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Conductometric Studies on Erbium Soaps of Higher Fatty Acids

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Abstract: Conductivity measurements of the solutions of erbium soaps (laurate, myristate, palmitate, and stearate) in mixture of xylene and DMSO (60% xylene + 40% DMSO). Erbium soaps behave as simple weak electrolytes in dilute solutions and Debye-Hückel-Onsager's equation is not applicable to these soap solutions. The values of the dissociation constant remain almost constant in dilute solutions but show a drift at higher soap concentrations which may be due to the failure of the Debye-Huckel's activity equation at higher soap concentrations. Critical micelle concentrations and dissociation constants decreased with increasing numbers of carbon atoms in the soap molecules. The thermodynamic results indicate that the micellization process is favored over the dissociation process.

Keywords: Erbium Soaps, Higher fatty Acids, Conductivity, Dissociation Constant, CMC.

I. Introduction

The study of metallic soaps has various prospects in technical and academic field. Soaps are widely used in industry and allied science as anti-oxidants, detergents, softeners, plasticizers, catalysts, lubricants, cosmetics, medicines, preservatives, fungicides, insecticides, emulsifier's water proofing agents. Application of metallic soaps depends largely on their physico-chemical properties such as physical state, thermal stability, chemical reactivity and solubility in polar and non-polar solvents.

Several researchers¹⁻¹² have prepared transition metallic soaps by treating the fatty acid with the requisite amount of metal oxide or hydroxide in the presence of organic solvent or organic base. Mehrotra et al^{13,14} investigated acoustical and thermodynamic properties of lanthanide soaps and concluded that these soaps behave as weak electrolyte in dilute solutions. Upadhyaya et al¹⁵ studied the thermodynamics of dissociation, micellization and conductance behaviour of alkaline-earth metal soaps. Topallar et al¹⁶ investigated conductance behaviour of erbium soaps in different solvents. A comparative study on micellization and electrolytic behaviour of dysprosium soaps in methanol was carried out by Shukla et al¹⁷. The present paper deals with the study of conductance of solutions of erbium soaps in a mixture of xylene and DMSO (60% xylene + 40% DMSO) (v/v) at different temperatures.

II. Experimental

Sodium hydroxide (NaOH), erbium nitrate, higher fatty acids (lauric acid, myristic acid, palmitic acid, and stearic acid) used in this study were supplied by Merck. The conductivity measurements of erbium soap solutions in a mixture of xylene and DMSO (40:60, v/v) were made with a Digital Conductivity Meter "Toshniwal model-CL 01.10 A" and with a dipping type conductivity cell with platinized electrodes at 40, 50 and 60 °C. The accuracy of the measurements was checked by repeating the observations several times.

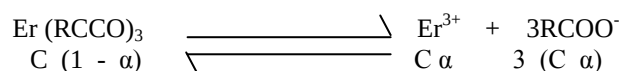
Erbium soaps were prepared by the direct metathesis of corresponding sodium soap with slightly excess of the required amount of erbium nitrate solution with vigorous stirring. The precipitated soaps were washed with distilled water and then with alcohol to remove excess of metal salt, sodium soap and unreacted fatty acid and obtained soaps were first dried in an oven and finally under reduced pressure. The solutions of soaps were prepared by dissolving a known amount of soap in a xylene-DMSO mixture (60:40, vol/vol) and were kept for 2 hr in a thermostat at the desired constant temperature.

III. Results and discussion

The plots of specific conductance, k , vs. soap concentration, C are characterized by a break, corresponding to CMC, indicating that micelle formation takes place at a definite soap concentration. Molar conductance, μ , of erbium soaps solutions in (60/40) xylene-DMSO mixture (v/v) decreases with increasing concentration and chain-length of the soaps. The specific conductance, k of the solutions of erbium soaps in mixture of xylene and DMSO (60% xylene + 40% DMSO) increases with the increase in the temperature, soap concentration and decreasing chain length of fatty acid constitute of soap. The increase in the specific conductance with soap concentration may have been due to partial dissociation of these soaps in mixed organic solvent in dilute solutions. However, an increase in specific conductance at higher soap concentration is probably due to formation of ionic micelles.

