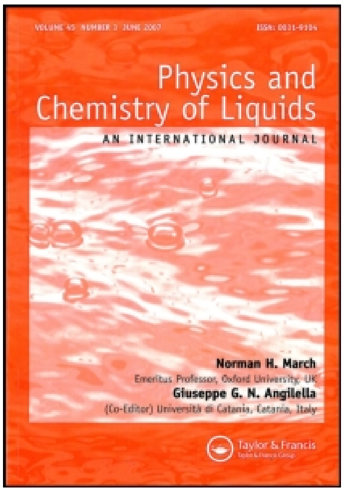

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EFFECT OF ELECTROLYTES AND NON-ELECTROLYTES ON THE MICELLIZATION OF SAMARIUM SOAPS IN WATER METHANOL MIXTURE

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The conductometric studies of the solutions of samarium valerate and caproate in methanol and in a mixture of water and methanol in presence of electrolytes (uni-, bi- and tri-valent) and non-electrolytes were used to evaluate the critical micelle concentration (CMC) and the free energy change for the micellization process. The CMC was found to decrease with increasing ionic radii of counterions. The results suggest that these soaps behave as weak electrolytes in dilute solutions below the CMC.

KEY WORDS: Specific conductance, ionic radii, surface charge density

INTRODUCTION

While a large number of studies have been carried out on the effect of various additives on the micellization of surfactants[1–9], physico-chemical studies on lanthanide soaps in the presence of additives have not been made so far. The studies on the nature and structure of these soaps are of great importance for their uses in industries and for explaining their characteristics under different conditions. The methods of preparation and properties of lanthanide soaps have been reviewed by Mehrotra[10] and Marwedel[11].

The present work deals with the effect of the electrolytes of varying valency (K^+, Mg^{2+} and Al^{3+}) and non-electrolytes (urea and sudan dye) on the micellization of valerate and caproate of samarium in methanol and in a mixture of water and methanol.

EXPERIMENTAL

All the chemicals used were of BDH/AR grade. Solvent methanol was purified by distillation under reduced pressure. The soaps were prepared and purified by the method described in our earlier communication[12]. Samarium soaps (valerate and

Table 1 The values of specific conductance (milli mhos), K of samarium caproate (S.C.) solution in presence of different electrolytes and non-electrolytes at (30 ± 0.05)°C

Conc. C × 10² *mol/dm³*	*S.C.* CH_3OH	*S.C.* $H_2O—CH_3OH$	*S.C.* $H_2O—CH_3OH$ $+Al(NO_3)_3$	*S.C.* $H_2O—CH_3OH$ $+Mg(NO_3)_3$	*S.C.* $H_2O—CH_3OH$ $+KNO_3$	*S.C.* CH_3OH *+ Urea*	*S.C.* CH_3OH *+ Sudan dye* $(7 \times 10^{-5}\ M)$
5.00	0.146	0.336	0.560	0.494	0.370	0.187	0.168
4.17	0.133	0.307	0.556	0.478	0.338	0.172	0.151
3.57	0.123	0.284	0.552	0.464	0.315	0.162	0.139
3.12	0.115	0.266	0.540	0.452	0.297	0.153	0.128
2.77	0.108	0.250	0.527	0.440	0.278	0.145	0.121
2.27	0.098	0.230	0.505	0.420	0.251	0.132	0.108
1.92	0.090	0.213	0.488	0.404	0.230	0.123	0.099
1.66	0.083	0.198	0.477	0.393	0.212	0.115	0.091
1.39	0.076	0.181	0.464	0.383	0.195	0.106	0.083
1.25	0.072	0.172	0.445	0.375	0.190	0.101	0.078
1.04	0.065	0.156	0.424	0.359	0.180	0.092	0.071
0.89	0.060	0.144	0.408	0.345	0.170	0.086	0.065
0.78	0.056	0.134	0.394	0.334	0.160	0.081	0.061
0.69	0.054	0.127	0.384	0.328	0.153	0.077	0.058
0.66	0.053	0.124	0.380	0.325	0.151	0.075	0.056

caproate) were insoluble while the electrolytes were highly soluble in water. The solution of soap and electrolytes were prepared separately in methanol and water, respectively, and then these solutions were mixed in required amounts. On the other hand the calculated amounts of non-electrolyte (urea and sudan dye) were directly added to the solutions of soaps in methanol. The conductance of the soap solutions was measured with a digital conductivity meter (Toshniwal CL 01.10 A) and a dipping type conductivity cell with platinized electrodes (cell constant 0.875) at (30 ± 0.05)°C in a thermostat.

