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K. N. Mehrotra<sup>a</sup>; Kirti Tandon<sup>a</sup>

<sup>a</sup> Department of Chemistry, Institute of Basic Sciences, Agra, India

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## MICELLIZATION AND CONDUCTANCE BEHAVIOUR OF YTTRIUM CAPROATE IN PROPANOL-1 AND BUTANOL-1

K. N. MEHROTRA and KIRTI TANDON

*Department of Chemistry, Institute of Basic Sciences, Khandari Road, Agra-282 002,  
India*

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The critical micelle concentration, degree of dissociation and dissociation constant of yttrium caproate in propanol-1 and butanol-1 at different temperatures were determined by using conductometric measurements. The results show that the soap behaves as a weak electrolyte in dilute solutions below the CMC and the CMC was found to increase with decreasing dielectric constant of the solvent. The various thermodynamic parameters were also evaluated for both dissociation and micellization processes.

KEY WORDS: Weak electrolyte, dielectric constant.

### INTRODUCTION

The transition metal soaps are being widely used in many industries. The methods of preparation and structural characteristics of transition metal soaps<sup>1-13</sup> and lanthanide metal soaps<sup>14-17</sup> have been investigated. Varma *et al.*<sup>18-20</sup> studied the critical micelle concentration of nickel, cobalt, manganese and iron soaps at different temperatures conductometrically. Fogg and Pink<sup>21</sup> carried out the electrical conductance and dielectric constant measurements for zinc, manganese and copper soaps in isobutanol and benzaldehyde.

The present work deals with the studies of conductance and micellar behaviour of the solutions of yttrium caproate in propanol-1 and butanol-1 at different temperatures.

### EXPERIMENTAL

The chemicals used were of AR/GR grade. Yttrium caproate was prepared by direct metathesis of potassium caproate with the required amount of aqueous solution of yttrium nitrate at 50-55°C under vigorous stirring. The precipitated soap was washed with distilled water and alcohol, recrystallized with a mixture of benzene and methanol and dried under reduced pressure. The absence of hydroxyl group in the soap was confirmed by studying its IR spectrum. The melting point of the purified yttrium caproate was 81.0°C.

A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type of conductivity cell with platinized electrodes were used for measuring the conductance of the solution. All measurements were made at constant temperatures (30, 40 and  $50 \pm 0.05^\circ\text{C}$ ) in a thermostat.

## RESULTS AND DISCUSSION

### *Specific conductance, $k$*

The specific conductance,  $k$  of the solutions of yttrium caproate in propanol-1 and butanol-1 increases with increasing soap concentration and temperature (Table 1). The increase in specific conductance with the increase in soap concentration may be due to the ionisation of yttrium caproate into simple metal cations,  $\text{Y}^{3+}$  and fatty acid anions,  $\text{C}_5\text{H}_{11}\text{COO}^-$  in dilute solutions and due to the formation of micelles at higher concentrations. The plots of specific conductance Vs soap concentration are characterised by an intersection of two straight lines at a definite soap concentration which corresponds to the critical micelle concentration of the soap in these solvents (Figures 1 and 2). The results show that the specific conductance of the soap solutions increases while the CMC decreases with increasing dielectric constant of the solvent. The CMC also increases with the increase in temperature. The higher values of specific conductance in propanol-1 than in butanol-1 may be due to the fact that the high dielectric constant of the solvent reduces the electrostatic attractive forces between positive and negative ions and thus favours dissociation of the solute molecule which ultimately results in the micellization. The values of the CMC show

**Table 1** Specific conductance,  $k \times 10^6$ (mhos) of the solutions of yttrium caproate at different temperatures ( $^\circ\text{C}$ ).

