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Investigations into the Conductance, Micellization and Dissociation Behaviour of Zinc Soaps in 70/30 Benzene-Methanol Mixture

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The conductance of zinc caprylate and laurate was measured in 70/30 benzene-methanol mixture at several temperatures. The values of the CMC increase with an increase in temperature. The dissociation constant, degree of dissociation and limiting molar conductance were evaluated from conductivity measurements. The results showed that these soaps behaved as weak electrolytes in dilute solutions and the micellization process was dominant over the dissociation process.

INTRODUCTION

The most striking feature of metal soaps is their increasing importance in various industries. The proven utility of divalent or trivalent metal soaps of saturated and unsaturated higher fatty acids as dispersants, lubricants, catalysts, stabilizers and corrosion inhibiting agents has fascinated research workers. The critical micellar concentration of cobalt[1] and copper[2] soaps in non-aqueous medium has been determined by density measurements. The colloidal behaviour and time effect in the supramolecular formation of cobalt monooleate in apolar solvents have been investigated by Benjamin Chu *et al.*[3] The studies on transition metal soaps have not been carried out systematically so far with the result that only few references[4–13] are available in this field.

The present work deals with the study of conductivity of the solutions of zinc caprylate and laurate in a mixture of 70% benzene and 30% methanol (v/v) with a view to study the micellar behaviour and to evaluate the various thermodynamic parameters both for the dissociation and micellization process.

EXPERIMENTAL

AnalaR-grade zinc acetate and fatty acids (Glaxo Labs., Bombay) were used without further purification. The methanol and benzene used were AnalaR grade (EM/BDH) chemicals. Zinc caprylate and laurate were prepared by the direct metathesis of corresponding potassium soaps with required amount of zinc acetate in water-alcohol medium (1:1). The precipitated soaps were washed with distilled water and acetone to remove excess of zinc ions and unreacted caprylic and lauric acids. The purity of the soaps was checked by the elemental analysis and IR spectra. The purified soaps have the following melting points. Zinc caprylate: 88.0°C, Zinc laurate: 125.0°C.

The reproducibility of the results was checked by preparing two samples of the same soap under similar conditions. The solutions of these soaps were prepared by dissolving a known amount of soap in a mixture of 70% benzene and 30% methanol (v/v) and were kept for 2 h in a thermostat at the desired constant temperature.

The conductance of the solutions was measured with a Systronics Conductivity Bridge 305 (SR No. 993) and dipping type conductivity cell (cell constant 1.6) with platinized electrodes. All measurements were made at 35–50°C (± 0.05°C) (308–323 K). The specific and molar conductance were expressed in mhos cm^{-1} and mhos cm^2/g mole, respectively.

RESULTS AND DISCUSSION

The increase in specific conductance of the solutions of zinc caprylate and laurate with an increase in soap concentration (Fig. 1) may be due to the fact that zinc soaps behave as a simple electrolyte in dilute solutions, and are considerably

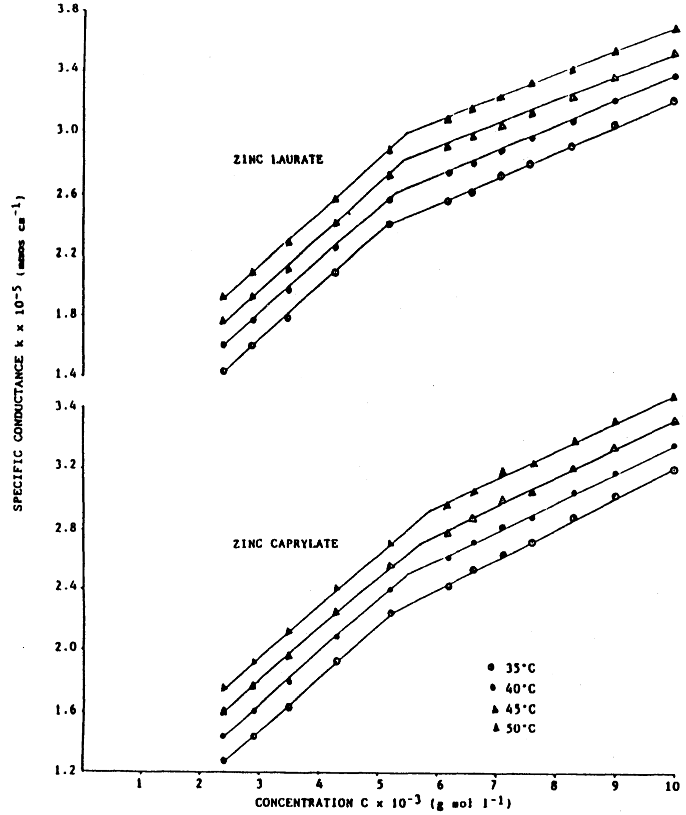

Fig.1 SPECIFIC CONDUCTANCE Vs CONCENTRATION ZINC CAPRYLATE AND ZINC LAURATE IN 70/30 BENZENE-METHANOL MIXTURE.

