



Conductometric Studies and Thermodynamic Behaviour of Neodymium Soaps in 60/40 Benzene-dimethylsulphoxide Mixture (V/V)

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(Received 10 July, 2015; Accepted 19 July, 2015; Published 23 July, 2015)

ABSTRACT: Conductometric measurements of the solution of Neodymium Caprylate and Laurate in 60/40 benzene-dimethylsulphoxide (V/V) mixture were employed to determine the critical micellar concentration (CMC), limiting molar conductance at infinite dilution, degree of dissociation and dissociation constant. The values of CMC decreases with increasing chain length of fatty acid component of soaps. The results shows that these soaps behaves as a weak electrolyte in dilute solutions below the CMC and Debye-Huckel-Onsager equation is not applicable to these soap solutions. The thermodynamic parameters indicate that the micellization process is favoured over the dissociation process.

Keywords: Critical micellar concentration; micellization; thermodynamic parameters; Neodymium caprylate and laurate respectively.

INTRODUCTION: Metallic soaps are widely used in many industries as anti-oxidants, catalyst, lubricants, cosmetics, medicines, preservatives, fungicides, insecticides, emulsifiers, water-proofing agents, plasticisers, softeners and detergents. The technological application of these soaps depends on the physico-chemical properties like their physical state, thermal stability, chemical reactivity and solubility in polar and non-polar solvents. Several workers¹⁻⁶ have used different techniques for studying the preparation, properties and uses of metal soaps. Metal soaps with element of lanthanide series were synthesized for the first time by Mishra et al⁷. Mehrotra et al⁸⁻⁹ investigated acoustical and thermodynamic properties of lanthanide soaps and concluded that these soaps behaves as weak electrolyte in dilute solutions. Upadhyaya et al¹⁰ studied the thermodynamics of dissociation, micellization and conductance behaviour of alkaline-earth metal soaps. Topallar et al¹¹ investigated conductance of erbium soaps in different solvents.

The present paper deals with the study of conductance, micellar behaviour and thermodynamic parameter of Neodymium soaps in a mixture of 60/40 benzene-dimethylsulphoxide mixture (V/V) at different temperatures.

MATERIAL AND METHODS: Anal R grade higher fatty acid (caprylic acid and lauric acid), potassium hydroxide, neodymium acetate (purity 99% received from Indian Rare Earth Limited, Kerala) were used for the present investigation. Neodymium soaps (caprylate and laurate) were prepared by the direct metathesis of corresponding Neodymium soaps by pouring a slight stoichiometric excess of aqueous neodymium acetate solution into the clear dispersion at raised temperature with vigorous stirring. The precipitated soaps were filtered off and washed with hot distilled water and acetone. After initial drying the final drying was carried out under reduced pressure. The soaps were purified by recrystallization and the purity of the soaps was established by observing their melting points, IR spectra and elemental analysis.

Solutions of Neodymium caprylate and Neodymium laurate were prepared by dissolving a known amount of soap in a mixture of 60% benzene and 40% dimethylsulphoxide and kept for 2 hours in a thermostat at a desired temperature.

Measurements: The conductance of solutions were measured with a “Systronics conductivity Bridge 305” and a dipping type conductivity cell (cell constant 1.0 cm⁻¹) with platinised electrodes at 25-40°C (±0.05°C).

The specific and molar conductance were expressed in mhos cm^{-1} and $\text{mhos cm}^{-1}(\text{g mol})^{-1}\text{litre}$ respectively.

RESULTS AND DISCUSSION:

Specific Conductance: The specific conductance, k of the solutions of Neodymium caprylate and neodymium laurate in 60/40 benzene-dimethylsulphoxide mixture (V/V), increases linearly with increase in the temperature and increase in soap concentration. The increase in specific conductance may be due to partial dissociation of these soaps in mixed solvent in dilute solution and due to formation of micelles at higher soap concentration. The specific conductance decreases with increase in chain length of fatty acid constituent of the soap molecule may be due to increasing size and decreasing mobility of anions. The plots of specific conductance, k Vs. Soap concentration C are characterized by an intersection of two straight line at a

concentration which corresponds to the CMC of the Neodymium soaps which indicates that these soaps are considerably ionized in dilute solutions and the formation of ionic micelles takes place at this concentration.

