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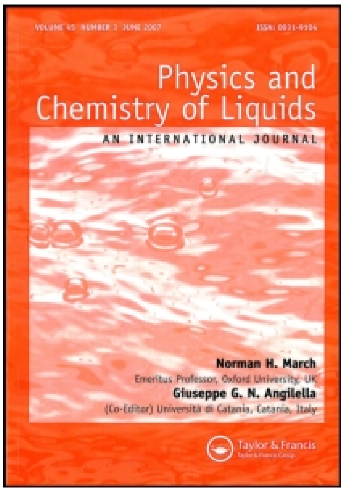

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MICELLIZATION AND CONDUCTANCE BEHAVIOUR OF THORIUM SOAP SOLUTIONS

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The critical micelle concentration, degree of dissociation and dissociation constant of dilute solutions of thorium soaps in methanol-benzene mixtures were determined from conductivity measurements. The results showed that these soaps behave as weak electrolytes in dilute solutions below the CMC and the CMC increases in presence of Sudan (IV) dye. The various thermodynamic parameters were also evaluated for both dissociation and micellization processes.

KEY WORDS: Rare-earth metal soaps, heat of dissociation, micellization, conductance.

INTRODUCTION

During the last decade, considerable work has been reported on alkali, alkaline-earth and transition metal soaps whereas only few references[1–16] are available on rare-earth metal soaps although these soaps are being widely used in many industries.

The present work deals with the studies on the conductance and micellor behaviour of thorium soaps in methanol-benzene mixtures of varying compositions at different temperatures.

EXPERIMENTAL

All the chemicals were used of BDH/AR grade. Thorium soaps (caprate and laurate) were prepared by the direct metathesis of corresponding potassium soap with the required amount of aqueous solution of thorium nitrate at 50–55°C under vigorous stirring. The soaps were purified by recrystallization and analysed for elemental and metal contents. The melting points of purified soaps were:

Caprate : 115°C
Laurate : 118°C

The solutions of thorium soaps were prepared by dissolving requisite amount of soap in methanol-benzene mixtures of desired compositions and were kept for two hours in a thermostat at desired constant temperature.

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The conductance measurements of the solutions of thorium soaps were taken with a Toshniwal digital conductivity meter model CL 01.10A and a dipping type conductivity cell with platinised electrodes at a constant temperature.

RESULTS AND DISCUSSION

The specific conductance of dilute solutions of thorium soaps in methanol-benzene mixtures of varying composition (30, 40, 50 and 60% methanol) increases with the increase in the concentrations of soap, methanol and dye and with increasing temperature. The values of critical micelle concentration, (CMC) of thorium soap

