

Conference Paper

Micellization Behavior of Ionic Surfactants in Presence of Butanol Isomers in Non-aqueous Solutions

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Abstract

Electrical conductivity and surface tension measurements of various surfactants, such as sodium caprylate, sodium laurate, sodium palmitate and sodium stearate micellar solution, containing 1-butanol (1-BuOH), 2-butanol (2-BuOH) and tertiary butanol (t-BuOH) in *n,n*-dimethyl acetamide have been determined at various temperatures. Both methods show that micelles are formed in *n,n*-dimethyl acetamide (DMA) solution in the presence of butanol isomers. Critical micelle concentration (cmc) has been determined for each of the surfactants. Critical micelle concentrations have also been measured as a function of temperatures and concentration of butanol isomers added. It is suggested that the addition of alcohol leads to an increase in *n,n*-dimethyl acetamide penetration into the micellar interface that depends on the alkyl chain configuration for three isomeric alcohols. Thermodynamic parameters of micellization, enthalpy (ΔH_m^o), entropy (ΔS_m^o), and free energy (ΔG_m^o) were determined from temperature dependence of CMC. The solvent composition dependence of these thermodynamic parameters is determined in terms of the effect of additives on micellization of ionic surfactants. It is observed that both ΔH_m^o and ΔS_m^o bear out not only the observed order of decrease in cmc but also account reasonably the effects produced by differences in alkyl chain configuration for these isomeric alcohols. In all cases $\Delta G_m^o < 0$, and remained practically constant over the entire solvent composition range studied. It is suggested that due to different structural consequences of intermolecular interactions, both enthalpy and entropy must differ in a mutually compensating manner so that ΔG_m^o is not significantly affected.

Keywords: *n,n*-dimethyl Acetamide, Micelle, Cmc, Conductivity, Surface tension, Butanol Isomers

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1. Introduction

The effect of the presence of additives on the critical micelle concentration (cmc) of surfactant has been widely studied [1-3]. Recently, increasing attention is being devoted to the study of the incorporation or solubilization of neutral molecules into micelle in aqueous solution. Some of the most studied solubilizes are alcohols, because of the important role they have in the preparation of microemulsions [4-15]. It is generally accepted that the alcohol binds to the micelle in the surface region, leading to three principal effects: a) the alcohol molecules intercalate between the surfactants ionic head groups to decrease the micelle surface area per head group and increase of ionization [16-19]. This effect is correlated with modification of the growth and shape of the micelle [20-21]. It seems to be a function of the mole fraction of the type of alcohol used [22-23]. b) The dielectric constant at the micellar interface decreases probably due to the replacement of water molecules in the interface region by alcohol molecules [24]. c) The molecular order of the interface region of the micelle changes [5]. So for the literature cited here are mainly the solubility measurements on alcohols in aqueous surfactant solutions, and it seems that the effect of addition of alcohol in micellar solution of various surfactants in non-aqueous solvents has not been studied. In continuation of our work on micelle formation in non-aqueous solvents [25-31], a systematic attempt has been made to study the effect of butanol isomers of varying polarities on the micelle of various surfactants in *n,n*-dimethyl acetamide, using conductivity and surface tension methods. The various aspects of interaction of these surfactants in *n,n*-dimethyl acetamide during micelle formations in presence of butanol isomers are also discussed.

2. Experimental Details

n,n-dimethyl acetamide (DMA) after drying for 72 hours on freshly ignited quick lime, was repeatedly vacuum distilled and the middle fraction of DMA having a specific conductivity (k) in the range of $2.5 \times 10^{-6} \text{ S cm}^{-1}$ was collected.

The surface tension of surfactant solutions was measured at various temperatures using a TRAUBE'S STALAGMOMETER Model 4855. The instrument consists of a straight tube which widens out in the upper part to form a bulb and narrows to a capillary tube in lower part, the open of which is ground smooth. The instrument is calibrated using water and *n,n*-dimethyl acetamide.

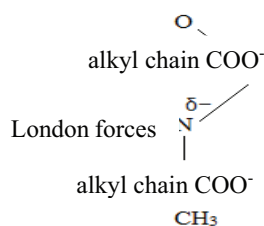
All the surfactants used in the present work obtained from FLUKA (Purity > 99 %), and were used without further purification. The alcohol, 1-butanol (1-BuOH), 2-butanol (2-BuOH) and tertiary butanol (t-BuOH) were either from FLUKA, BDH or MERCK products (research grade), and were used without purification. Specific conductivities of the solutions were measured at various temperatures using a CRISON Model 255 CONDUCTIMETER and a dipping cell with platinum electrodes (cell constant = 0.12 cm^{-1}). The reproducibility of the instruments was better than 0.1 % accuracy better than 0.2 %.

