Conductometric Studies and Thermodynamics of Dissociation and Micellization of Praseodymium and Neodymium Linoleates in Mixed Organic Solvents

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The results show that the praseodymium and neodymium linoleates behave as a weak electrolyte in dilute solutions (60% benzene + 40% methanol v/v) below the critical micellar concentration, and the conductance result can be explained on the basis of Ostwald's formula and Debye-Huckel's theory of weak electrolytes. The dissociation constant and thermodynamic parameters for dissociation and micellization processes of lanthanide linoleates are also evaluated. The micellization process has been found to be predominant over the dissociation process.

A survey of literature (1–14) reveals that the physicochemical properties and structure of lanthanide and actinide soaps have not yet been thoroughly investigated in spite of their considerable industrial applications. The study of metallic soaps is becoming increasingly important in technological as well as in academic fields. It has been a subject of intense investigation in the recent past on account of its role in such diversified fields as detergents, softeners, lubricants, plasticizers, stabilizers, catalysts, cosmetics, medicines, emulsifiers and waterproofing agents. However, technological application of these soaps is based mostly on empirical know-how. The selection of a soap is dependent largely on economic factors.

The present work deals with the studies on the conductance and micellar behavior of praseodymium and neodymium linoleate soaps in a mixture of 60% benzene and 40% methanol at different temperatures.

EXPERIMENTAL

The praseodymium and neodymium linoleates were prepared by the direct metathesis of potassium linoleate with the required amount of praseodymium and neodymium nitrates in a water-alcohol medium (1:1). The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreached linoleic acid. Both the preparation and purification processes were carried out under nitrogen atmosphere to protect against possible oxidation of these soaps. The purity of the soaps was checked by the elemental analysis, and the results were found in agreement with the theoretically calculated values for dry praseodymium and neodymium soaps. The reproducibility of the results was checked by preparing two samples of the soaps under similar conditions. The solutions of soaps were prepared by dissolving a known amount of soap in a mixture of 60% benzene and 40% methanol (v/v) and were kept for 2 hr in a thermostat at the desired constant temperature.

The conductance of the soap 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 at different temperatures. The reproducibility (±0.1%) of the measurements was examined by repeating them several times.

RESULTS AND DISCUSSION

The soaps of rare earth metals are soluble in the mixture of organic solvents. The solubility depends on the temperature, on the metal involved and on the solvent employed. But the nature of acid radical, its carbon chain length, degree of unsaturation, etc. are of considerable importance. Investigations have been made of the electrical properties of the solutions of rare earth metal soaps in mixed organic solvents, the subject being of interest to electrical engineers and others concerned in the transmission of electric power.

The specific conductance, k, of the solutions of praseodymium and neodymium linoleate soaps in 60% benzene and 40% methanol (v/v) increases with the increase in soap concentration and temperature. The plots of specific conductance vs soap concentration (Fig. 1) are characterized by an intersection of two straight lines at a concentration which corresponds to the critical micellar concentration (CMC) (Table 1).

TABLE 1

Critical Micellar Concentration of Praseodymium and Neodymium Linoleates in 60% Benzene and 40% Methanol (v/v)

Soap	CMC × 10^3 dm^{-3} mol			
	30°C	40°C	50°C	60°C
Praseodymium linoleate	4.3	4.8	5.1	5.4
Neodymium linoleate	4.2	4.6	4.9	5.3

The values of molar conductance, μ, of the dilute solutions of soap decrease with increasing soap concentration. The decrease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of micelles. However, the CMC values cannot be obtained from the plots of molar conductance vs square root of soap concentration because the plots are concave upwards with increasing slopes, indicating that these soaps behave as weak electrolytes in dilute solutions. Debye-Huckels-Onsagers equation is not applicable to these soap solutions. Since the praseodymium and neodymium linoleates behave as weak electrolytes in dilute solutions, an expression for the dissociation of these soaps may be developed in Ostwald's manner. The dissociation of soaps can be expressed as follows:

$$\underset{C(1-\alpha)}{M(C_{17}H_{31}COO)_3} \rightleftharpoons \underset{C\alpha}{M(C_{17}H_{31}COO)_2^+} + \underset{C\alpha}{C_{17}H_{31}COO^-} \quad [1]$$