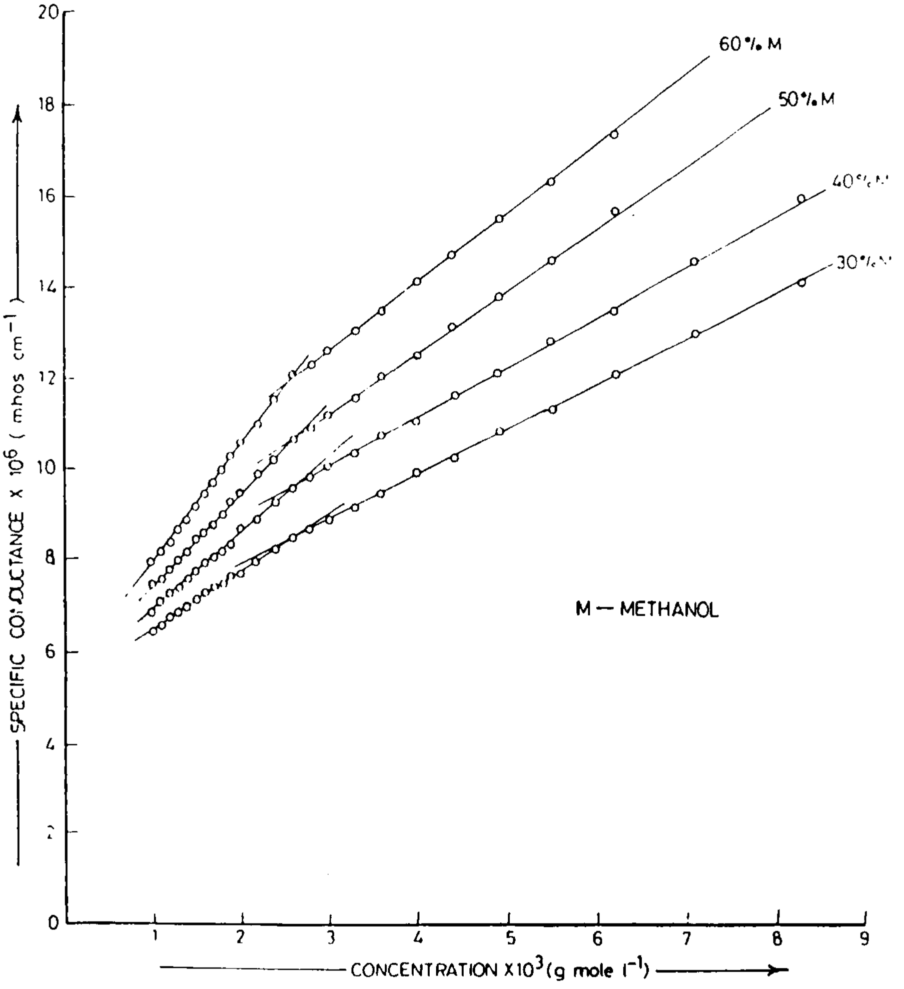

Figure 1 Specific conductance vs. concentration plots for thorium caprate in methanol-benzene mixtures at 30 ± 0.05°C.

solutions were determined from the plots of specific conductance vs. soap concentration which are characterised by an intersection of two straight lines at the CMC (Figure 1).

The increase in temperature and concentration of dye results in the increase of the CMC and the values of CMC were found to be almost independent of solvent composition (Table 1).

The molar conductance of the dilute solutions of thorium soaps decreases with increasing soap concentration. However, the CMC cannot be obtained from the plots of molar conductance vs. square root of soap concentration (Figure 2) which are concave upwards with increasing slopes indicating that thorium soaps behave as weak

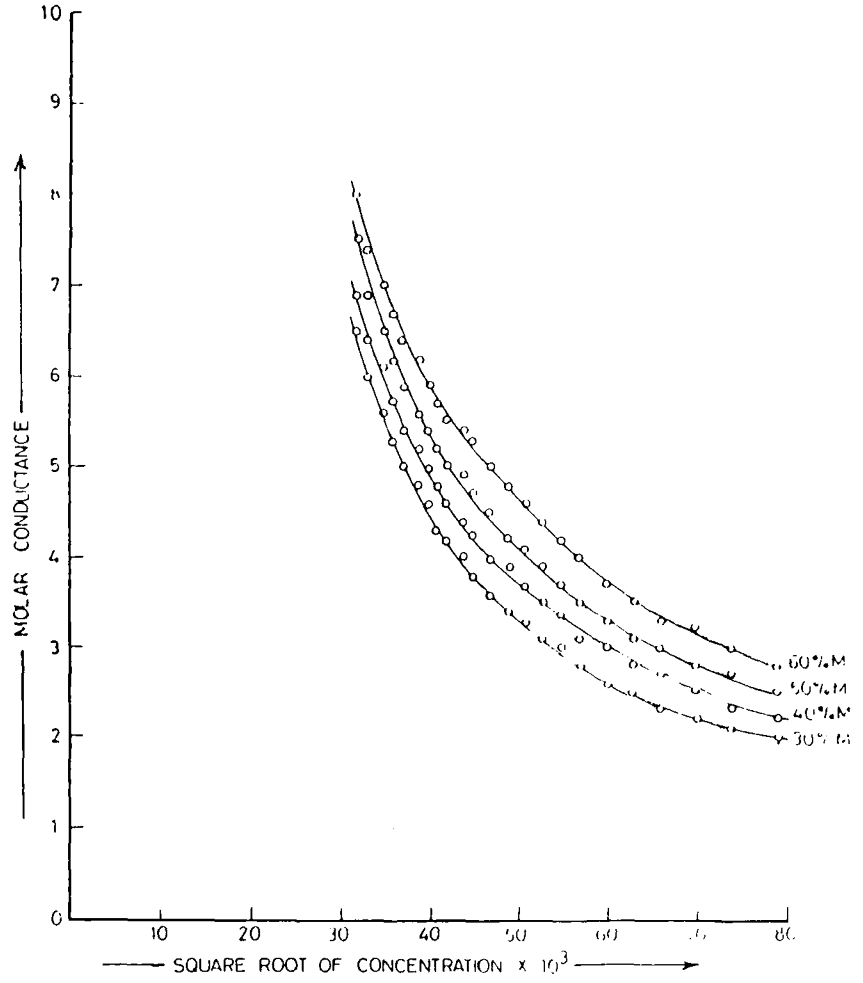

Figure 2 Molar conductance vs. square root of concentration plots for thorium caprate in methanol-benzene mixtures at 30 ± 0.05°C.