For each of the surfactants the cmcs were determined precise to $\pm 1\%$ from an apparent discontinuity in the plot of Λ vs c as described elsewhere [25–31]. Similarly, a discontinuity in surface tension is also observed at certain concentration, for each of the surfactants. The average cmc values by these methods are reported in Table 1.

3. Results and Discussion

As it is reported in Table I that as the number of carbon atoms in the anionic surfactant increases the cmc decreases. Similar behavior has been observed by some workers [32–36].

The change in cmc with 1-butanol (1-BuOH), 2-butanol (2-BuOH) and tertiary butanol (t-BuOH) at concentration of 0.1 M in *n,n*-dimethyl acetamide at different temperatures are reported in table 2. Table 2 shows that the cmc of sodium surfactants are lower in presence of butanol isomers in *N,N*-dimethyl acetamide than in *N,N*-dimethyl acetamide [25–27]. The ion-solvent interaction in presence of butanol isomers in DMA, in terms of a molecular picture, can be looked upon somewhat as follows: The micelle formation in DMA could be due to the effects like ion-solvent interactions, hydrogen bonding, and dispersion forces, even though the dielectric constant of *N,N*-dimethyl acetamide (DMA) is much lower than acetamide and *N*-methyl acetamide (28–30). It could be suggested that the micelle formation in DMA in presence of butanol isomers, is due to the orientation of the opposite end of the solvent dipole, which causes ion-solvent interaction. It could also be suggested that in DMA, the ability of nitrogen to participate in resonance with the carbonyl group is more likely than in *N*-methyl acetamide and acetamide. The process can be seen as follows



An increase in cmc is seen for 1-BuOH, 2-BuOH and t-BuOH at 25, 30, 35, and 40°C. Increase in cmc upon addition of 1-BuOH, 2-BuOH and t-BuOH is due to the solvent power of the n,n-dimethyl acetamide-alcohol mixture. The hydrophobic effect associated with the hydrophobic moiety of alcohol molecules also favors micellization and increases as dipole of 1-BuOH, 2-BuOH and t-BuOH increases.

TABLE 1: Critical micelle concentration of sodium surfactants in N,N, dimethylacetamide at 25°C in the presence of 1-BuOH, 2-BuOH, t-BuOH at different concentrations.

SURFACTANT	ALCOHOL	≠C.M.C. x 10 ⁻³ M				
		0.1 M	0.5 M	1.0 M	2.0 M	4.0 M
Sodium Caprylate (C ₈)	*	24	27	33	38	47
	1-BuOH	21	24	29	33	42
	2-BuOH	18	22	26	31	38
	t-BuOH	14	17	23	29	33
Sodium Laurate (C ₁₂)	*	19	23	28	37	45
	1-BuOH	16	19	23	33	40
	2-BuOH	14	18	21	28	34
	t-BuOH	10	14	18	24	29
Sodium Palmitate (C ₁₆)	*	18	19	30	36	41
	1-BuOH	12	14	27	32	37
	2-BuOH	10	13	20	26	37
	t-BuOH	8	12	17	22	31
Sodium Stearate (C ₁₈)	*	10	13	21	27	37
	1-BuOH	6	9	16	22	30
	2-BuOH	4	6	13	18	26
	t-BuOH	2	3	9	13	20

* In pure N, N-dimethyl acetamide
 ≠ Average values obtained from conductance and surface tension measurements at 25°C.± 0.01°C

The changes in cmc with increasing the concentration of 1-BuOH, 2-BuOH and t-BuOH are also reported in Table 1 and are shown in figure [1-4].

Change in cmc of sodium surfactants with increasing concentration of **Fig (1)**: N, N Dimethyl acetamide (DMA) **Fig. (2 - 4)** 1-BuOH, 2-BuOH, t-BuOH in N,N Dimethyl acetamide (DMA)

TABLE 2: Critical micelle concentration of sodium surfactants in presence of 0.1M of 1-butanol (1-BuOH), 2-butanol (2-BuOH) and tertiary-butanol (t-BuOH) solution in N-N-dimethyl acetamide (DMA) at different temperatures.