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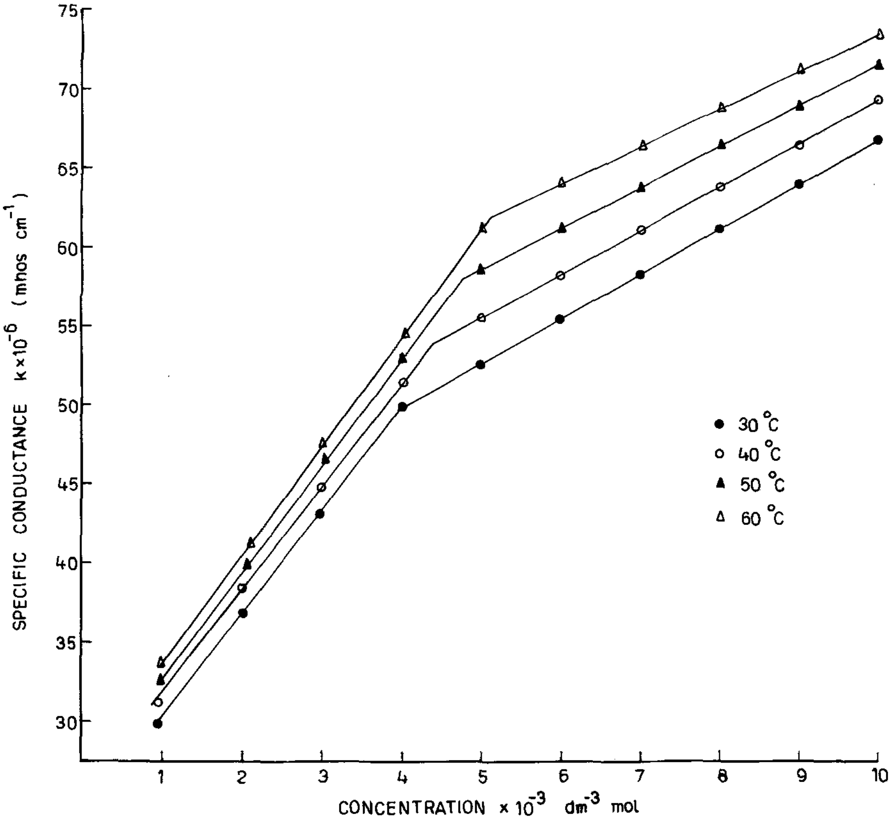

FIG. 1. Specific conductance vs concentration plots of praseodymium linoleate in 60% benzene and 40% methanol (v/v).

where C is the concentration of soap (dm^{-3} mol), α is the degree of dissociation and M is used for the cations praseodymium and neodymium, respectively. The dissociation constant K for the above mentioned method of dissociation of soap can be represented as:

$$K = \frac{[M(C_{17}H_{31}COO)_2^+][C_{17}H_{31}COO^-]}{[M(C_{17}H_{31}COO)_3]}$$

$$= \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \qquad [2]$$

Since the degree of dissociation of praseodymium and neodymium linoleates in dilute solutions is small, the ionic concentrations are low and interionic effects are almost negligible. Therefore, the dilute soap solutions do not deviate appreciably from ideal behavior, and the activities of ions can be taken as almost equal to the concentrations. The degree of dissociation, α, may be determined by the conductance ratio, μ/μ_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 (2) can be written as:

$$\mu C = \frac{K\,\mu_0^2}{\mu} - K\,\mu_0 \qquad [3]$$

The values of limiting molar conductance, μ_0 and dissociation constant K have been calculated from the slope [K μ_0^2] and intercept [$-$K μ_0] of the linear plots of μC vs 1/μ below the CMC (Table 2).

The results indicate the values of molar conductance at infinite dilution increase while the dissociation constant decreases with increasing temperature. The values of limiting molar conductance and dissociation constant decrease with the increase in the size of the cations. The values of degree of dissociation, α, at different soap concentrations and temperatures have been determined by assuming it as equal to the conductance, μ/μ_0. The results show that soaps behave as weak electrolytes in dilute solutions. The values of degree of dissociation of the soaps decrease rapidly in dilute solutions with the increase in soap concentrations whereas it decreases slowly above the CMC.