Table 1 CMC values of thorium soaps in g moles l^{-1}.

Name of soaps	*CMC × 10³*			
	30°	*40°*	*50°*	*60°*
Thorium caprate	2.6	3.0	3.3	3.5
Thorium laurate	1.5	1.8	2.1	2.3

electrolytes in dilute solutions and Debye-Huckel-Onsager's equation is not applicable to these soap solutions. Since thorium soaps behave as weak electrolytes in dilute solutions, the expression for the dissociation may be developed in Ostwald's manner:

$$\begin{array}{ccccc} (\mathrm{RCOO})_4\mathrm{Th} & \rightleftharpoons & \mathrm{Th}^{4+} & + & 4.\mathrm{RCOO}^- \\ \mathrm{C}(1-\alpha) & & \mathrm{C}\alpha & & 4.\mathrm{C}\alpha \end{array}$$

where C and α are the concentration and degree of dissociation of soap, respectively. The dissociation constant, K and be expressed as:

$$K = \frac{256\mathrm{C}^4\alpha^5}{1-\alpha} \tag{1}$$

Since α is very small, interionic effects may be treated as negligible. Assuming α as equal to the conductance ratio, μ/μ_0 and rearranging, Eq. (1) can be written as:

$$\mu^4 c^4 = \frac{K\mu_0^5}{256\mu} - \frac{K\mu_0^4}{256}$$

The values of μ_0 and K were determined from the slope, $[K\mu_0^5/256]$ and intercept, $[-K\mu_0^4/256]$ of the plots of $\mu^4 c^4$ vs. $1/\mu$ are recorded in Tables 2 and 3.

Table 2 Values of limiting molar conductance of thorium soaps.

Percentage of	*Thorium caprate*			
Methanol	*30°*	*40°*	*50°*	*60°*
30	12.66	14.87	17.41	23.11
40	13.01	15.59	18.49	23.39
50	13.71	16.41	19.00	24.31
60	14.65	17.21	19.49	24.78
	Thorium laurate			
30	10.77	12.64	14.93	16.99
40	11.81	13.44	15.71	17.78
50	12.85	15.24	17.01	18.88
60	13.96	16.03	18.22	19.61

Table 3 Values of dissociation constant.

Percentage of methanol	*Thorium caprate* $K \times 10^{11}$ 30°	40°	50°	60°
30	2.7	1.6	1.0	0.7
40	5.1	2.3	1.4	0.9
50	9.4	3.9	1.9	1.2
60	17.6	6.1	2.7	1.6
	Thorium laurate			
30	4.7	2.7	1.6	1.0
40	6.8	3.5	1.9	1.1
50	10.5	4.7	2.2	1.2
60	15.5	6.6	2.8	1.4

The values of degree of dissociation and dissociation constant decrease rapidly in dilute solutions but decrease slowly above the CMC with increasing soap concentration. The dissociation constant increase with increasing amount of methanol in solvent mixture and with the chainlength of the soap while it decreases with increase of temperature. The decrease in the values of K with increasing temperature indicates the exothermic nature of thorium soaps in methanol-benzene mixtures.

The values of heat dissociation, ΔH_D for thorium soap solutions in methanol-benzene mixtures of varying compositions were obtained from the slope of linear plots of log K vs. $1/T$ (Figure 3) and are tabulated (Table 4). The heat of dissociation from thorium soaps is negative indicating that the dissociation of thorium soap is exothermic. However, the heat of dissociation decreases with the increase in chainlength of the soap and amount of methanol in the solvent mixture.

The free energy for the dissociation process, ΔF_D was calculated by using the relationship:

$$\Delta F_D = -RT \ln K_D = RT \ln K_A$$

where K_A and K_D are the equilibrium constants for the association and dissociation processes, respectively. The free energy values for dissociation (ΔF_D) and micellization (ΔF_A) have been calculated per mole of monomer and are recorded in Tables 5 and 6. The higher values of decrease in free energy for micellization process than dissociation process favours micellization.