SURFACTANT	ALCOHOL	≠C.M.C. x 10 ⁻³ M			
		298K	303K	308K	313K
Sodium Caprylate (C ₈)	*	24	27	31	34
	1-BuOH	21	23	27	30
	2-BuOH	18	20	22	27
	t-BuOH	14	16	18	23
Sodium Laurate (C ₁₂)	*	19	23	27	30
	1-BuOH	16	20	22	26
	2-BuOH	14	17	19	22
	t-BuOH	10	12	14	18
Sodium Palmitate (C ₁₆)	*	14	18	23	27
	1-BuOH	12	14	20	23
	2-BuOH	10	11	17	20
	t-BuOH	8	10	13	17
Sodium Stearate (C ₁₈)	*	8	12	18	23
	1-BuOH	6	9	15	20
	2-BuOH	4	7	13	16
	t-BuOH	2	4	9	12

* In pure solvent (DMA)
 ≠ Average values obtained from conductance and surface tension methods.

For 1-BuOH, 2-BuOH and t-BuOH, cmc increases on increasing 1-BuOH, 2-BuOH and t-BuOH concentration in n,n-dimethyl acetamide which can be explained on the basis of increased solubility of non-polar part of the anionic surfactants in non-aqueous medium. This is because the addition of 1-BuOH, 2-BuOH and t-BuOH disrupts the n,n-dimethyl acetamide structure or solvates the solute molecules preferentially and can be explained as follows: it is known that the major factor that determines the intermicellar solubility of 1-BuOH, 2-BuOH and t-BuOH is the change in hydrophilic balance of the micelle during the inclusion of alcohol in it [4, 37]. At the minimum cmc, micelles become saturated with 1-BuOH, 2-BuOH and t-BuOH so that molecules move into n,n-dimethyl acetamide causing it to be more hydrophobic. This causes an increase in cmc on further addition of 1-BuOH, 2-BuOH and t-BuOH.

The thermodynamic parameters for sodium surfactants in n,n-dimethyl acetamide in presence of 1-BuOH, 2-BuOH and t-BuOH were calculated. The free energies of micelle formation are calculated using the relationship

$$\Delta G_m^0 = -RT \ln \text{cmc}$$

Even though the size of the micelle is not known at present. Also the high cmc values in *n,n*-dimethyl acetamide may invalidate the use of above mentioned equation, because the monomer activity would be quite different from the monomer concentration. Such ΔG° values should therefore, be taken as only approximation. The results for sodium surfactants in *n,n*-dimethyl acetamide in presence of 1-BuOH, 2-BuOH and *t*-BuOH are mentioned in Table 3.

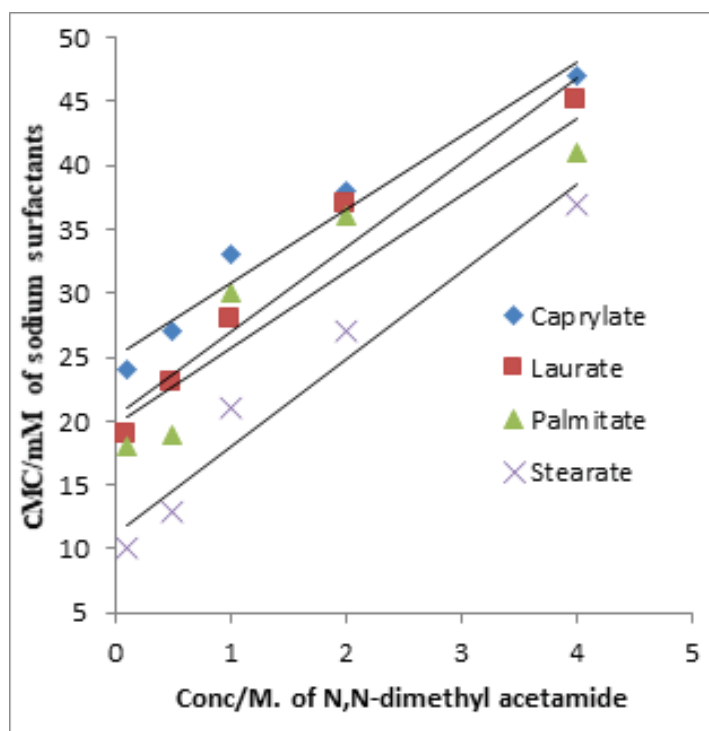


Figure 1

It is evident from Table 3, that there is a decrease in the standard Gibbs energy of micelle formation as the number of carbon atoms in alkyl chain of various surfactant increases. It suggests that a strong solvophobic interaction takes place for longer alkyl chain in *n,n*-dimethyl acetamide.