Concentration $\text{mol l}^{-1}$	Propanol-1			Butanol-1		
	30	40	50	30	40	50
0.0500	27.7	29.5	35.4	12.2	13.6	16.8
0.0456	25.9	28.2	32.7	11.3	13.0	16.0
0.0417	24.8	26.9	31.6	10.9	12.7	14.7
0.0385	23.4	25.3	29.7	10.4	12.0	13.8
0.0357	23.2	24.3	28.4	9.7	11.9	13.2
0.0333	22.4	23.0	27.5	9.2	11.2	12.4
0.0313	21.1	22.1	26.4	8.7	10.6	11.9
0.0294	20.7	21.5	25.6	8.2	10.1	11.6
0.0278	19.9	20.9	24.9	7.9	9.7	11.2
0.0263	19.3	20.0	24.7	7.5	9.2	11.0
0.0250	18.8	19.9	24.1	7.2	8.8	10.6
0.0227	18.4	19.0	22.7	6.6	8.6	10.4
0.0208	18.0	18.3	21.9	6.1	8.1	10.1
0.0192	17.4	17.5	20.8	5.7	7.6	9.7
0.0179	16.3	17.2	20.4	5.4	7.2	9.0

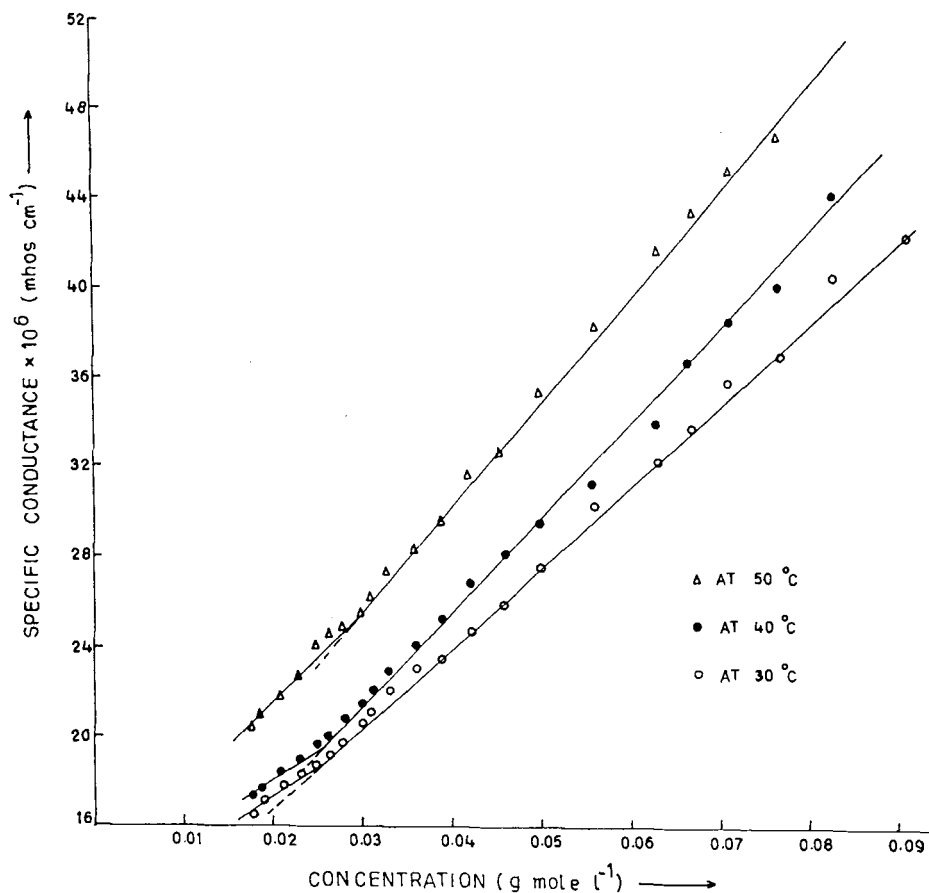


Figure 1 Specific conductance vs concentration of yttrium caproate in propanol-1.

that the micelle formation occurs more easily in propanol-1 than in butanol-1 (Table 3).