Table 1: Critical Micellar Concentration, CMC (g mole l^{-1}) of Neodymium Caprylate and laurate in a mixture of 60/40 benzene-dimethylsulphoxide (V/V) at various temperatures.

Name of the Soap	CMC $\times 10^3$ (gm mol l^{-1})			
	25 °C	30 °C	35 °C	40 °C
Neodymium Caprylate	4.50	4.70	4.80	5.10
Neodymium Laurate	4.0	4.15	4.50	4.80

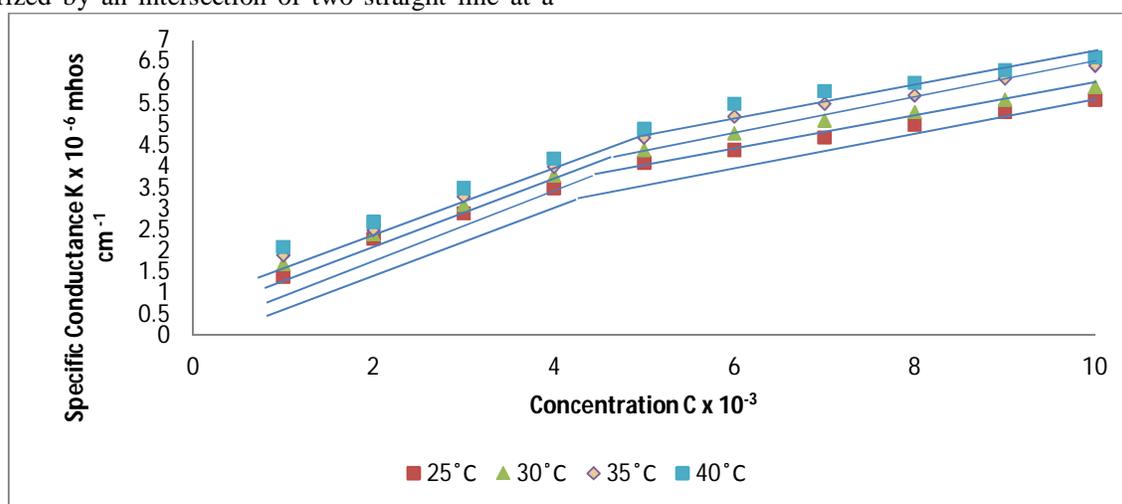
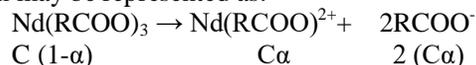


Figure 1: Specific Conductance Vs Concentration Plots of Neodymium Caprylate in 60% Benzene & 40% dimethylsulphoxide (V/V).

Molar Conductance: The molar conductance μ of the solutions of Neodymium caprylate and laurate in 60% Benzene and 40% Dimethylsulphoxide (V/V) decreases with increasing concentration of soap as well as the chain length of soap. The decrease in molar conductance may be attributed to combined effects of ionic atmosphere, solvation of ions, decrease in mobility and due to formation of micelles. The plots of molar conductance μ Vs \sqrt{C} (Square root of concentration) are not linear but are concave upwards indicating that these soaps behave as weak electrolyte in dilute solutions. The limiting molar conductance μ cannot be obtained by usual extrapolating method and Debye-Huckel-Onsager equation¹²⁻¹³ is not applicable to these soap solutions.

The result of the molar conductance of the dilute solution of neodymium soaps behave as weak electrolyte so an expression for dissociation of these metal soaps in 60/40 benzene-dimethylsulphoxide may be explained by Oswald's formula. If C is the concentration of soaps in g mol/ litre and α is the degree of dissociation of the Neodymium soaps then molar concentration may be represented as:



Where R is C_7H_{15} , $\text{C}_{11}\text{H}_{23}$ for caprylate and laurate respectively.

The dissociation constant K_D can be written as:

$$K_D = \frac{4C^2\alpha^3}{(1-\alpha)} \quad (1)$$

Since the number of ions for weak electrolyte are relatively low in dilute solutions and the interionic effects are almost negligible, the activities of ions may be taken as proportional to the concentration. Thus the degree of dissociation, α may be defined by conductance ratio μ/μ_0 where μ is the molar conductance at finite dilution and μ_0 is the limiting molar conductance of ions.