Table 2 gives the cmc values of sodium surfactants in *n,n*-dimethyl acetamide in presence of 1-BuOH, 2-BuOH and *t*-BuOH at different temperatures. It was observed that with increase in temperature, cmc increased in pure solvent (DMA) and also in the presence of 0.1M butanol isomers in DMA as shown below in figures [5-8].

Change in cmc of sodium surfactants as function of temperature in presence of **fig (5)** pure solvent (DMA) **fig (6)** 1-BuOH in DMA

Change in cmc of sodium surfactants as function of temperature in presence of **fig (7)** 2-BuOH in DMA **fig (8)** *t*-BuOH in DMA

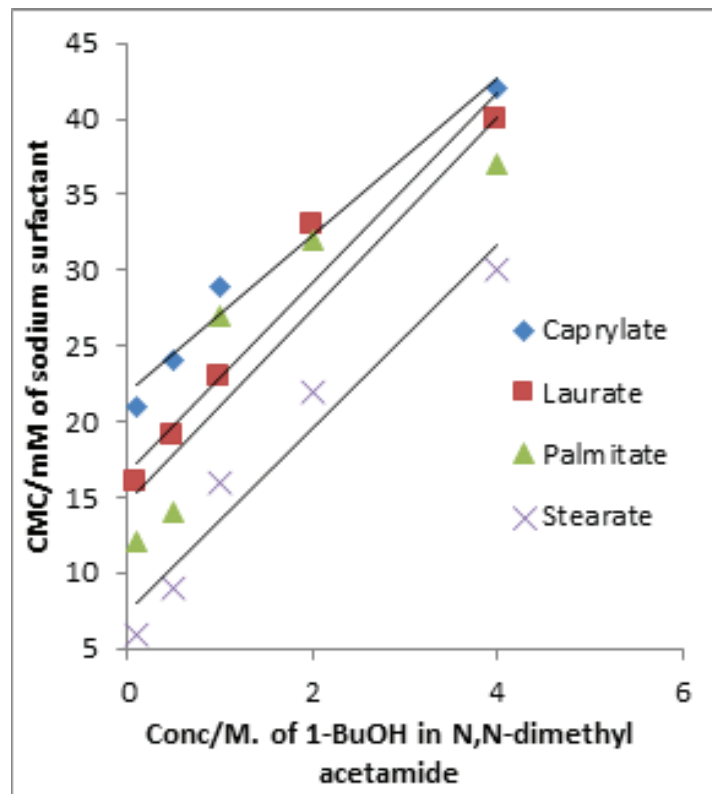


Figure 2

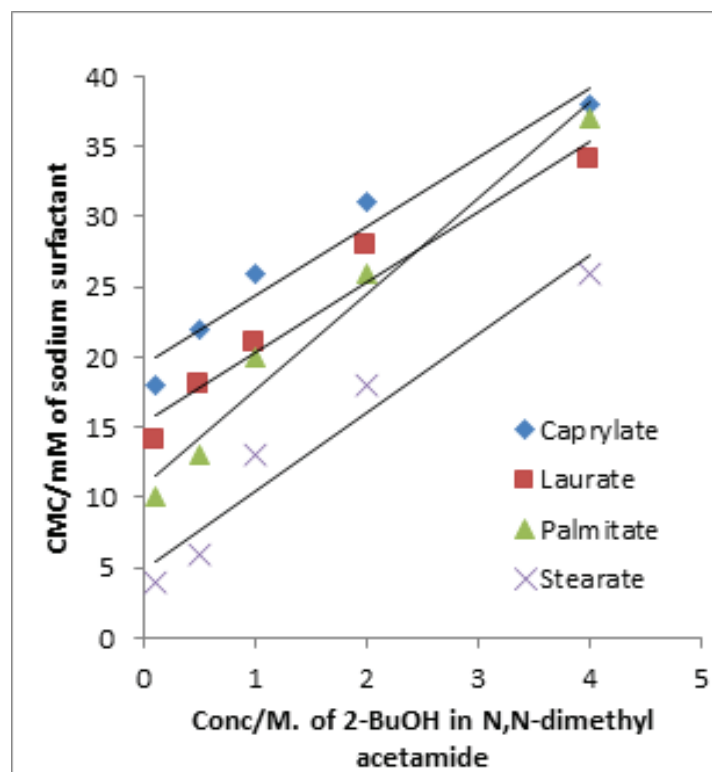


Figure 3

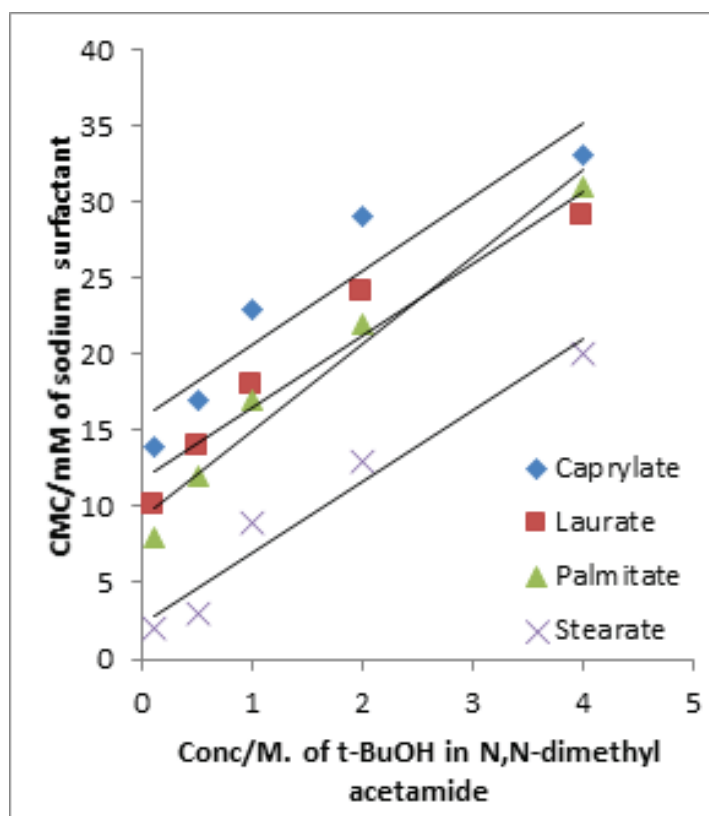


Figure 4

TABLE 3: Thermodynamic parameters ($\Delta G_m^\circ, \text{kJmol}^{-1}$, $\Delta H_m^\circ, \text{kJmol}^{-1}$, $\Delta S_m^\circ, \text{JK}^{-1}$) for sodium surfactants in N,N-dimethylacetamide in presence 1-BuOH, 2-BuOH and t-BuOH (0.1M).