*Molar conductance  $\mu$ , and dissociation constant,  $K$*

The molar conductance,  $\mu$  of the dilute solutions of yttrium caproate in propanol-1 and butanol-1 decreases with increasing soap concentration (Table 2 and Figure 3). The decrease may be due to the tendency of the soap to form aggregates at higher soap concentrations. It is suggested that the mobility of the soap decreases with the increase in the size of the molecules and hence the molar conductance decreases as the concentration increases. However, the CMC can not be obtained from the plots of molar conductance,  $\mu$  Vs square root of soap concentration,  $C^{1/2}$  which are concave upwards with increasing slopes indicating that yttrium caproate behaves as a weak

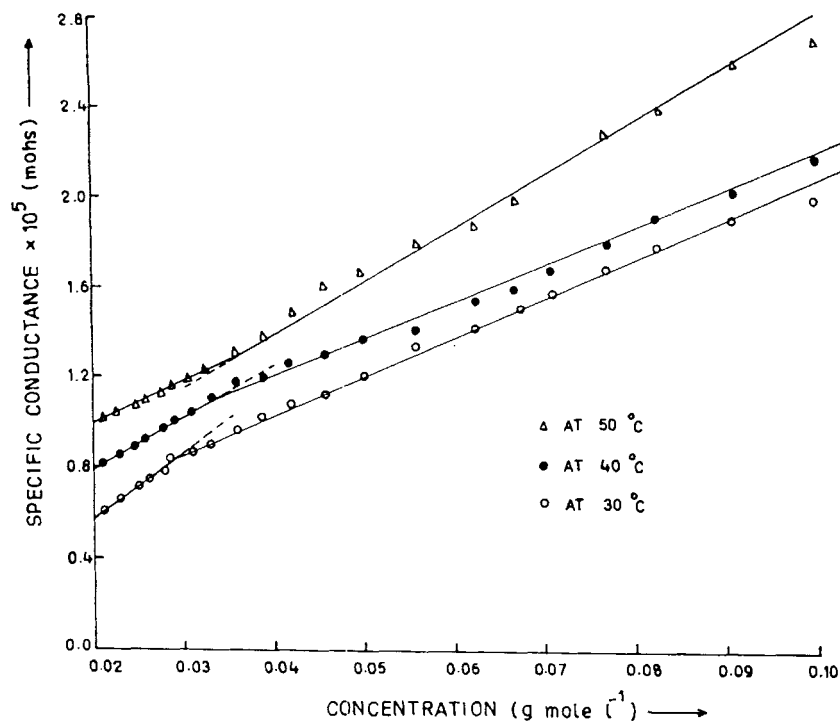


Figure 2 Specific conductance vs concentration of yttrium caproate in butanol-1.

Table 2 Molar conductance,  $\mu$  of the solutions of yttrium caproate at different temperatures ( $^{\circ}\text{C}$ ).

