Thermodynamics of Micellization and Conductance Behaviour of Lanthanide Palmitates in Mixed Organic Solvents

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The conductivity measurements of the solutions of palmitates of lanthanides (La, Ce, Pr and Nd) in 60% benzene and 40% dimethylsulphoxide show that these soaps behave as a weak electrolyte in dilute solutions; Debye-Huckel-Onsager's equation is not applicable to these solutions. The results show that the values of the CMC increase with increasing temperature and micellization process is predominent over the dissociation process.

The study of metallic soaps is becoming increasingly important in technological as well as academic fields [1]. Some work has been carried out on lanthanide soaps [1-12]. But often the technological applications of these soaps are based on empirical know-how and the selection of a soap is dependent largely on economic factors. There is a need for some systematic study of these soaps to optimise conditions for selection. Studies on the nature and structure of lanthanide soaps are of great importance for their uses in industries and for explaining their characteristics under different conditions.

The present work deals with the studies on the conductance and micellar behaviour of palmitates of some lanthanides (La, Ce, Pr and Nd) in a mixture of 60% benzene and 40% dimethylsulphoxide at different temperatures (30° - 60°C).

EXPERITMENTAL

The lanthanide (La, Ce, Pr and Nd) palmitates were prepared by the direct metathesis of corresponding potassium soaps with the required amount of lanthanide metal chlorides / nitrates in water-alcohol medium (1:1). The precipitated soaps were washed with water followed by acetone to remove the excess of metal ions and unreacted palmitic acid. The purity of the soaps was checked by elemental analysis and the results were found in agreement with the theoretically calculated values. The solutions of soaps were prepared by dissolving a known amount of soap in a mixture of 60% benzene and 40% dimethylsulphoxide and were kept for 2 hours in a thermostat at the desired constant temperature before measurement. The reproducibility of the results was checked with two samples of the soap prepared under similar conditions.

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The conductance of the solutions was measured with a Toshniwal digital conductivity meter (Model CL 01 10A) and a dipping type conductivity cell (cell constant 0.90) with platinized electrodes.

RESULTS AND DISCUSSION

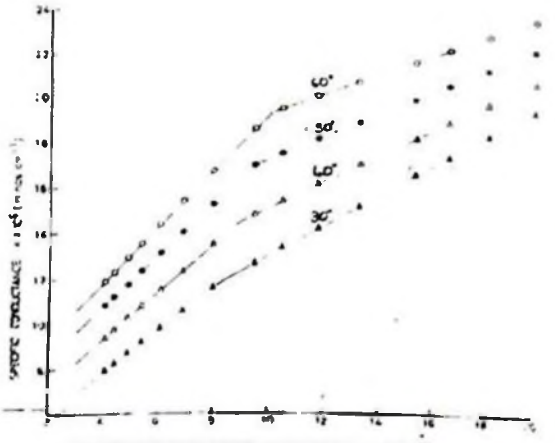
The specific conductance (k) of the solutions of lanthanide palmitates in a mixture of 60% benzene and 40% dimethylsulphoxide (V/V) was plotted as a function of soap concentration (Fig 1). These plots are characterised by an intersection of two straight lines. The concentration at the intersecton point corresponds to the critical micellar concentration (CMC). The CMC is presented in Table 1.

Table 1

Values of CMC of Lanthanide palmitates
Medium: Benzene-DMSO 60:40

CMC x10⁴ (g mol.l⁻¹)at	30°	40°	50°	60°C
Lanthanum palmitate	6.5	7.0	7.5	8.1
Cerium palmitate	8.5	9.1	9.6	10.2
Prasedymiun palmitate	9.5	10.2	10.7	11.2
Neodymium palmitate	10.5	11.0	11.5	12.2

The results show that the CMC increases directly with temperature and inversely with size of the rare earth metal ion. The micellization is assumed to occur when the energy released as a result of aggregation of



Specific conductance Vs Concentration plots of cerium palmitate in 60% benzene and 40% dimethyl Sulfoxide mixture

hydrocarbon chains of the monomers is sufficient to overcome the electrical repulsion between the ionic head groups and to balance the decrease in entropy accompanying aggregation. The kinetic energy of the monomers increase with rising temperature. So, it is expected that increase in temperature would increase the CMC value. The values of the CMC of these soaps are in good agreement with those obtained from viscosity, density and ultrasonic measurements.

The molar conductance (μ) of the dilute solutions of soaps decrease with increasing soap concentration as expected. However, the plots of μ *vs* square root of concentration are concave upwards with increasing slopes, indicating that these soaps behave as weak electrolytes in dilute solutions. The dissociation of these soaps can be represented as follows:

$$\underset{C(1-\alpha)}{M(C_{11}H_{11}COO)_3} \rightleftharpoons \underset{C\alpha}{M(C_{11}H_{11}COO)^{++}_2} + \underset{C\alpha}{C_{11}H_{11}COO^-} \quad (1)$$

where C is the concentration of soap (g mol.l^{-1}), α is the degree of dissociation and M stands for lanthanum, cerium, praseodymium and neodymium. Since the degree of dissociation of these soaps in dilute solutions is small, the ionic concentrations are low and interionic effects are almost negligible. Therefore, one can assume that 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 dissociation constant K for the above mentioned dissociation of soap can be expressed as :

$$K = C\ \alpha^2/ (1-\alpha) \qquad \ldots (2)$$

As an approximation, the degree of dissociation, α, may be taken as the conductance ratio, μ/μ_o, where μ is the molar conductance at finite concentration and μ_o is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging, equation (2) can be written as :

$$\mu C = \frac{K \mu_o^2}{\mu} - K\mu_o$$

The values of μ_o and K have been calculated from the slope, ($K\mu^2_o$) and intercept ($-K\mu_o$) of the linear plots of μC *vs* $1/\mu$ below the CMC. The values are recorded in Table 2.