SURFACTANT	PURE SOLVENT			1-BuOH			2-BuOH			t-BuOH		
	ΔG_m°	ΔH_m°	ΔS_m°	ΔG_m°	ΔH_m°	ΔS_m°	ΔG_m°	ΔH_m°	ΔS_m°	ΔG_m°	ΔH_m°	ΔS_m°
Sodium Caprylate(C8)	-9.24	-14.2	16.6	-9.58	-14.8	17.5	-9.96	-15.2	17.6	-10.6	-15.8	17.4
Sodium Laurate(C12)	-9.82	-14.6	16.0	-10.3	-15.0	15.8	-10.6	-15.7	17.1	-11.4	-16.3	16.4
Sodium Palmitate(C16)	-10.6	-15.1	15.1	-11.0	-15.9	16.4	-11.4	-16.2	14.4	-12.0	-17.0	16.8
Sodium Stearate (C18)	-12.0	-15.7	12.4	-12.7	-16.4	12.4	-13.7	-17.0	11.1	-14.2	-17.6	11.4

The plot of $\ln \text{cmc}$ of sodium surfactants against $1/T$ gives a good straight line with a negative slope. This shows that the micelle size does not change within the temperature range studied. In the present work, the Van't Hoff equation

$$\frac{d \ln \text{cmc}}{dT} = \frac{-\Delta H^0}{RT^2}$$

is applicable. The values of ΔH^0 , enthalpy of micellization, have been calculated from the slope of the line and are included in Table 3.

