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Conductivity of Titanium(III) Soaps in Benzene-Cyclohexane Mixture

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In present work, the effects of temperature on the conductance behaviour of titanium (laurate, myristate, palmitate and stearate) in benzene + cyclohexane mixtures were studied. Attempts have been made to determine critical micelle concentration dissociation constant (K), molecular conductance and infinite dilution (λ_∞) heat of dissociation (ΔH°) and activation energy of conductance (ΔE_λ) of these soaps under different conditions.

Key Words: Conductivity, Titanium(III) soaps, Benzene-Cyclohexane mixture.

INTRODUCTION

The soaps are useful on account of their fundamental properties and state of molecule in the solution. The soap conductance was measured as well as observed the micelle formation in lower aliphatic alcohols[1,2]. The critical micelle concentration (CMC) has been determined for magnesium soaps in alcohols[3]. The thermodynamic properties of aqueous solution of lithium and manganese chloride presence of surfactant were also measured[4,5].

Conductance of magnesium soaps of caprylate, laurate, myristate and palmitate was measured at different temperature[6] and also in mixed organic solvents[7]. In the present study, the conductance behaviour of titanium(III) soaps in benzene and cyclohexane mixture is studied.

EXPERIMENTAL

AnalaR (BDH) lauric acid, myristic acid, palmitic acid and stearic acid were used and purified by distillation under reduced pressure. Conductivity water was prepared in glass apparatus and was used throughout the experiment.

The conductivity measurements were taken from Elico conductivity Bridge. A dipping type conductivity cell constant 1 cm^{-1} was used. The error in conductivity measurement was within ± 0.5 %. All the measurements were made in a thermostatically controlled bath (± 0.05 °C).

Preparation of titanium(III) soaps: The calculated amount of titanium chloride dissolved in distilled water using a hot solution of sodium soaps. The later being added dropwise while stirring at 50-55 °C. The precipitate was filtered in a buckner funnel and washed with hot distilled water until the filtrate gave a negative test for sulphate ions present. The precipitate was recrystallized by benzene.

RESULTS AND DISCUSSION

The critical micelle concentrations (CMC) values obtained from the plot of specific conductivity (K) *vs.* soap concentration (C). The values increase with increasing soap concentration. But these values increase with much slower rates above a certain definite concentration. It is due to the fact that CMC of the soap molecules associate to form aggregates and the number of free ions do not increase as rapidly as at concentrations below CMC.

The conductance behaviour of soap solutions may be represented by an equation:

$$\log \lambda = A + B \log C \quad (1)$$

where A and B are constants and C is the concentration of soap solutions in moles dm^{-3} and λ is molecular conductivity in $ohm^{-1}\ cm^{2}\ mol^{-1}$.

Since, the soaps behave as a weak electrolyte in dilute solution, an expression for calculating the values of K and λ_∞ can be derived if α is the degree of dissociation, the equivalent concentration; the equivalent concentration of the different in species in dilute solutions may be represented as follows[8-10]:

$$\underset{C(1-\alpha)}{(RCOO)_3Ti} \rightleftharpoons \underset{3C\alpha}{3RCOO^-} + \underset{C\alpha}{Ti^{3+}} \quad (2)$$

$$K = \frac{[Ti^{3+}][RCOO^-]^3}{[[COOR]_3Ti]}$$

$$= \frac{[C\alpha][3C\alpha]^3}{C(1-\alpha)} \quad (3)$$

$$= \frac{27.C^3.\ \alpha^4}{1-\alpha} \quad (4)$$

Since, the degree of dissociation (α) of soap in dilute solution is very small, ionic concentration will be very low and hence inter-ionic effects are almost negligible. Such solutions do not deviate from ideal behaviour and therefore, the activity of ions is almost equal to the concentration. On substituting the value of α the eqn. 4 can be written as[11]:

$$K = \frac{27.c^3(\lambda/\lambda_\infty)^4}{\left(1-\dfrac{\lambda}{\lambda_\infty}\right)}$$

$$K = \frac{27.c^3\ \lambda^4 \times \lambda_\infty}{(\lambda_\infty - \lambda).\lambda_\infty^4}$$

$$i.e.,\ c^3\lambda^3 = \frac{k\lambda_\infty^4}{27\ \lambda} - \frac{k\lambda_\infty^3}{27} \tag{5}$$

The plots of $c^3\ \lambda^3$ *vs.* $1/\lambda$ should be linear at low concentrations. On extrapolating the lines intercept, $K\lambda_\infty^3/27$ and slope, $K\lambda_\infty^4/27\lambda$ are obtained. The ratio of slopes to the intercept yield the value of l8 which when substituted in the equation.