The values of dissociation constant, K, show approximate constancy in dilute solutions, but exhibit a drift

TABLE 2

Values of Dissociation Constant of Praseodymium and Neodymium Linoleates in 60% Benzene and 40% Methanol at Different Temperatures

	Dissociation constant K × 10^7			
Soap	30°C	40°C	50°C	60°C
Praseodymium linoleate	11.091	7.762	5.559	4.477
Neodymium linoleate	8.710	6.761	5.012	4.102

with increasing soap concentration which indicates that these soaps do not behave as very weak electrolytes in non-aqueous medium. The drift in the values of dissociation constant with increasing soap concentration may be due partly to the fact that the degree of dissociation, α, is not exactly equal to the conductance ratio, μ/μ_0 but mainly due to the fact that the activity coefficient of ions is not equal to unity at higher soap concentrations. The deviation in the values of dissociation constant at higher soap concentration may be due to the failure of simple Debye-Huckel's activity equation. The decrease in the values of dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of praseodymium and neodymium linoleates in mixed organic solvents.

The heat of dissociation, ΔH°_{D}, for praseodymium and neodymium linoleates has been determined by using the equation:

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

or

$$\log K = -\frac{\Delta H_D}{2.303\ RT} + C$$

The values of heat of dissociation, ΔH°_{D}, have been obtained from the slope of the linear plots of log K vs 1/T (Fig. 2), and are mentioned in Table 3. The negative values of heat of dissociation, ΔH°_{D}, again indicate that the dissociation process is exothermic in nature.

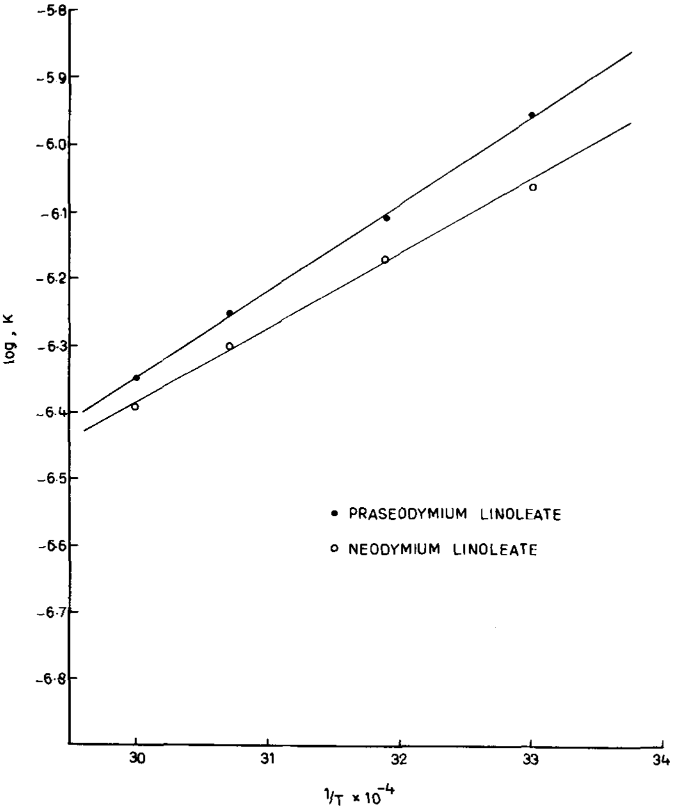

FIG. 2. The log K vs 1/T; 60% benzene and 40% methanol (v/v).

TABLE 3

Thermodynamic Parameters of Lanthanide Linoleates Per Mole of Monomers

Soap	Heat of dissociation ΔH_D kJ mol^{-1}	Heat of micellization ΔH_m kJ mol^{-1}
Praseodymium linoleate	−8.32	10.87
Neodymium linoleates	−7.04	11.51

The values of change in free energy, ΔG°_{D} and entropy, ΔS°_{D} per mole for the dissociation process have been calculated by using the relationships:

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

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

The calculated values of ΔG°_{D} and ΔS°_{D} are recorded in Table 4.