RESULTS AND DISCUSSION

The specific conductance of the solutions of samarium soaps (valerate and caproate) in methanol and water-methanol mixture increases with increasing soap concentration (Table 1) which may be due to the fact that samarium soaps behave as an electrolyte in dilute solution and are ionized into simple metal cations, Sm^{3+} and fatty acid anions, $RCOO^-$ (where R is C_4H_9 and C_5H_{11} for valerate and caproate) respectively. The increase of specific conductance at higher soap concentrations may be due to the formation of ionic micelles of higher conducting power than the simple ions. The plots of specific conductance vs. soaps concentration exhibit two breaks. The first break occurs at a concentration, CMC (I), at which anions begin to aggregate to form ionic micelles and the second break which is observed at higher soap concentration, CMC (II), may be due to the probable formation of neutral colloid. The particles of neutral colloid are charged due to the attachment of ions.

The specific conductance of the dilute solutions of samarium soaps increases with the addition of electrolytes (Table 2). It is observed that the values of CMC (I) for samarium valerate and caproate without any additive are higher than the corresponding values for soap solutions in presence of ions of varying valency (Table 2). On the other hand, the addition of nonelectrolytes (urea and sudan dye) has no effect on the CMC of these soap solutions.

Table 2 The values of CMC and free energy for micellization, ΔGm of samarium soaps

	Samarium valerate (0.05 M)			*Samarium caproate (0.05 M)*		
	CMC × 10^2 (mol/dm^3)		*−ΔGm KJ mol^{-1}*	*CMC × 10^2 (mol/dm^3)*		*−ΔGm KJ mol^{-1}*
	I	*II*		*I*	*II*	
No additive	1.80	3.10	41.92	1.60	3.00	42.61
Al^{3+}	1.70	3.75	42.25	1.50	3.35	42.98
Mg^{2+}	1.50	3.60	42.98	1.30	3.25	43.81
K^+	1.35	3.20	43.59	1.20	3.05	44.28
Urea	1.80	3.10	41.92	1.60	3.00	42.61
Sudan dye	1.80	3.10	41.92	1.60	3.00	42.61

The values of the CMC of samarium soaps in methanol–water mixture in the presence of cations of varying valency are in the order:

$$\text{CMC (I): } Al^{3+} > Mg^{2+} > K^{+}$$

$$\text{CMC (II): } Al^{3+} > Mg^{2+} > K^{+}$$

It is concluded that the increase in ionic radii and decrease in valency of added cation (Al^{3+}, Mg^{2+} and K^{+}) result in the decrease of the CMC in a curvilinear manner (Figure 2). The results are in agreement with the observations of Goddard *et al.*[7] and Mukerjee *et al.*[13]. The addition of electrolyte causes a reduction in the thickness of the ionic atmosphere surrounding the polar head groups and a consequent decrease in repulsion between them. These effects are manifest as reduction in CMC and an increase in aggregation number[14].