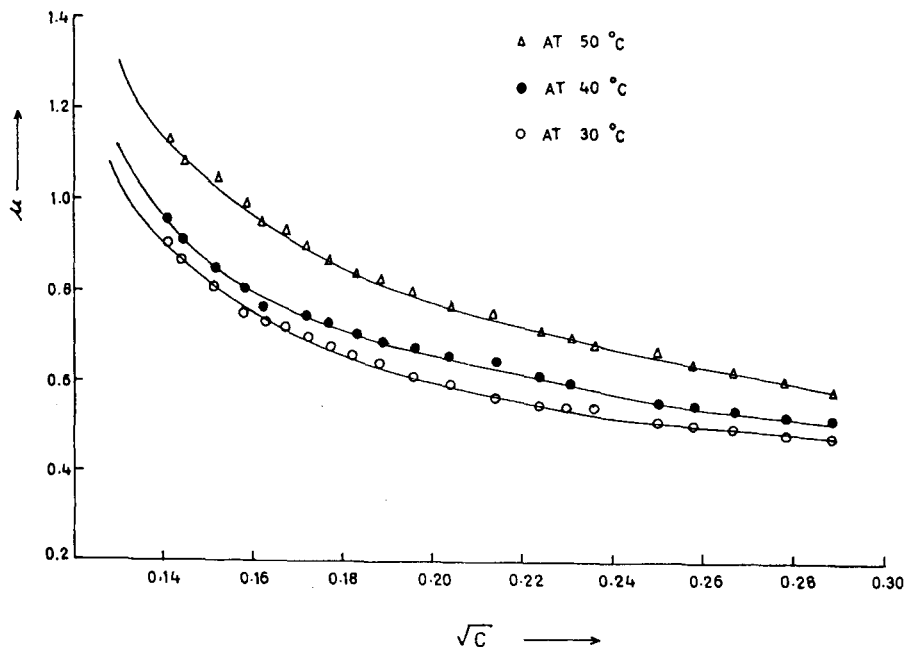
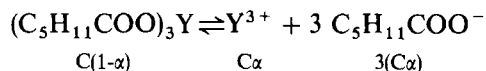
Concentration $\text{mol l}^{-1}$	Propanol-1			Butanol-1		
	30	40	50	30	40	50
0.0500	0.554	0.590	0.708	0.244	0.272	0.336
0.0456	0.569	0.618	0.717	0.248	0.285	0.351
0.0417	0.595	0.645	0.758	0.261	0.305	0.353
0.0385	0.608	0.657	0.771	0.270	0.312	0.358
0.0357	0.650	0.681	0.796	0.271	0.333	0.370
0.0333	0.673	0.691	0.826	0.276	0.336	0.372
0.0313	0.674	0.706	0.844	0.278	0.339	0.380
0.0294	0.704	0.731	0.871	0.282	0.344	0.395
0.0278	0.716	0.752	0.896	0.284	0.349	0.403
0.0263	0.734	0.761	0.939	0.285	0.350	0.418
0.0250	0.752	0.796	0.964	0.288	0.352	0.424
0.0227	0.811	0.837	1.000	0.291	0.379	0.458
0.0208	0.865	0.880	1.053	0.293	0.389	0.486
0.0192	0.906	0.912	1.083	0.297	0.396	0.500
0.0179	0.911	0.916	1.140	0.302	0.402	0.503

**Table 3** Critical micelle concentration, CMC ( $\text{mol l}^{-1}$ ) of yttrium caproate.

Temperature (°C)	Propanol-1	Butanol-1
30	0.025	0.029
40	0.027	0.033
50	0.031	0.036

electrolyte in dilute solutions and Debye-Huckel-Onsagar equation is not applicable to these soap solutions and the limiting molar conductance,  $\mu_0$  for these soap solutions can not be obtained by usual extrapolation method.

Since the soap behaves as a weak electrolyte in dilute solutions, an expression for the dissociation of yttrium caproate can be developed in Ostwald's manner. If  $C$  is the concentration in  $\text{mol l}^{-1}$  and  $\alpha$  is the degree of dissociation of yttrium caproate, the equivalent concentrations of different species can be represented as



**Figure 3** Molar conductance vs square root of concentration in propanol-1.

The dissociation constant,  $K$  can be expressed as

$$\begin{aligned}
 K &= \frac{[Y^{3+}][C_5C_{11}COO^-]^3}{[Y(C_5H_{11}COO)_3]} \\
 &= \frac{C\alpha(3 - C\alpha)^3}{C(1 - \alpha)} \\
 &= \frac{27 C^3 \alpha^4}{(1 - \alpha)} \quad (1)
 \end{aligned}$$

The ionic concentrations in dilute solutions are low and so the interionic effects may be treated as negligible. Therefore, the dilute soap solutions do not deviate appreciably from ideal behaviour and the activities of ions can be taken as almost equal to the concentrations. The degree of dissociation,  $\alpha$  may be replaced by the conductance ratio,  $\mu/\mu_0$  where  $\mu$  is the molar conductance at finite concentration and  $\mu_0$  is the limiting molar conductance at infinite dilution. On substituting the values of  $\alpha$  and rearranging, Eq. (1), can be written as

$$\mu^3 C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \quad (2)$$

The values of  $K$  and  $\mu_0$  have been obtained from the slope,  $K\mu_0^4/27$  and intercept  $-K\mu_0^3/27$  of the linear plots of  $\mu^3 C^3$  Vs  $1/\mu$  for soap solutions (Table 4).