For the aggregation process, when counter ions are bound to micelle, the standard free energy of micellization (per mole of monomer) ΔF_A, for the phase separation model[17,18] is given by the relationship:

$$\Delta F_A = 2RT \ln x_{\text{CMC}}$$

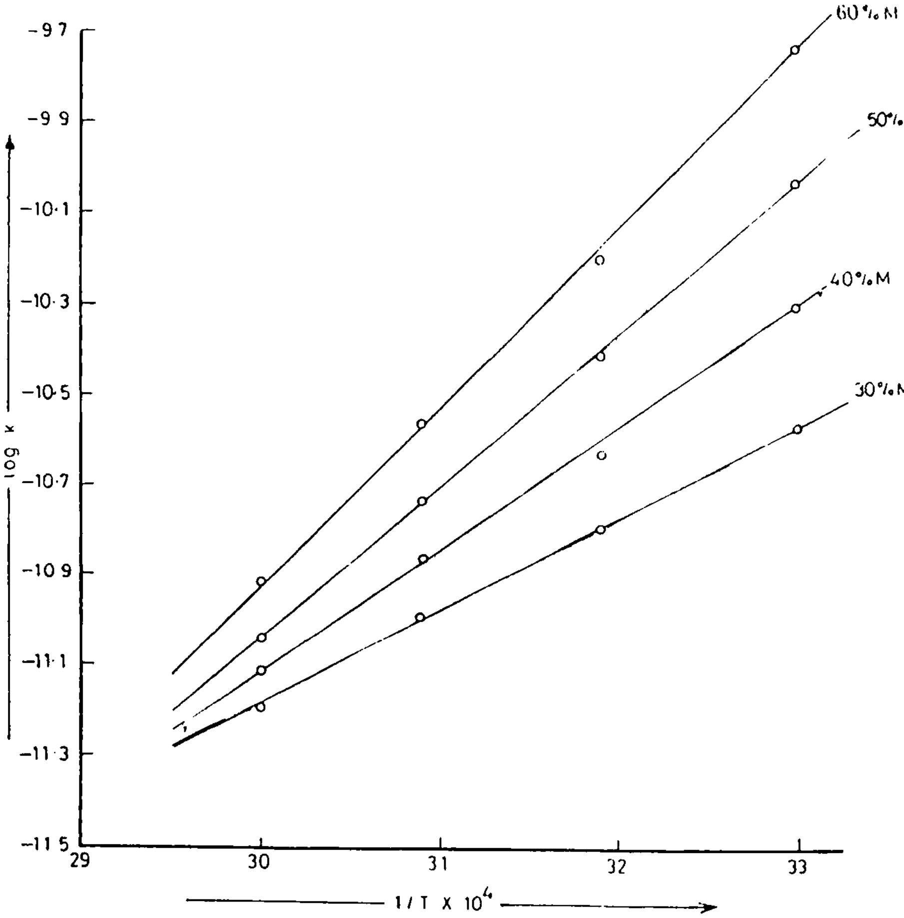

Figure 3 log k vs. $1/T$ plots for thorium caprate in methanol benzene mixtures.

Table 4 Thermodynamic parameters of dissociation process.

Name of soaps	$-\Delta H_D (kJ\ mol^{-1})$			
	Percentage of methanol			
	30	*40*	*50*	*60*
Thorium caprate	38.51	51.95	59.68	65.43
Thorium laurate	46.16	55.82	63.50	69.26

Table 5 Thermodynamic parameters for dissociation process.

Percentage of methanol	*Thorium caprate*							
	$\Delta F_D (kJ\ mol^{-1})$				$-\Delta S_D \times 10^2\ (kJ\ k^{-1}\ mol^{-1})$			
	30°	*40°*	*50°*	*60°*	*30°*	*40°*	*50°*	*60°*
30	15.49	16.34	17.18	17.96	17.82	17.52	17.24	16.96
40	15.08	16.10	16.95	17.79	22.12	21.74	21.33	20.94
50	14.69	15.75	16.75	17.59	24.54	24.09	23.66	23.20
60	14.29	15.46	16.51	17.38	26.31	25.84	25.37	24.87
	Thorium laurate							
30	15.13	15.99	16.86	17.71	20.23	19.86	19.51	19.18
40	14.89	15.83	16.75	17.65	23.33	22.89	22.47	22.06
50	14.62	15.63	16.65	17.59	25.78	25.28	24.81	24.35
60	14.37	15.41	16.48	17.48	27.60	27.05	26.54	26.05

where x_{CMC} is the CMC expressed as a mole fraction and is defined by:

$$x_{CMC} = \frac{n_s}{n_s + n_0}$$

Since the number of moles of free surfactant, n_s is small as compared to the number of moles of solvent, n_0. Therefore,

$$x_{CMC} = n_s/n_0$$

The standard entholpy change of micellization per mole of monomer for the phase

Table 6 Thermodynamic parameters for association process.

