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Conductometric And Thermodynamic Investigation of Zirconyl Soaps of Lower Saturated Fatty Acids In Mixed Solvents

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ABSTRACT

The critical micelle concentration (CMC) of zirconyl soaps in mixture of xylene-methanol were determined by using conductometric studies. The result show that zirconyl soaps behave as simple electrolyte in dilute solutions and critical micelle concentration was found to decrease with increasing chain length of the soap and increase with increasing temperature. Various thermodynamic parameters for dissociation and micellization process were evaluated and it is found that the dissociation of zirconyl soaps is exothermic while the association process is endothermic in nature.

Keywords: Zirconyl soaps, Specific conductance, Micellization, Heat of dissociation, Heat of association.

INTRODUCTION

The most striking feature of metal soaps has been their increasing importance in technological and academic fields. The uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non-polar solvents. Mehrotra et al studied the various physico-chemical properties of metal soaps in various mixed solvents[1-4]. Several workers have reported thevarious use of metal soaps in industries as binding and molding material, adhesive for rubber steel cord, lubricants, greases etc. [5-11]. In view of the increasing interest in the field of metal soaps, the present work has been initiated with a view to determine the CMC and evaluate the various thermodynamic parameters for the dissociation and association process.

MATERIALS AND METHODS

All chemicals used were of AR grade. Zirconyl soaps were prepared by direct metathesis of the corresponding sodium soaps with slight excess of the solution of zirconyl nitrate under vigorous stirring. The precipitated soaps were washed with water, methanol and acetone to remove excess of metal salt, sodium soaps and unreacted fatty acid. The soap thus obtained was dried in an air oven and the final drying of the soap were carried out under reduced pressure. The purity of the soaps were confirmed by determination of their melting point and IR spectral analysis. Solutions of zirconyl soaps were prepared by dissolving a known amount of soap in xylene-methanol solvent (4:1 v/v). The conductance were measured by Toshniwal Digital Conductivity Meter "Type CL 01.10 A" using dipping type conductivity cell with plantinized electrode.

RESULTS AND DISCUSSION

The specific conductance of the solutions of zirconyl soaps in xylene-methanol (4:1 v/v) mixture increases with increasing soap concentration and temperature (Table 1). The increase in specific conductance may be due to the ionization of zirconyl soaps into zirconyl cations ZrO^{+2} and fatty acid anion, $RCOO^-$[Where R is C_3H_7, C_4H_9, C_5H_{11} and C_7H_{15}] and due to the formation of micelles at higher soap concentration. The plot of specific conductance Vs. soap concentration are characterized by an intersection of two straight lines at a definite soap concentration which correspond to the critical micelle concentration (Figure 1). The values of the CMC decrease with increasing chain length of fatty acid constituent of the soap molecule and increase with increasing temperature (Table 2).
An expression for the dissociation of zirconyl soaps may be obtained in Ostwald's manner.

$$\begin{array}{ccc} ZrO[RCOO]_2 & \rightleftharpoons & ZrO^{+2} + 2RCOO^- \\ C(1-\alpha) & c\alpha & 2(c\alpha) \end{array}$$

Where C is the concentration and α is the degree of dissociation of soap. The dissociation constant, K for the above dissociation may be expressed as-

$$K = \frac{(ZrO^2)(RCOO^-)^2}{[ZrO(COO)_2]}$$

Table 1. Specific conductance of zirconyl butyrate and zirconyl caprylate at different temperatures

Concentration C × 10^2(mol dm^{-3})	Specific Conductance k×10^6 (mhos cm^{-1})					
	Butyrate			Caprylate		
	20°C	30°C	40°C	20°C	30°C	40°C
1.0	7.00	7.25	7.60	4.77	5.30	5.92
2.0	8.65	8.95	9.38	6.25	7.02	7.72
3.0	10.34	10.70	11.15	7.82	8.80	9.57
4.0	11.98	12.40	12.88	9.31	10.60	11.34
5.0	13.52	14.10	14.60	10.23	11.85	12.87
6.0	14.55	15.24	15.85	11.10	12.83	13.83
7.0	15.51	16.28	16.90	11.91	13.89	14.73
8.0	16.50	17.35	17.95	12.75	14.68	15.70
9.0	17.48	18.40	18.99	13.60	15.60	16.68
10.0	18.49	19.50	20.00	14.45	16.55	17.61

Table 2.