The critical micellar concentration, CMC, cannot be, however obtained from the plots of molar conductance vs. square root of soap concentration, which are concave upwards with increasing slopes indicating that soaps behave as weak electrolyte in dilute solutions. The decrease in molar conductance is attributed to the combined effects of ionic atmosphere, solvation of ions and decrease in mobility and ionization with the formation of micelles. The increase in specific conductance with soap concentration may have been due to dissociation of erbium soaps into simple erbium metal cations (Er^{3+}) and fatty acid anions (RCOO^-), where R is $\text{C}_{11}\text{H}_{23}$, $\text{C}_{13}\text{H}_{27}$, $\text{C}_{15}\text{H}_{31}$ and $\text{C}_{17}\text{H}_{35}$ for laurate, myristate, palmitate, and stearate, respectively, in dilute solutions and due to the formation of micelles at higher soap concentrations ($C > 0.005 \text{ M}$). The decrease in specific conductance with increasing number of carbon atoms in the fatty acid chain of the soap molecules may have been due to the higher molecular weight and decreasing mobility of anions.

Since the molar conductance of the solutions of erbium soaps does not vary linearly with the square root of soap concentration, the Debye-Huckel-Onsager equation¹⁸ is not applicable to these solutions. Molar conductance results show that erbium soaps behave as weak electrolytes in solution. Ionization of erbium soaps may be explained by Ostwald's formula. If C is the concentration and α is the degree of dissociation of the erbium soap, molar concentration may be represented as follows:



Where R is $\text{C}_{11}\text{H}_{23}$, $\text{C}_{13}\text{H}_{27}$, $\text{C}_{15}\text{H}_{31}$, and $\text{C}_{17}\text{H}_{35}$ for lauric acid, myristic acid, palmitic acid and stearic acid, respectively. The dissociation constant, K can be expressed as :

$$K = \frac{[\text{Er}^{3+}][\text{RCOO}^-]^3}{[\text{Er (RCCO)}_3]} = \frac{C\alpha(3C\alpha)^3}{C(1-\alpha)} = \frac{27C^3\alpha^4}{(1-\alpha)}$$

The degree of dissociation α may be replaced by the conductance ratio, α/α_0 where μ is the molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging equation can be written as :

$$\mu^3 C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27}$$

Table 1: Dissociation constants, K (from the plot of $\mu^3 C^3$ vs. $1/\mu$), of erbium soaps in a xylene-DMSO mixture (60:40, vol/vol) at various temperatures.

Soaps	Dissociation Constant $-\log K \times 10^7$		
	Temp. 40 °C	Temp. 50 °C	Temp. 60 °C
Erbium Laurate	4.380	3.543	1.447
Erbium Myristate	4.094	2.968	1.820
Erbium Palmitate	3.983	1.672	0.984
Erbium Stearate	4.620	2.871	0.879

The values of the dissociation constant, K and limiting molar conductance, μ_0^0 have been obtained from the slope, $(K\mu_0^3/27)$ and intercept, $(-K\mu_0^4/27)$ of the linear plots of $\mu^3 C^3$ vs $1/\mu$. The values of the change in free energy ΔG_D^0 and entropie ΔS_D^0 per mole for the dissociation process have been calculated by using the relationship -

$$\Delta G_D^0 = -RT \ln K_D$$

$$\Delta S_D^0 = \left[\frac{\Delta H_D^0 - \Delta G_D^0}{T} \right]$$

The results show that the values of ΔG_D^0 are positive and of ΔS_D^0 are negative indicating that the dissociation process is not favoured.

Table 2: The values of heat of dissociation, ΔH_d , of erbium soaps in a xylene-DMSO mixture (60:40 vol/vol)

Soaps	Heat of dissociation Soap $\Delta H_d / \text{kJ mol}^{-1}$
Erbium Laurate	-21.43
Erbium Myristate	-39.19
Erbium Palmitate	-43.83
Erbium Stearate	-45.56

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