\circ < 0$  is not significantly affected.

Finally counterion binding,  $\beta$  values for CTAB and SDS are reported in Table 1 & 2 respectively. It is interesting to note that irrespective of the nature of polar head group and nature of alcohols,  $\beta$  values for these surfactants remain practically constant  $\sim 0.6 - 0.8$  at 25°C indicating that the size and shape of micelle of SDS and CTAB probably remain constant [26]. This has been found to be in fairly good agreement with the general observation that for large number o systems,  $\beta$  lies in the range (0.5 – 0.8) [27].





**Fig. 3. Critical micelle concentration (CMC) of SDS as a function of mole % MeOH (a), mole%EtOH (b), mole% n-PrOH (c) and mole% i-PrOH (d) in aqueous solutions at different temperatures.**

### CONCLUSION

The results of present investigation indicate that the nature of alcohols play a very vital role on micellization process of surfactants. To aid to this evaluation thermodynamic properties such as  $\Delta H_m^\circ$ ,  $\Delta S_m^\circ$  and  $\Delta G_m^\circ$  have been estimated for SDS and CTAB in aqueous solutions of organic solvents at 25°C.  $\Delta G_m^\circ < 0$  remains practically constant, which indicates different arrangements of water molecules in the presence of alcohols. It is therefore, believed that both  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  changes in a mutually compensating manner so that  $\Delta G_m^\circ < 0$  is not practically affected. However the general observation is that micelle formation is entropy driven process. Thus it is concluded that the observed changes in the solution behaviour of CTAB and SDS are primarily due to different structural consequences of intermolecular interactions preferentially at relatively large hydrocarbon water interface of surfactant molecules and the nature of their polar head groups. The counterion binding,  $\beta$  is found to be practically constant, which concludes that no structural transitions of micelles of CTAB and SDS takes place.

### Acknowledgement

GK thanks UGC New Delhi for financial assistance in the form of a minor research project (No : F6-1(53/2006(mrp / nrcb)).

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