By substituting the values of α and rearranging equation (1), the following expression¹⁴ for the dissociation of neodymium soaps can be written as:

$$\mu^2 C^2 = \frac{K_D \mu_0^3}{4\mu} - \frac{K_D \mu_0^2}{4} \quad (2)$$

The values of dissociation constant K_D and limiting molar conductance μ_0 were calculated from the slope $K_D \mu_0^3/4$ and the intercept, $-K_D \mu_0^2/4$ of the linear portion of the plots of $\mu^2 C^2$ Vs $1/\mu$ for dilute solution of neodymium soap. The values of limiting molar con-

ductance increases while the dissociation constant decreases with the rise in concentration.

The decrease in the value of dissociation constant with temperature indicates the exothermic nature of dissociation of neodymium soaps in 60/40 benzene-DMSO mixture. The value of dissociation constant, K_D obtained from above said plots were found in agreement with the values determined by using equation (1) but show a drift at higher concentration which may be due to the failure of Debye-Huckel's activity equation at higher soap concentration.

The heat of dissociation, ΔH_D , for Neodymium caprylate and laurate is determined by using following equation:

$$\text{Log } K_D = \frac{-\Delta H_D}{2.303RT} + C \quad (3)$$

The negative values of the enthalpy of dissociation, ΔH_D , were obtained from the slope of the linear plots of $\log K_D$ Vs $1/T$ (Figure 2) which indicates the dissociation process of Neodymium soaps (caprylate and laurate) is exothermic in nature.

Table 2: Molar Conductance at infinite dilution μ_0 and dissociation constant K_D of Neodymium Caprylate and laurate in a mixture of 60/40 benzene-dimethylsulphoxide (V/V) at various Temperatures.

Name of the soap	25 °C		30 °C		35 °C		40 °C	
	μ_0	K_D	μ_0	K_D	μ_0	K_D	μ_0	K_D
Neodymium Caprylate	24	6.01	29	4.52	31.5	3.50	37	2.62
Neodymium Laurate	20.46	5.6	26.32	4.25	29.4	3.27	30.55	2.48

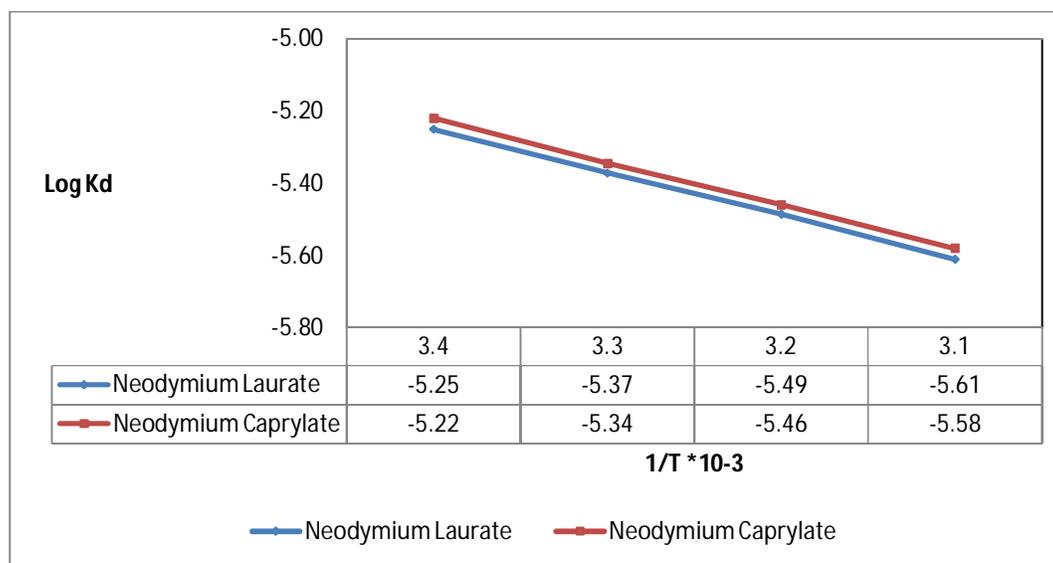


Figure 2: $\log K_D$ vs $1/T$ for Neodymium Caprylate and Laurate.

