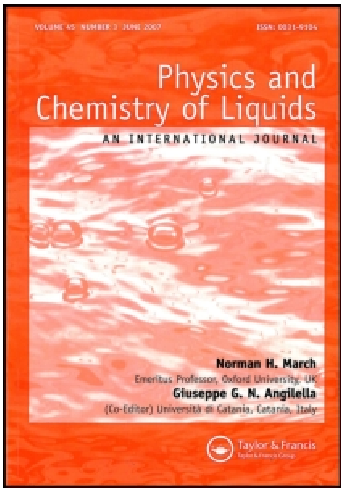

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Effect of electrolytes and non-electrolyte on micellar behaviour of lanthanum soaps in non-aqueous solvents

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The miceller behaviours of the solution of lanthanum butyrate and caprylate in a mixture of benzene and methanol in presence of uni-, bi- and trivalent electrolytes and non-electrolytes were studied by the means of conductivity measurements, and the results were used to evaluate the critical micelle concentration (CMC) and the free energy change for the process of micellization. The CMC was found to decrease with increasing ionic radii of electrolytes. The results show that these soaps behave as weak electrolytes in dilute solutions below the CMC.

Keywords: Micellization; Electrolyte; Free energy; Ionic radii; CMC

1. Introduction

The inner transition metal soaps are being widely used in industries and the play an important role in surface chemistry [1–3]. The effect of additives, i.e. electrolytes and non-electrolytes on the CMC of soaps in non-aqueous solvents are of great importance for their applications in industries and for explaining their characteristics under different conditions [4]. Several workers [5–10] paid attention in the study of lanthanide soaps.

In the present work, attempts have been made to compute the effect of the electrolytes of different valenceies (K^+, Mg^{+2} and Al^{+3}) and non-electrolyte (urea) on the CMC of butyrate and caprylate of lanthanum in a mixture of benzene and methanol (50% v/v).

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2. Experimental

All the chemicals used were of BDH grade. Benzene was purified by keeping over sodium wire for several hours and then distilled. Methanol was purified by keeping over potassium hydroxide and then distilled. Lanthanum soaps (butyrate and caprylate) were prepared by direct metathesis of the corresponding potassium soap. These soaps were purified by recrystallization with benzene–methanol mixture and checked by elemental analysis [12,14].

The solution of soap and electrolytes were prepared in benzene and methanol mixture separately and after that these solutions were mixed in required amount. The calculated amount of non-electrolyte had been added to the solutions of soap in benzene–methanol mixture directly [11]. The conductivity measurements were made with a *Toshniwal Digital conductivity Meter "Type CL 01.10 A"* using dipping-type conductivity cell with platinized electrodes.

3. Results and discussion

The specific conductance, κ of the dilute solution of lanthanum soaps (butyrate and caprylate) in a mixture of benzene and methanol (50% v/v) increases with the increase in soap concentration, C (g mol L^{-1}). The increase of specific conductance is more rapid in dilute solutions due to greater ionization of metal soaps into simple metal cation (La^{3+}) and fatty acid anions, $RCOO^-$ (where R is C_3H_7 and C_7H_{15} for butyrate and caprylate). The increase of specific conductance at higher soap concentration is due to the formation of ionic micelles of higher conducting power than the simple ions.

The specific conductance of the dilute solutions of lanthanum soaps (butyrate and caprylate) increases with the addition of electrolytes. Tables 1 and 2 show that the values of CMC for lanthanum soaps without additive are higher than the corresponding

Table 1. The values of specific conductance of lanthanum butyrate solution in benzene methanol mixture (50% v/v) and in presence of different electrolytes and non-electrolyte at (40 ± 0.05)°C.