Percentage of methanol	*Thorium caprate*							
	$-\Delta F_A (kJ\ mol^{-1})$				$\Delta S_A \times 10^2\ (kJ\ k^{-1}\ mol^{-1})$			
	30°	*40°*	*50°*	*60°*	*30°*	*40°*	*50°*	*60°*
30	43.81	44.48	45.40	46.49	20.81	20.36	20.01	19.74
40	44.31	45.02	45.95	46.99	20.97	20.53	20.18	19.89
50	44.71	45.49	46.41	47.50	21.10	20.68	20.32	20.04
60	45.15	45.91	46.87	47.96	21.25	20.81	20.47	20.18
	Thorium laurate							
30	46.58	47.17	47.84	48.85	24.27	23.68	23.16	22.76
40	47.08	47.67	48.38	49.35	24.43	23.84	23.32	22.91
50	47.54	48.13	48.85	49.85	24.59	23.99	23.47	23.06
60	47.96	48.59	49.31	50.32	24.73	24.14	23.61	23.21

separation model,[17,18] ΔH_A is given by the relationship:

$$\frac{\partial(\ln x_{\mathrm{CMC}})}{\partial T} = \frac{\Delta H_A}{2RT^2}$$

or $\ln x_{\mathrm{CMC}} = -\Delta H_A/2RT + C$

The values of ΔH_A have been obtained from the slope of the linear plots of $\ln x_{\mathrm{CMC}}$ vs. $1/T$ (Figure 4) and found to be 19.24 and 26.96 KJ mol^{-1} for thorium caprate and laurate, respectively. The positive values of ΔH_A indicate that the association process of these soaps is endothermic in methanol-benzene mixtures. The results show that the association process is dominant over the dissociation process.

The standard entropy changes for dissociation and association process, ΔS_D and ΔS_A have been calculated by the relationship:

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

The values of ΔS_D and ΔS_A for thorium soaps have been recorded in Tables-5 and 6. The higher values of ΔS_A indicate that the association is dominant over dissociation process.

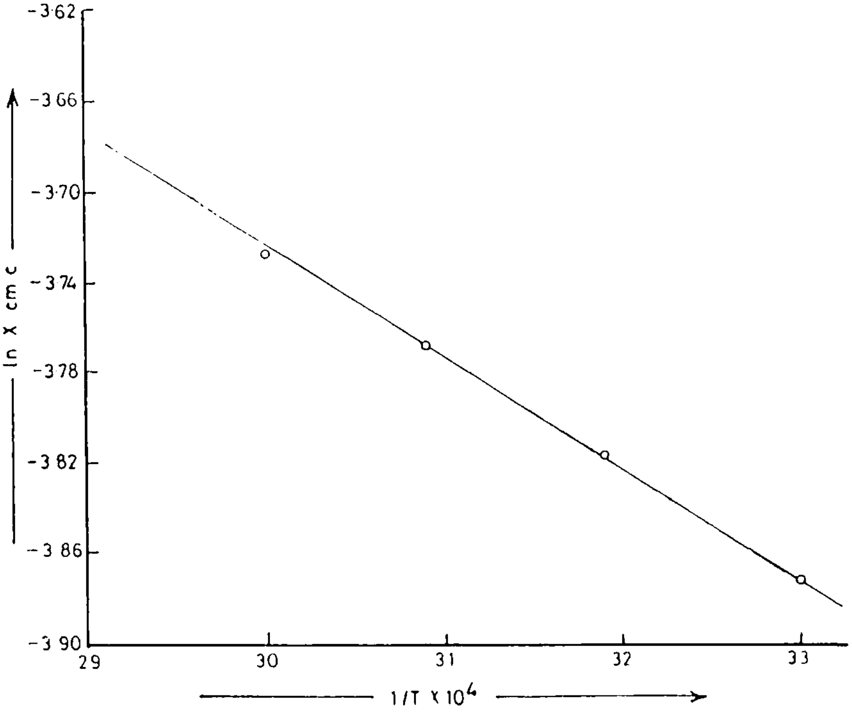

Figure 4 ln X_{CMC} vs. $1/T$ plots for thorium caprate in methanol-benzene mixture.

It is, therefore, concluded that the thermodynamics of dissociation and association can be satisfactorily explained in the light of phase separation model by conductivity measurements. The results showed that dissociation of thorium soaps was found to be exothermic while the association process was endothermic in nature.

Acknowledgements

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