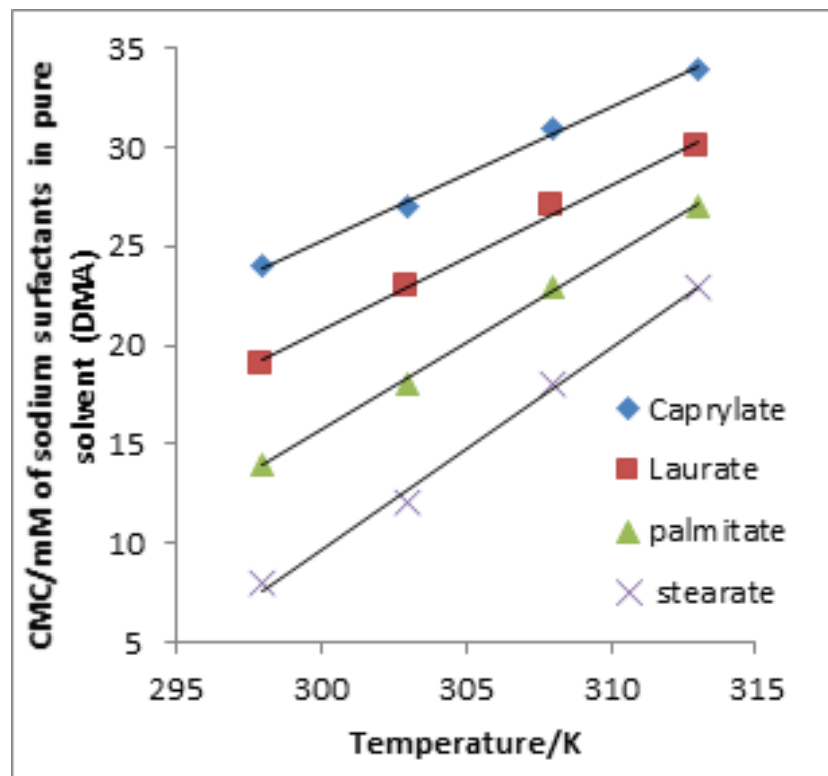


Figure 5

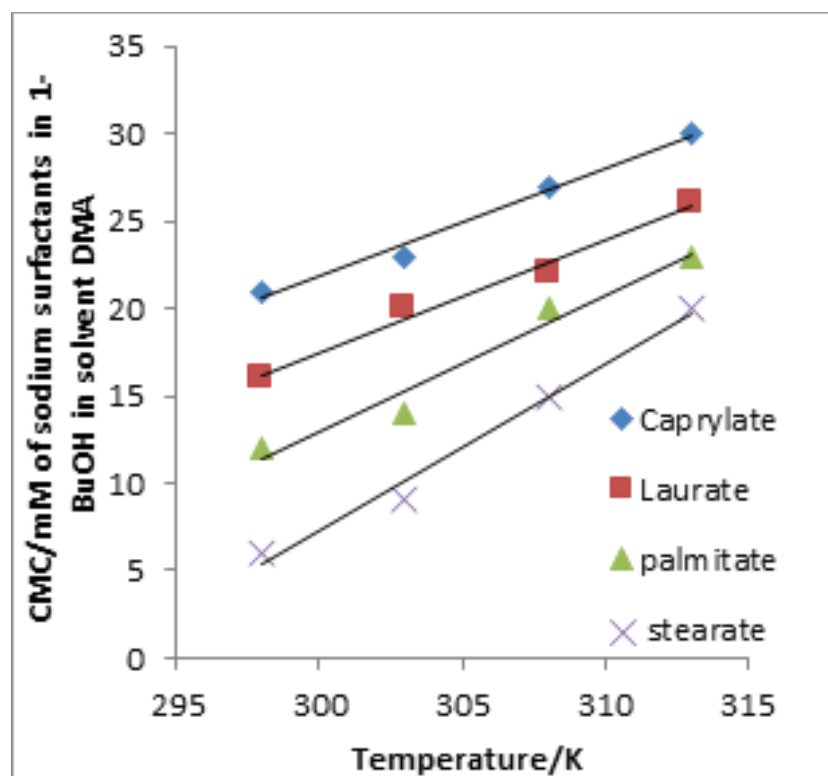


Figure 6

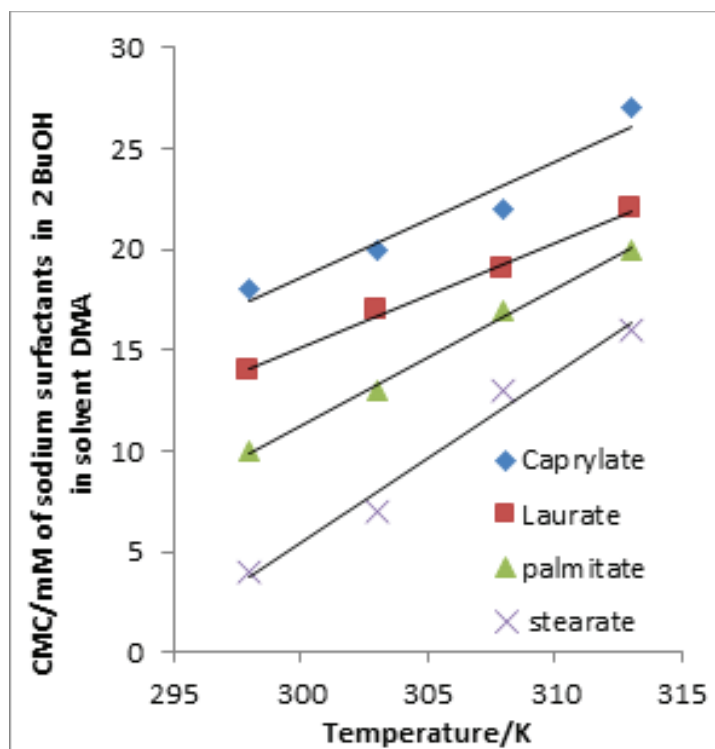


Figure 7

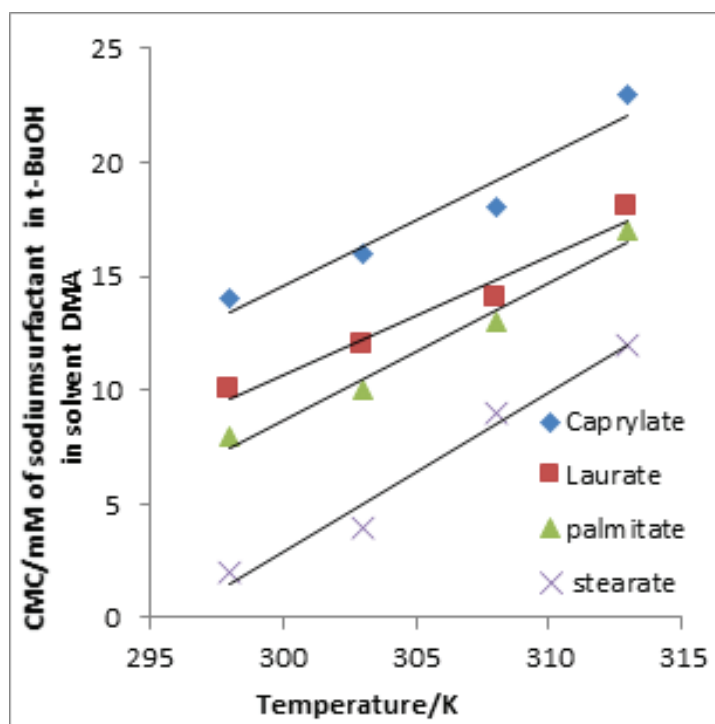


Figure 8

These values are in the range of the hydrogen bond energy. *n,n*-dimethyl acetamide has a strong tendency to form hydrogen bonding. Negative values for ΔH were obtained for the micelle formation of the surfactant tetra decyl-trimethylammonium

bromide (C₁₄ TAB) in water and hydrazine [38]. The standard entropies of micellization were calculated from the values of ΔH_m^o and ΔG_m^o using $\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o$ and are also included in Table 3.

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 ice-berg structure surrounding the hydrocarbon chains of the monomeric surfactants.

The effects on the enthalpy and entropy were small in 0.1 M 1-BuOH, 2-BuOH and t-BuOH. Possibly this effect is operative primarily on the hydrophobic group of the sodium surfactants while only secondarily on the hydrophilic group.

It was also observed that in presence of 1-BuOH, 2-BuOH and t-BuOH, the enthalpy is more negative and entropy is less positive. Therefore, the contribution of the enthalpy to the micellization becomes increasingly important with 1-BuOH, 2-BuOH and t-BuOH in contrast to the predominance of entropy in the aqueous solution. Similar behavior of more negative enthalpy in presence of organic additives has been observed [39–41].

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