Intercept = $\frac{K\lambda_\infty^3}{27}$ gives the value of K. The heat of dissociation, ΔHº may be calculated from the linear plots log K *vs.* 1/T.

The values of free energy ΔGº have been calculated from the relationship:

$$\Delta G^o = RT \ln K \tag{6}$$

where K, is dissociation constant the values of entropy of dissociation, ΔSº have also been obtained from the values of ΔGº and ΔHº.

The effect of temperature on the conductance may also be discussed in the light of expression:

$$\lambda = Ae^{-\Delta E}\lambda/RT \tag{7}$$

where, A and ΔEλ are constants and activation on energy of conductance respectively.

The plots of log λ *vs.* log C are linear at all temperatures. The values of log λ are zero value of log C (1 M) have been obtained by extrapolation of the linear plots at various temperatures and are recorded[12] as constant (A). In Table-1, the constant (A) increases with increasing temperature and decreasing soap chain. The values of constant (B) obtained from the slops of linear plots of eqn. 1 (Table-1) are independent of temperature and vary with soap chain.

The plots $c^3\lambda^3$ *vs.* $1/\lambda$ are linear below critical micelles concentrations and the values of K and λ_∞ have been obtained from the slops and intercepts of these linear plots at different temperatures. The dissociation constant (K) (Table-2) of the soaps decreases with rise in temperature.

The molecular conductivity at infinite dilution increases (Table-3) with increasing temperature which may be due to decrease in the viscosity of the solvent. The rise in temperature causes the increase in ion mobility despite fact that the addition of soaps increases the viscosity of the solvent. The values of λ_∞ decreases as chain length of fatty acids in the soap increases.

TABLE-1
VALUES OF CONSTANT A AND B OF TITANIUM(III) SOAPS IN MIXED ORGANIC SOLVENT (BENZENE + CYCLOHEXANE) AT 35-50 ºC

Temperature (ºC)	Soaps name			
	Laurate	Myristate	Palmitate	Stearate
	Constant A			
35	1.04	2.96	2.71	2.64
40	1.06	2.97	2.72	2.68
45	1.07	2.98	2.74	2.70
50	1.08	1.50	2.91	2.81
	Constant B			
35	0.86	0.88	0.89	0.93
40	0.86	0.86	0.88	0.92
45	0.86	0.86	0.88	0.92
50	0.86	0.86	0.88	0.92

TABLE-2
VALUE OF DISSOCIATION CONSTANT K OF TITANIUM SOAPS IN MIXED ORGANIC SOLVENTS (BENZENE + CYCLOHEXANE) AT 35-50 ºC

Soaps name	$K \times 10^8$ Temperature (ºC)			
	35	40	45	50
Laurate	8.758	8.532	8.408	7.842
Myristate	45.824	44.806	43.922	43.142
Palmitate	86.972	85.966	84.988	83.126
Stearate	122.594	114.086	103.304	92.116

TABLE-3
VALUES OF MOLECULAR CONDUCTIVITY OF INFINITE DILUTION, λ_∞, OF TITANIUM(III) SOAP IN MIXED ORGANIC SOLVENTS (BENZENE + CYCLOHEXANE) AT 35-50 ºC

Soaps name	λ_∞ Temperature (ºC)			
	35	40	45	50
Laurate	217.390	221.904	224.526	233.642
Myristate	98.654	100.882	103.006	105.044
Palmitate	57.342	57.798	58.250	59.148
Stearate	39.584	41.236	44.003	47.058

The plots of log K *vs.* 1/T are found to be linear. Heat of dissociation, ΔH^o (Table-4) calculated from the slopes of these plots, varies with soap chain as follows:

Stearate > Laurate > Myristate > Palmitate

TABLE-4
VALUES OF CMC AND HEAT OF DISSOCIATION, ΔHº OF TITANIUM(III) SOAPS IN MIXED ORGANIC SOLVENTS (BENZENE + CYCLOHEXANE)

Soaps name	Tested concentration range (mol dm^{-3}) C × 10^5	CMC × 10^5 (mol dm^{-3})	ΔHº (KJ mol^{-1})
Laurate	3-12	7.0	9.572
Myristate	3-12	6.5	5.742
Palmitate	3-12	6.0	3.828
Stearate	3-12	5.0	11.487

This shows that the dissociation of stearte is more endothermic than any other soap of titanium.

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