MOLAR CONDUCTANCE, μ

The molar conductance, μ, of the solutions of samarium valerate and caproate in methanol and in water–methanol mixture decreases with increasing soap concentration (Figure 1). The decrease may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of micelles. The plots of molar conductance, μ vs. square root of soap concentration, $\sqrt{C}$ (Figure 1) are not linear which indicates that the soap behaves as a weak electrolyte in dilute solutions. The molar conductance of the dilute solutions of samarium soaps increases with the addition of additives but the nature of the curves (Figure 1: μ vs. $C^{1/2}$) remain the same. The standard free energy of micellization, ΔGm, at constant temperature is related to the critical micellar concentration by the following equation[14]:

$$\Delta Gm = 2RT \text{ In } XCMC \tag{1}$$

Where XCMC is the CMC expressed as a mole fraction and is defined as:

$$XCMC = \frac{ns}{ns + nsol} \simeq \frac{ns}{nsol} \tag{2}$$

Since the number of moles of soap, ns is small as compared to the number of moles of the solvent, nsol.

The values of free energy for micellization for samarium soap solutions in absence of additives (Valerate; -42.61 KJ mol^{-1} and caproate; -41.92 KJ mol^{-1}) are lower than the corresponding values in presence of additives. The free energy of micelle formation is less negative for ions of small ionic radii (Table 2). For ionic system, the free energy includes a contribution due to the involvement of the counterion with the micelles. This contribution may be taken into account either by a chemical