ionized into a zinc cation Zn^{2+} and fatty acid anions ($C_7H_{15}COO^-$ and $C_{11}H_{23}COO^-$). However, the increase in the specific conductance at higher soap concentration is probably due to the formation of ionic micelles. The values of critical micellar concentration of zinc caprylate and laurate are summarised in Table 1. It is apparent (Table 1) that the CMC increases with increasing temperature because the micellization is assumed to occur when the energy released as a result of aggregation of the hydrocarbon chains of the monomer is sufficient to overcome the electrical repulsion between the ionic head groups and to balance the decrease in entropy accompanying aggregation. Therefore, increase in temperature would have been expected to increase the CMC value since the kinetic energy of the monomer would have been increased.

TABLE 1

CRITICAL MICELLAR CONCENTRATION (CMC), LIMITING MOLAR CONDUCTANCE μ_0 AND DISSOCIATION CONSTANT K OF ZINC CAPRYLATE AND ZINC LAURATE IN 70% BENZENE AND 30% METHANOL MIXTURE (V/V).

Zinc Caprylate

Temperature (°C)	35	40	45	50
CMC × 10^{-3} (g. mol l^{-1})	5.20	5.45	5.70	5.90
μ_0	8.10	8.86	9.86	11.17
$K_D \times 10^{-5}$	2.41	1.59	1.04	0.66

Zinc Laurate

Temperature (°C)	35	40	45	50
CMC × 10^{-3} (g. mol l^{-1})	5.25	5.35	5.45	5.55
μ_0	9.88	11.30	12.98	14.28
$K_D \times 10^{-5}$	1.15	0.92	0.73	0.58

The molar conductance of the dilute solutions of zinc soaps decreases with an increase in soap concentration. The values of the critical micellar concentration (CMC) cannot be, however, obtained due to the concave nature of the plots of molar conductance *vs.* square root of soap concentration. This shows that zinc soaps behave as weak electrolyte in dilute solutions and Debye-Hückel-Onsager's equation is not applicable to these soap solutions. Since these metal soaps behave as weak electrolyte in dilute solutions, the following expression[14] for their dissociation can be derived:

$$\mu^2C^2 = \frac{K_D\mu_0^3}{4\mu} - \frac{K_D\mu_0^2}{4} \tag{1}$$

The values of the dissociation constant K_D and limiting molar conductance μ_0 have been determined from the slope, $\frac{K_D\mu_0^3}{4}$ and the intercept, $-\frac{K_D\mu_0^2}{4}$ of the linear plots of μ^2C^2 *vs.* $1/\mu$ for dilute soap solutions. The results show that the values of molar conductance at infinite dilution and dissociation constant K_D increase with increasing temperature. The values of degree of dissociation, α, at different concentrations and temperatures have been determined by assuming it as equal to the conductance ratio, μ/μ_0. These results show that zinc soaps behave as weak electrolytes in 70% benzene and 30% methanol (v/v) mixture. The values of degree of dissociation of the soap decrease rapidly in dilute solutions with increasing soaps concentration whereas it decreases slowly above the CMC.

The values of dissociation constant are almost constant in very dilute solutions but exhibit a drift with increasing concentration which indicates that zinc caprylate and laurate do not behave as very weak electrolyte in benzene-methanol mixture. The drift in the values of dissociation constant with increasing concentration may be due to the fact that the degree of dissociation is not exactly equal to the conductance ratio, μ/μ_0, but mainly due to the fact that the activity coefficient, of ions are not equal to unity at higher soap concentrations.

The heat of dissociation, $\Delta H_D°$ for zinc caprylate and laurate have been calculated by using the following expression.

$$\frac{\partial(\log K)}{\partial T} = \frac{\Delta H_D}{RT^2}$$

or,

$$\log K = -\frac{\Delta H_D}{2.303RT} + C \qquad (2)$$

The values of heat of dissociation $\Delta H_D°$ which have been obtained (Table 2) from the slope of the linear plots of log K *vs.* 1/T are −35.69 KJ mol^{-1} and −18.79 KJ mol^{-1} for zinc caprylate and laurate respectively. The negative values indicate that the dissociation is exothermic.