Table 3: Thermodynamic Parameters of the dissociation of Neodymium Caprylate and Laurate in mixture of 60/40 benzene-dimethylsulphoxide (V/V) at various temperatures.

		Dissociation (Kilo calorie per mole)								
S.No	Name of the Soap	25 °C		30 °C		35 °C		40 °C		ΔH_D
		ΔG_D	$-T\Delta S_D$	ΔG_D	$-T\Delta S_D$	ΔG_D	$-T\Delta S_D$	ΔG_D	$-T\Delta S_D$	
1	Neodymium Caprylate	12.96	27.22	13.5	27.76	14.03	28.29	14.6	28.86	14.26
2	Neodymium Laurate	12.93	27.31	13.42	27.8	13.93	28.31	14.54	28.92	14.38

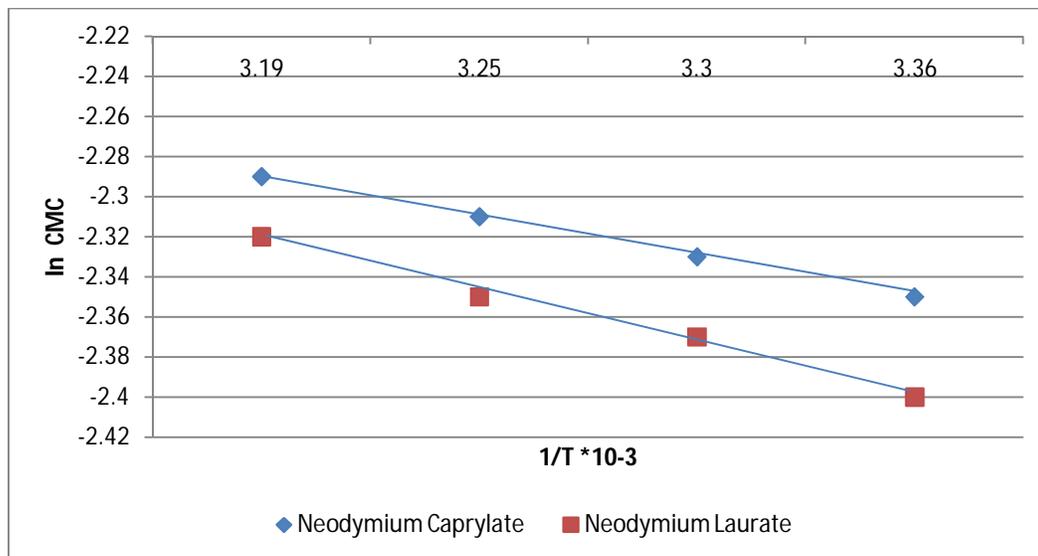


Figure 3: $\ln X_{CMC}$ vs $1/T$ for Neodymium Caprylate and Laurate.

The values of change in free energy, ΔG_D and standard entropy change, $T\Delta S_D$ for the dissociation process are calculated by using the following relationships.

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

$$T\Delta S_D = \Delta H - \Delta G \quad (5)$$

The calculated values of ΔG_D and $T\Delta S_D$ are recorded in Table 3.

In case of micellization the standard free energy change of micellization, ΔG_M for phase separation model [15-17] is given by the equation.

$$\Delta G_M = 2RT \ln X_{CMC} \quad (6)$$

The standard enthalpy change of micellization, ΔH_M for the phase separation model is evaluated as follows:

$$\ln X_{CMC} = \frac{\Delta H_M}{2RT} + C \quad (7)$$

The values of ΔH_M have been determined from the slope of linear plots of $\ln X_{CMC}$ vs $1/T$. The positive

enthalpy for micellization, ΔH_M , indicates that the association of neodymium caprylate and laurate in 60/40 benzene-dimethylsulphoxide (V/V) is endothermic.