CMC of zirconyl soaps in a mixture of xylene-methanol at different temperatures

Temperature	CMC [mol dm^{-3}]			
	Butyrate	Valerate	Caproate	Caprylate
20°C	4.85	4.80	4.50	4.20
30°C	5.10	5.00	4.70	4.50
40°C	5.30	5.20	5.00	4.70

$$k = \frac{(c\alpha)(2c\alpha)^2}{C(1-\alpha)} = \frac{4C^2\alpha^3}{(1-\alpha)} \qquad (1)$$

Since the degree of ionization for dilute solutions of zirconyl soaps are small, the degree of ionization α may be taken as equal to the conductance ratio μ/μ_o.
On substituting the value of α and rearranging equation (1)–

$$\mu^2 c^2 = \frac{K\mu_o^3}{4\mu} - \frac{K\mu_o^2}{4} \qquad (2)$$

The plots of molar conductance μ Vs. square root of soap concentration $C^{1/2}$ for the solutions in mixed organic solvents are not-linear which indicate that Debye-Huckel-Onsagar's equation is not applicable to these soap solutions. The results were explained on the basis of Ostwald's formula. The value of degree of dissociation show that these soaps behave as simple electrolyte in mixed organic solvents. The molar conductance, μ of the dilute solutions of zirconyl soaps decrease with increasing soap concentration.

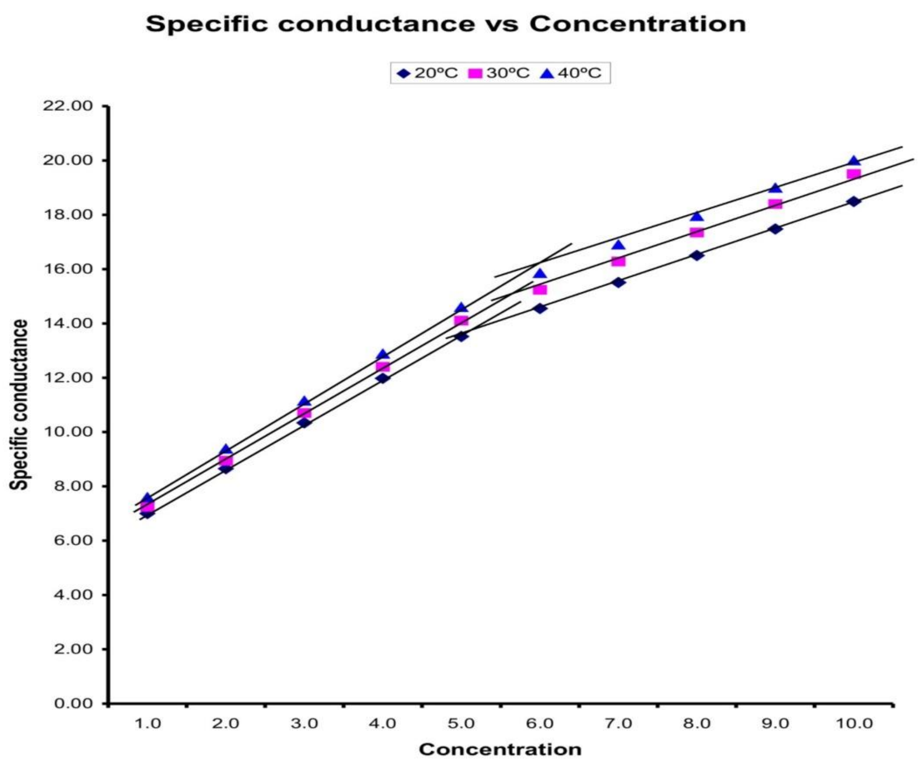

Fig 1. Specific conductance Vs. Concentration of zirconyl butyrate in xylene-methanol at different temperature