The values of the degree of dissociation,  $\alpha$  at different soap concentration have been calculated by assuming it as equal to the conductance ratio,  $\mu/\mu_0$ . The plots of degree of dissociation,  $\alpha$  Vs soap concentration,  $C$  show that the degree of dissociation,  $\alpha$  of the soap decreases rapidly in dilute solutions with increasing soap concentration. The dissociation constant,  $K$  increase with increasing dielectric constant of the solvent while it decreases with increase of temperature. The decrease in the values of  $K$  with increasing temperature indicates the exothermic nature of yttrium caproate in propanol-1 and butanol-1.

**Table 4** Dissociation constant,  $K$  and thermodynamic parameters for solutions of yttrium caproate at different temperatures ( $^{\circ}C$ )

	<i>Propanol-1</i>			<i>Butanol-1</i>		
	30	40	50	30	40	50
$K \times 10^6$	5.86	4.02	3.04	3.4	2.9	2.1
$\Delta G_D^{\circ} (kJ mol^{-1})$	7.25	7.73	8.15	7.58	7.93	8.39
$\Delta G_A^{\circ} (kJ mol^{-1})$	-7.56	-7.71	-7.78	-7.13	-7.20	-7.72
$\Delta S_D^{\circ} \times 10^2 (kJ mol^{-1})$	-2.74	-2.81	-2.85	-2.79	-2.81	-2.72
$\Delta S_A^{\circ} \times 10^2 (kJ mol^{-1})$	2.45	2.42	2.37	2.29	2.24	2.21

The heat of dissociation is given by the relationship

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_D^\circ}{RT^2}$$

or

$$\log K = \frac{-\Delta H_D^\circ}{2.303RT} + C$$

The values of heat of dissociation,  $\Delta H_D^\circ$  have been obtained from the linear plots of  $\log K$  Vs  $1/T$  and are found to be  $-1.05$  and  $-0.86 \text{ kJ mol}^{-1}$  for solutions in propanol-1 and butanol-1, respectively. The negative values of heat of dissociation indicate that the dissociation process is exothermic in nature.

The values of change in free energy,  $\Delta G_D^\circ$  and entropy,  $\Delta S_D^\circ$  per mole for dissociation process have been calculated (Table 4) by using the relationship

$$\Delta G_D^\circ = -RT \ln K_D$$

$$\Delta S_D^\circ = [\Delta H_D^\circ - \Delta G_D^\circ]/T$$

For the aggregation process, the standard free energy of micellization (per mole of monomer),  $\Delta G_A^\circ$ , for the phase separation model<sup>22,23</sup> is given by the relationship

$$\Delta G_A^\circ = 2RT \ln X_{CMC}$$

where  $X_{CMC}$  is the CMC expressed as a mole fraction and defined as

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

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 enthalpy change of micellization per mole of monomer for the phase separation model<sup>22,23</sup>,  $\Delta H_A^\circ$  is given by the relationship

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

or

$$\ln X_{CMC} = -\frac{\Delta H_A^\circ}{2RT} + C$$



The values of  $\Delta H_A^\circ$  have been obtained from the slope of the linear plots of  $\ln X_{\text{CMC}}$  Vs  $1/T$  and are found to be  $-0.13$  and  $-0.19 \text{ kJ mol}^{-1}$  for solutions in propanol-1 and butanol-1, respectively.

A careful scrutiny of the thermodynamic parameters (negative values of  $\Delta G^\circ$  and positive value of  $\Delta S^\circ$  for the micellization process and positive values of  $\Delta G^\circ$  and negative values of  $\Delta S^\circ$  for dissociation process) indicates that the association process is favoured over the dissociation.

The results of conductivity measurements show that the soap behaves as a weak electrolyte in dilute solutions below the CMC and the thermodynamics of dissociation and association processes can be satisfactorily explained in the light of phase separation model.

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