The standard entropy change for micellization is calculated as,

$$T\Delta S_M = \Delta H_M - \Delta G_M \quad (8)$$

The micellization of the soaps in a mixture of 60/40 benzene-dimethylsulphoxide (v/v) consistent with $\Delta H_M > 0$, $\Delta G_M < 0$, $T\Delta S_M > 0$. However, dissociation of these soaps is consistent with $\Delta H_D < 0$, $\Delta G_D > 0$, $T\Delta S_D < 0$. The results are in consistent with other data¹⁸⁻²¹.

The negative value of free energy of micellization, ΔG_M , positive value of ΔS_M for micellization and positive value of ΔG_D and negative value of $T\Delta S_D$ for the dissociation indicate that micellization process is favoured over the dissociation process. It may therefore be inferred that in a mixture of 60/40 benzene-dimethylsulphoxide (V/V) neodymium caprylate and laurate behave as weak electrolytes. The value of the

CMC increases with increasing temperature and the micellization process is predominating over dissociation process.

Association (Kilo Calorie per mole)										
S.No	Name of the Soap	25 °C		30 °C		35 °C		40 °C		ΔHm
		-ΔG m	TAS m							
1	Neodymium Caprylate	13.23	30.45	13.40	30.62	13.60	13,82	13.74	30.96	17.22
2	Neodymium Laurate	13.35	32.21	13.53	32.39	13.65	32.52	13.89	32.75	18.86

Table 4: Thermodynamic Parameters of the association of Neodymium Caprylate and Laurate in mixture of 60/40 benzene-dimethylsulphoxide (V/V) at various temperatures.

ACKNOWLEDGEMENT: The authors are grateful to Principal, Head of Chemistry department, S. S. L. Jain P.G. College, Vidisha for providing all necessary facilities.

REFERENCES:

- Mehmet Gonen, Serdar Oztarki , Devrin Balkose , Salih Okur and Semra Ulku (2010) *Ind. Eng. Chem. Res.*, 49(4), 1732.
- Robert W. Corkery (2004) *Phys. Chem. Phys.*, 6, 1534.
- Norichika Matsumoto (2002) *Jpn. Kokai Tokkyo Koho*,198, 38.
- Norichika Matsumoto (2002) *Jpn. Kokai Tokkyo Koho*, 199, 317.
- S. P. Verghese, Suleman and F. M. Prasad (2008) *J. Ind. Chem. Soc.*, 85, 252.
- H. W. Lawureck and K. A. Samurai (2008) *J. Appl. Prob.*, 76, 401.
- S. N. Mishra, T. N. Mishra, R. C. Mehrotra (1963) *J. Inorg. Nucl. Chem.*, 25, 195.
- K. N. Mehrotra, A. S. Gahlaut and M. Sharma (1987) *J. Colloid and Interface Sci.*, 120, 110.
- K. N. Mehrotra and S. K. Upadhyaya (1990) *J. Am. Oil Chemists Soc.*, 67, 464.
- S. K. Upadhyaya and C. Singh, (2001) *Asian J. Chem.*, 13(3), 977.
- H. Topallar and Y. Bayrak , Tr. (1988) *J. Chem.*, 22, 167.
- P. Debye and E. Huckel Z. (1923) *Phys.*, 24, 305.
- P. Debye and E. Huckel, Onsager Z. (1926) *Phys.*, 27, 388.
- C. A. Kraus and W. C. Bray (1913) *J. Am. Chem. Soc.*, 35, 1315.
- B. W. Barry and G. F. Russel (1972) *J. Colloid Interface Sci.*, 40(2), 174.
- D.C. Robins and I.L. Thomas (1968) *J. Colloid Interface Sci.*, 26(4), 407.
- D. Attwood and A.T. Florence (1983) *Surfactant Systems* , London-New York, 100.
- K. Kishore and S. K. Upadhyaya (2010) *Tenside Surf. Det.*, 47, 184.
- K. Kishore and S. K. Upadhyaya (2010) *Port. Electrochimica Acta*, 28, 213.
- A. Gupta and S.K. Upadhyaya (2012) *J. Indian chem.Soc.*, 89,1539-1542.
- Anubhuti Jain and S. K. Upadhyaya (2014) *J. Indian Chem.*, 91, 859-863.