For the process of micellization, when counter ions are bound to a micelle, the standard free energy of micellization, ΔG°_{m} (per mole of monomer) for phase separation model (15,16) is given by the relationship:

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

where X_{CMC} is the critical micellar concentration expressed in terms of mole fraction and it may be expressed by the relationship:

$$X_{CMC} = n_s/(n_s + n_o)$$

where n_s and n_o are the number of moles of surfactants and solvent, respectively. Since the number of moles of

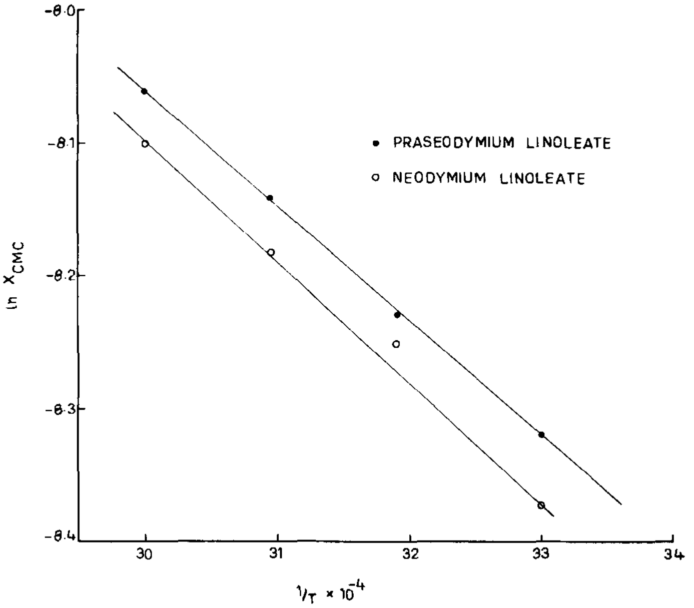

FIG. 3. The ln X_{CMC} vs 1/T; 60% benzene and 40% methanol (v/v).

TABLE 4

Thermodynamic Parameters of Lanthanide Linoleates 60% Benzene and 40% Methanol (v/v) for Dissociation Process at Various Temperatures

	ΔG_D kJ mol^{-1}				$\Delta S_D \times 10^2$ kJ			
Soap	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Praseodymium linoleate	11.54	12.23	12.92	13.52	−6.55	−6.57	−6.58	−6.56
Neodymium linoleate	11.74	12.35	13.01	13.60	−6.20	−6.19	−6.21	−6.20

TABLE 5

Value of ln X_{CMC} at Different Temperatures

Soap	30°C	40°C	50°C	60°C
Praseodymium linoleate	−8.323	−8.228	−8.141	−8.061
Neodymium linoleate	−8.374	−8.251	−8.183	−8.100

TABLE 6

Thermodynamic Parameters of Lanthanide Linoleates 60% Benzene and 40% Methanol (v/v) for Micellization Process at Various Temperatures

	ΔG_m kJ mol^{-1}				$\Delta S_m \times 10^2$ kJ			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Praseodymium linoleate	−3.35	−3.42	−3.49	−3.56	4.69	4.57	4.45	4.33
Neodymium linoleate	−3.37	−3.43	−3.51	±3.58	4.91	4.77	4.65	4.53

free surfactant, n_s, is too small as compared to the number of moles of solvent, n_o, it follows the relationship (Table 5).

$$X_{CMC} = n_s/n_o$$

The standard enthalpy change of micellization per mole of monomer for the phase separation model (14,15), ΔH°_m, is given by the relationship:

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

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

The values of ΔH°_m of praseodymium and neodymium linoleates have been obtained from the slope of linear plots of ln X_{CMC} vs 1/T (Fig. 3), and are recorded in Table 3.

A careful scrutiny of the thermodynamic parameter indicates that the negative value of ΔG° and positive values of ΔS° for the micellization process (Table 6) and positive values of ΔG° and negative values of ΔS° for the dissociation process (Table 4) show that the micellization process is favored over the dissociation process.

The results show that the increase in temperature results in an increase of the CMC (Table 5) because the process of micellization is assumed to occur when the energy released as a result of aggregation of the hydrocarbon chains of the monomer is sufficient to the electrical repulsion between the ionic head groups and to balancing 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 monomers would have been raised.

The thermodynamics of dissociation and micellization can satisfactorily be explained in the light of phase separation model. These results also indicate that the micellization process is predominant over the dissociation and praseodymium and neodymium linoleates behave as a weak electrolyte in a mixture of 60% benzene and 40% methanol (v/v).

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