The values of μ_o and K which were obtained from the slope, $(K\mu_o^3/4)$ and intercept, $(-K\mu_o^2/4)$ of the plots of μ^2c^2 Vs. $1/\mu$ shows that the value of limiting molar conductance μ_o increases while the dissociation constant, K decreases with increasing temperature and decreasing chain length of the soap molecules. The decrease in the values of K with increasing temperature indicate the exothermic nature of dissociation of soaps in xylene-methanol [4:1 v/v] mixture. The values of dissociation constant, K from equation-1 remains almost constant in dilute solutions but exhibit a drift at higher soap concentration.

Various thermodynamic parameters for the dissociation and association process have been calculated. The relation between dissociation constant, K and heat of dissociation, ΔH_D can be written as-

$$\text{Log}\,K = \frac{-\Delta H_D^o}{2.303RT} + constant \qquad (3)$$

The values of the heat of dissociation are negative indicating that the dissociation of zirconyl soaps are exothermic in nature. The values of change in free energy, ΔG_D^o and entropy ΔS_D^o per mole for the dissociation process have been calculated (Table 3).

Table- 3. Thermodynamic parameters for dissociation process

	ΔG_D^o (K cals mol^{-1})			$-\Delta S_D^o \times 10^2$ (K cals K^{-1} mol^{-1})			$-\Delta H_D^o$ (K cals mol^{-1})
Soaps	20°C	30°C	40°C	20°C	30°C	40°C	
Butyrate	6.758	7.027	7.306	2.678	2.679	2.682	1.090
Valerate	6.723	6.994	7.258	2.653	2.654	2.654	1.050
Caproate	6.688	6.957	7.223	2.619	2.621	2.623	0.986
Caprylate	6.667	6.926	7.178	2.519	2.521	2.521	0.713

In the aggregation process, when the counter ions are bound together to form micelles the standard free energy of Micellization, ΔG_A^o for phase separation model is given by the relationship-

$$\Delta G_A^o = 2RT In\, X_{cmc} \tag{4}$$

The standard enthalpy change of Micellization is given by the relationship-

$$\partial In\, Xcmc = \frac{\Delta H_A^o}{2RT} + C \tag{5}$$

The values of H_A^o which have been obtained from the plots of In X_{cmc} Vs. *1/T* [Table 3] indicate that the association of zirconyl soaps in a mixture of xylene-methanol [4:1] is endothermic (Table 4). The standard entropy change for the association process has been calculated by the relationship-

$$\Delta S_A^o = \frac{\Delta H_A^o - \Delta G_A^o}{T} \tag{6}$$

The positive values of ΔS_A^o and negative values of ΔG_A^o for Micellization process and the negative values of ΔS_D^o and positive values of ΔG_D^o for dissociation process indicate that the association process is favored over the dissociation.

Table 4. Thermodynamic parameter for association process

	$-\Delta G_A^o$ (K cals mol^{-1}			$\Delta S_A^o \times 10^2$ (K cals K^{-1} mol^{-1})			ΔH_A^o (K cals mol^{-1})
Soaps	20°C	30°C	40°C	20°C	30°C	40°C	
Butyrate	6.172	6.331	6.528	2.479	2.450	2.435	1.093
Valerate	6.282	6.442	6.600	2.704	2.667	2.632	1.640
Caproate	6.362	6.527	6.686	2.805	2.767	2.730	1.858
Caprylate	6.476	6.629	6.762	2.994	2.945	2.894	2.296

APPLICATIONS

The thermodynamics of dissociation and association can be satisfactorily explained in the light of phase separation model by conductivity measurement. The result show that the dissociation of zirconyl soaps is exothermic while the association process is endothermic in nature.

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