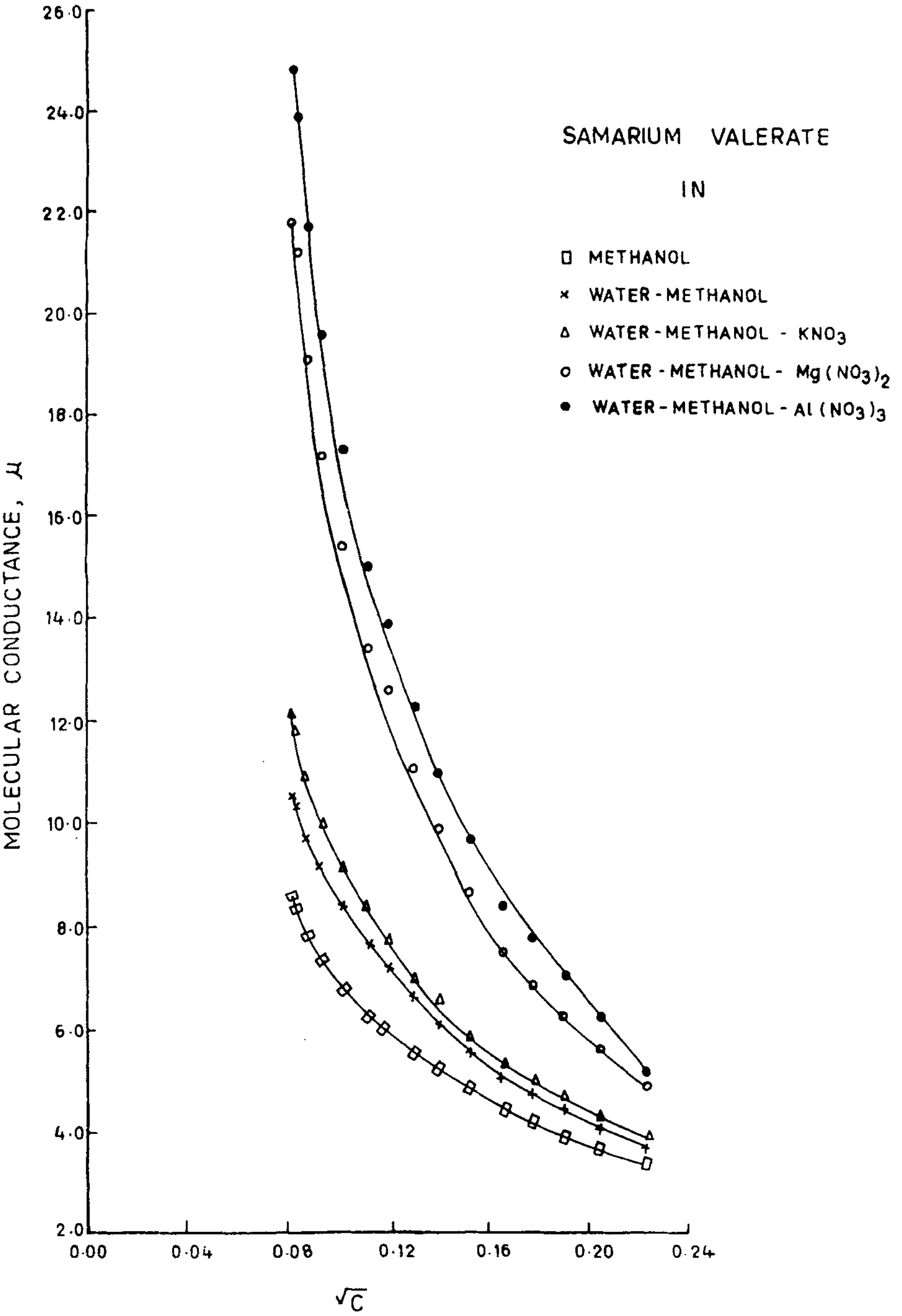

Figure 1 Molar conductance, μ, vs. square root of concentration, $C^{1/2}$.

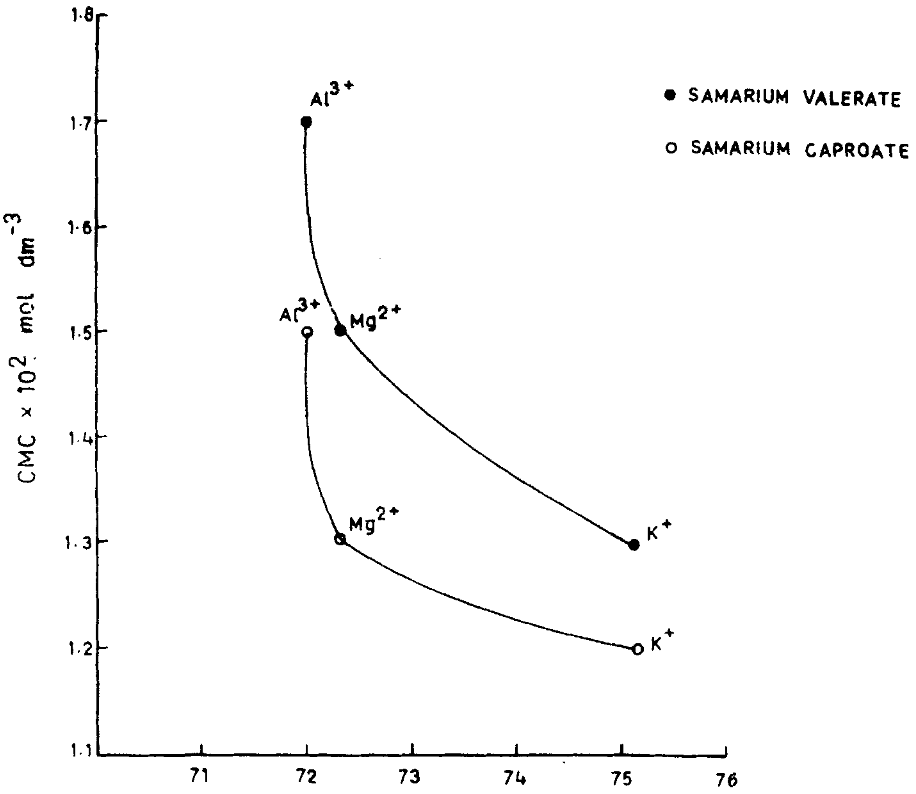

Figure 2 Variation of CMC of samarium valerate and samarium caproate with ionic radii in Å.

approach based on binding of some counterions to the micelles or by a physical approach using an electrostatic calculation based on a fully ionized model[14].

It is, therefore, concluded that the nitrates of potassium magnesium and aluminium are effective electrolytes in causing CMC lowering and that potassium nitrate is the most effective electrolyte. The main factor which causes a decrease in CMC appears to be the reduction of the free energy of the micelle due to the diluted surface charge density on the micelle. On the other hand, the addition of non-electrolyte (urea and sudan dye) has no effect on the CMC of these soap solutions.

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