	Specific conductance of ($\kappa \times 10^6$ mhos)				
Concentration, $C \times 10^2$ (g mol L^{-1})		Soap + $Al(NO_3)_3$	Soap + $Mg(NO_3)_2$	Soap + KNO_3	Soap + Urea
1.00	18.0	45.4	38.9	21.2	7.4
1.18	19.6	47.5	39.3	22.2	7.5
1.43	20.8	48.4	41.1	22.7	7.6
1.54	22.6	49.7	42.0	24.4	7.7
1.65	23.1	50.8	43.1	26.2	7.8
1.91	24.8	52.5	44.7	28.3	7.9
2.07	25.7	54.7	46.0	31.0	8.0
2.26	26.0	56.0	47.2	32.9	8.1
2.49	27.4	58.2	48.4	34.7	8.2
2.77	29.5	58.6	49.8	37.0	8.2
3.12	31.3	59.0	51.4	40.6	8.3
3.57	35.1	60.4	53.0	44.3	8.4
4.16	37.9	60.7	54.8	48.0	8.5
4.56	40.1	61.0	56.4	52.2	8.6
5.00	43.6	61.2	58.2	55.8	8.7

Table 2. The values of specific conductance of lanthanum caprylate solution in benzene–methanol mixture (50% v/v) and in presence of different electrolytes and non-electrolyte at (40 ± 0.05)°C.

	Specific conductance of ($\kappa \times 10^6$ mhos)				
Concentration, $C \times 10^2$ (g mol L^{-1})		Soap + $Al(NO_3)_3$	Soap + $Mg(NO_3)_2$	Soap + KNO_3	Soap + Urea
1.00	14.0	41.6	35.1	17.4	3.6
1.18	15.4	42.8	36.4	18.5	3.6
1.43	16.6	44.1	37.6	19.7	3.7
1.54	17.4	44.9	38.8	21.0	3.8
1.64	18.1	45.6	39.9	22.2	3.9
1.91	19.6	47.0	41.2	23.7	4.0
2.87	20.7	48.1	42.0	24.6	4.1
2.26	22.0	49.6	43.3	25.6	4.2
2.49	23.4	51.1	44.5	26.7	4.2
2.77	25.2	52.6	45.8	27.7	4.3
3.12	27.3	54.1	47.8	28.6	4.4
3.57	30.3	55.8	48.2	29.1	4.5
4.16	33.1	58.6	50.7	30.5	4.6
4.56	35.1	60.5	51.8	31.4	4.7
5.00	37.5	63.0	52.9	32.6	4.8

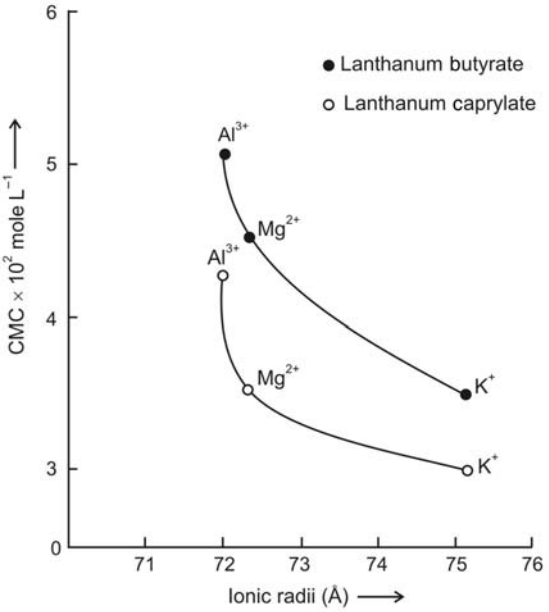

Figure 1. Variation of CMC of lanthanum butyrate and lanthanum caprylate with ionic radii.

values of lanthanum soaps solution in presence of ions of different valence. But no effect appears on the CMC of soap solutions by the addition of non-electrolyte (urea).

The values of CMC of lanthanum soaps in benzene–methanol mixture in the presence of cations of different valence are in order:

$$Al^{3+} > Mg^{2+} > K^{+}$$

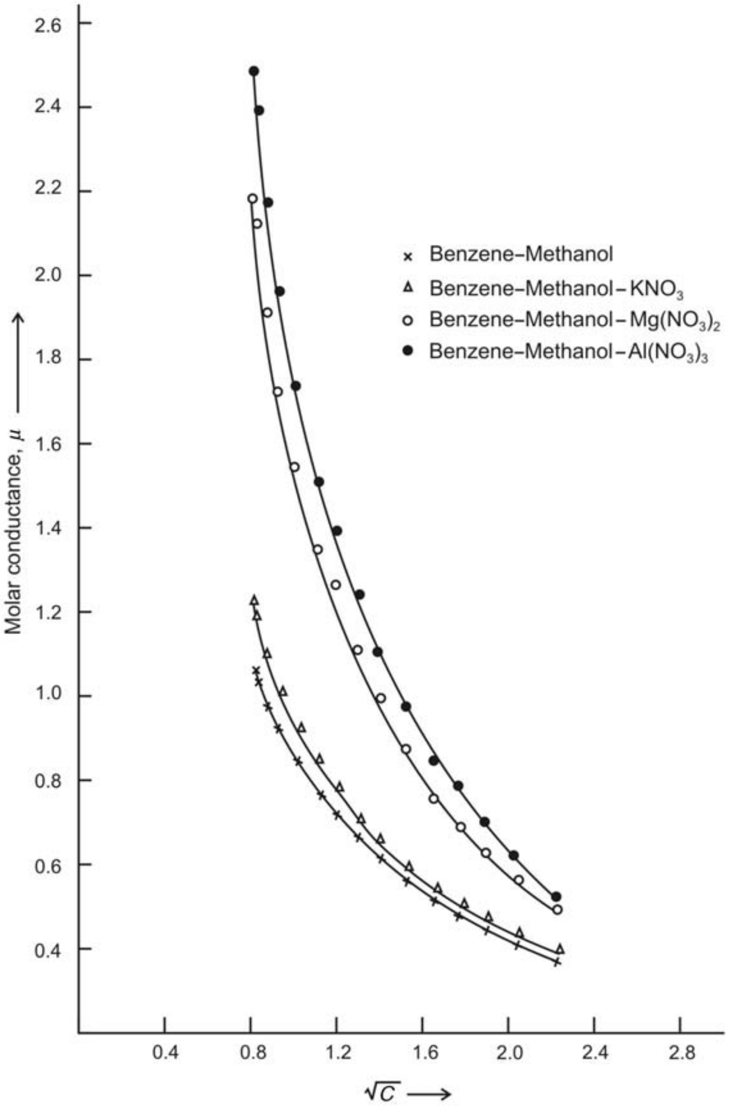

Figure 2. The plots of molar conductance, μ *vs*. square root of concentration $\sqrt{C}$ of lanthanum caprylate in various system.

It is concluded that the decrease of the CMC is due to the increase in ionic radii and decrease in valence of added cations (Al^{3+}, Mg^{2+} and K^{+}), see figure 1. The addition of electrolyte causes in the reduction of thickness of the ionic atmosphere surrounding the polar head groups and a consequent decrease in repulsion between them [6]. The results are in agreement with observations of Goddard *et al.* [17] and Mehrotra *et al.* [16].

The molecular conductance, μ of the solutions of lanthanum butyrate and caprylate in a mixture of benzene and methanol decrease with increasing soap concentrations.

Table 3. The values of CMC and free energy for micellization, ΔG_m of Lanthanum soaps.

	Lanthanum butyrate		Lanthanum caprylate	
	CMC ($\mathrm{g\,mol\,L^{-1}}$)	$-\Delta G_m$ ($\mathrm{kJ\,mol^{-1}}$)	CMC ($\mathrm{g\,mol\,L^{-1}}$)	$-\Delta G_m$ ($\mathrm{kJ\,mol^{-1}}$)
No additive	0.044	28.23	0.040	28.72
Al^{3+}	0.042	28.26	0.038	28.99
Mg^{2+}	0.039	28.86	0.035	29.42
K^+	0.035	29.42	0.032	29.72
Urea	0.044	28.23	0.040	28.72

The plot of molar conductance, μ *versus* square root of soap concentration, $\sqrt{C}$ are not linear, which indicates that soaps behave as a weak electrolyte in dilute solutions (figure 2). The standard free energy of micellization, ΔG_m at constant temperature is related to the CMC by the following relationship [15]:

$$\Delta G_m = 2RT \ln X_{CMC} \tag{1}$$

where

$$X_{CMC} = \frac{n_s}{n_s + n_{sol}} \approx \frac{n_s}{n_{sol}}$$

The values of free energy for the micellization of lanthanum soap solutions with and without additives are given in table 3.

Now, it is concluded that the main factor which causes a decrease in CMC appears to be the reduction of free energy of the micelle due to the diluted surface charge density on the micelle and that is why non-electrolyte posses no effect on the CMC of these soap solutions. So the electrolytes of potassium, magnesium and aluminium are effective in CMC lowering.

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