The results show that the values of molar conductance at infinite dilution increase while the value of dissociation constants decrease with increasing temperature. Both the values decrease with the increase in the size of the cations.

The values of degree of dissociation of soaps decrease rapidly in dilute solutions but quite slowly above CMC. The values of dissociation constant, K, show approximate constancy in dilute solutions but exhibit a drift with increasing soap concentration. The drift in the values with increasing soap concentration may be:

Table 2

Limiting Molar Conductance (μ_o) and Dissociation Constants (K)

Medium: Benzene - DMSO (60:40)

Soap	Molar Conductance at				log K x 10^4 at			
	30°	40°	50°	60°	30°	40°	50°	60°
Lanthanum palmitate	92.2	93.5	94.6	95.8	6.166	3.981	1.630	1.862
Cerium palmitate	36.2	37.1	39.1	40.5	5.370	3.548	2.399	1.738
Praseodymiun palmitate	28.1	29.6	30.2	31.7	4.786	3.236	2.291	1.660
Neodymium palmitate	27.5	28.6	29.3	30.6	2.818	3.090	2.188	1.622

1. partiay due to the degree of dissociation (α) not being exactly equal to the conductance ratio, μ/μ_o,

2. due to the activity coefficient of ions not being equal to unity at higher soap concentrations.

3 due to the failure of the simple Debye-Huckel's activity equation at higher concentrations.

The values of the thermodynamic parameters for dissociation of soaps - change in free energy (ΔG_D), heat of dissociation (ΔH_D) and enthalphy change (ΔS_D) - for lanthanide palmitates have been calculated using the following expressions:

$$\Delta G_D = -RT \ln K_D \quad \ldots (4)$$

$$\log K = -\frac{\Delta H_D}{2.303\ RT} + C \quad \ldots (5)$$

and

$$\Delta S_D = 1/T\ (\Delta H_D - \Delta G_D) \quad \ldots (6)$$

The log K *vs* 1/T are plotted from the data in Table 2 and found to be linear. ΔH_D is calculated fron these plots. ΔS_D is then calculated. The calculated parameters are recorded in Table 3. The negative values of heat of dissociation (ΔH_D) indicate that the dissociation process is exothermic in nature.

Micellization Process

During aggregation process, counter ions get bounded to a micelle [1b]. The standard free energy of such binding per mole of monomer (ΔG_A) is given for the phase separation model as [13, 14]:

$$\Delta G_A = 2RT \ln X_{CMC} \quad \ldots (7)$$

where X_{CMC} is the CMC expressed in terms of mole fraction and is given for a dilute solution (where n_s the number of moles of surfactant << n_o number of moles of solvent for dilute solution) by the relationship:

$$X_{CMC} \sim \eta_s / \eta_o \quad \ldots (8)$$

The standard enthalpy change of micellization per mole of monomer (ΔH_A) for the phase separation model [13, 14] is given by the relationship:

Table 3
Thermodynamic Parameters For Dissociation of Lanthanum Palmitates
Medium: Benzene - DMSO (60:40)

	ΔG_D k.cals.mole^{-1} at				ΔH_D	ΔS_D			
	30°	40°	50°	60°		30°	40°	50°	60°
Lanthanum palmitate	4.46	4.88	5.30	5.69	-7.90	-4.08	-4.08	-4.09	-4.08
Cerium palmitate	4.54	4.95	5.36	5.74	-7.33	-3.92	-3.92	-3.93	-3.92
Praseodymiun palmitate	4.61	5.01	5.30	5.77	-6.87	-3.79	-3.80	-3.80	-3.80
Neodymium palmitate	4.93	5.03	5.42	5.78	-6.76	-3.86	-3.77	-3.77	-3.77

Table 4
Thermodynamic Parameters For Micellization of Lanthanum Palmitates

Medium: Benzene - DMSO (60:40)

	ΔG_A k cal.mole^{-1} at				ΔH_D	ΔS_A x 10^2k cals at			
	30°	40°	50°	60°		30°	40°	50°	60°
Lanthanum palmitate	-11.88	-12.19	-12.48	-12.78	-6.87	16.53	16.96	17.37	17.69
Cerium palmitate	-11.56	-11.96	-12.16	-12.46	-5.96	18.48	18.85	19.20	19.52
Praseodymiun palmitate	-11.43	-11.71	-12.03	-12.34	-5.04	21.09	21.31	21.64	21.92
Neodymium palmitate	-11.31	-11.62	-11.93	-12.22	-4.58	22.21	22.49	22.76	22.94

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

The values of ΔH_A of lanthanide palmitates have been obtained from the slope of the linear plots of ln X_{CMC} *vs* 1/T and are recorded in Table 4.

The positive values of ΔG_D and negative values of ΔS_D for the dissociation process (Table 3) and the negative values of ΔG_A and positive values of ΔS_A for the micellization process indicate that association process is favoured over the dissociation process.

CONCLUSION

The thermodynamic parameters of dissociation and association (micellization) can be satisfactorily explained in the light of phase separation model and conductivity measurements. The results showed that the micellization process is predominant over the dissociation process and lanthanide palmitates behaves as a weak electrolytes in benzene dimethylsulphoxide mixture.

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