TABEL 2

HEAT OF DISSOCIATION AND MICELLIZATION (PER MOLE OF MONOMER) OF ZINC CAPRYLATE AND ZINC LAURATE IN 70% BENZENE AND 30% METHANOL MIXTURE (V/V)

Soap	Heat of dissociation ΔH_D KJ mol^{-1}	Heat of micellization ΔH_m KJ mol^{-1}
Zinc caprylate	-35.69	19.18
Zinc laurate	-18.79	7.94

The values of the change in free energy $\Delta G_D°$ and entropy, $\Delta S_D°$ per mole of monomer for the dissociation process have been calculated by using the following relationships.

$$\Delta G_D° = -RT \ln K_D \qquad (3)$$

$$\Delta S_D = (\Delta H_D - \Delta G_D)/T \qquad (4)$$

TABLE 3
VALUE OF ln X_{CMC} OF ZINC CAPRYLATE AND ZINC LAURATE

Soap	ln X_{CMC}			
	35°C	40°C	45°C	50°C
Zinc Caprylate	-7.99	-7.94	-7.90	-7.86
Zinc Laurate	-7.98	-7.96	-7.94	-7.92

The values of $\Delta G_D°$ and $\Delta S_D°$ at different temperatures are recorded in Table-4.

TABLE 4
THERMODYNAMIC PARAMETERS OF DISSOCIATION AND MICELLIZATION PROCESS OF ZINC CAPRYLATE AND ZINC LAURATE IN 70% BENZENE AND 30% METHANOL MIXTURE

Temperature °C	Dissociation Process		Micellization Process	
	$\Delta G_D°$ KJ mol^{-1}	$\Delta S_D \times 10^2$ KJ $mole^{-1}$	$\Delta G_m°$ KJ $mole^{-1}$	$\Delta S_m° \times 10^2$ KJ $mole^{-1}$
Zinc Caprylate				
35	13.64	-16.02	-20.49	12.88
40	14.39	-16.00	-20.69	12.74
45	15.19	-16.00	-20.92	12.61
50	16.02	-16.01	-21.14	12.48
Zinc Laurate				
35	14.60	-10.84	-20.46	9.22
40	15.10	-10.83	-20.74	9.16
45	15.65	-10.83	-21.02	9.11
50	16.22	-10.84	-21.30	9.05

For the micellization process, the standard free energy $\Delta G_m°$ per mole of monomer for the phase separation model[15-17] is calculated by the relationship,

$$\Delta G_m = 2RT \ln X_{CMC} \tag{5}$$

where X_{CMC} is the CMC expressed in terms of mole fraction (Table 3) and is represented by the relationship,

$$X_{CMC} = n_s/(n_s + n_0) \tag{6}$$

where n_s and n_0 are the number of moles of soap and solvent, respectively, since the number of moles of free soaps, n_s, is small as compared to the number of moles of solvent, n_0,. Now equation (6) can be written as

$$X_{CMC} = n_s/n_0 \tag{7}$$

The standard enthalpy change of micellization per mole of monomer for the phase separation model [15-17], ΔH_m is given by the relationship.

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

$$\ln X_{CMC} = \frac{\Delta H_m}{2RT} + C \qquad (8)$$

The values of $\Delta H_m{}^\circ$ of zinc soaps which have been determined from the slope of linear plots of $\ln X_{CMC}$ *vs.* $1/T$ are 19.18 KJ mol^{-1} and 7.94 mol^{-1} for zinc caprylate and laurate, respectively. The positive values of $\Delta H_m{}^\circ$ (Table 2) indicate that the micellization is endothermic in nature.

A careful scrutiny of the thermodynamic parameters indicate that negative values of $\Delta G_m{}^\circ$, positive values of $\Delta S_m{}^\circ$ for the micellization process (Table 4) and positive values of $\Delta G_D{}^\circ$ and negative values of $\Delta S_D{}^\circ$ for the association process are favoured over the dissociation process.

It is, therefore, concluded that the zinc caprylate and laurate behave as weak electrolytes in 70/30 benzene-methanol mixture. The values of the critical micellar concentration increase with increasing temperature and the micellization process is predominant over dissociation process.

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