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Acoustical Behaviour of Neodymium Soaps of Saturated Fatty Acids in 60/40 Benzene-Dimethylsulphoxide Mixture at Various Temperatures

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ABSTRACT: Ultrasonic velocity & density measurements of the solutions of neodymium caprylate and laurate in 60/40 benzene-dimethylsulphoxide mixture (V/V) at different temperatures have been carried out in order to determine the critical concentration of micelle formation, ultrasonic velocity, soap-solvent interactions and number of allied acoustical parameters. The value of critical micellar concentration of neodymium caprylate and laurate are in good agreement with those determined from other physico-chemical techniques .The results also confirm that there is a significant interaction between neodymium soaps and mixed organic solvent molecules in dilute solutions and the soap molecules do not aggregate below the CMC. The values of CMC for neodymium soaps increases with the rise in temperature.

Keywords: Ultrasonic velocity; neodymium caprylate; neodymium laurate; critical micellar concentration and acoustical parameters.

INTRODUCTION: Metallic soaps are being used in different industries as softener, plasticizers, water proofing agents and in the preparation of paints, varnish and enamels. Sound velocity is purely a thermodynamic function and with the help of this method[1], a number of other acoustical constants of electrolyte solutions can be determined. Mehrotra et al[2-4] determined acoustical parameters of lanthanide soaps in mixed organic solvents. Acoustical studies on uranyl soaps of lower fatty acids have been reported by Varsha et al[5]. Acoustical studies, compressibility behaviour and Rao formalism of lanthanide soap solutions was carried out by Upadhyaya et al[6].Ultrasonic studies on the molecular interaction of uranyl soaps in benzene-dimethylsulphoxide mixture was carried out by Anubhuti et al[7].

In continuation with earlier work on metal soaps we report the results of ultrasonic measurements in 60/40 benzene-dimethylsulphoxide mixture (V/V) at different temperatures, in this manuscript. This work has been initiated to calculate various allied parameters related to the acoustical properties of neodymium soaps and effect of temperature on these parameters have also been studied.

MATERIAL AND METHODS: AnalaR grade higher fatty acid (caprylic acid and lauric acid), potassium hydroxide, neodymium acetate (purity 99% Indian Rare- Earth Limited, Kerala) were used for the preparation of neodymium soaps. Neodymium soaps (caprylate and laurate) were prepared by the metathesis method. The precipitated soaps were filtered off and washed with hot double distilled water and acetone. After an initial drying in air oven at 50-60°C the final drying was carried out under reduced pressure. The purity of these soaps was established by carbon hydrogen analysis and the results of c were found to be in good agreement with theoretically calculated values.

Solutions of neodymium caprylate and laurate were prepared by dissolving a known amount of soap in a mixture of 60/40 benzene-dimethylsulphoxide mixture (V/V) and kept for 2 hours in a thermostat at a desired constant temperature.

The ultrasonic velocity of solutions of neodymium caprylate and laurate were measured with a multifrequency ultrasonic interferometer Model MX-3 (Mittal Enterprises New Delhi) at 25°C, 30°C, 35°C, 40°C using a crystal frequency of 1MHz. The uncertainty of velocity measurements was of ± 0.2%. The densities of the solutions were determined by a pyknometer calibrated with pure benzene.

Various acoustical parameters, such as adiabatic compressibility (β), molar compressibility (W), intermolecular free length (L_f), specific acoustical impedance (Z), apparent molar volume (ϕ_v), apparent molar compressibility (ϕ_k), molar sound velocity (R), relative association (Ra), primary solvation number (Sn), available volume (Va) and relaxation strength (r), have been evaluated by using the following relationships:

$$\beta = \rho^{-1} v^{-2} \quad \text{.....(1)}$$

$$W = Meff/\rho\ (\beta)^{-1/7} \quad \text{.....(2)}$$

$$L_f = K\ (\beta)^{1/2} \quad \text{.....(3)}$$

$$Z = \rho\, v \quad \text{.....(4)}$$

$$\phi_V = 1000/C\rho_o(\rho_o-\rho)+M/\rho_o \quad \text{.....(5)}$$

$$\phi_K = 1000/C\rho_o(\rho_o\beta-\beta_o\rho)+\beta_o xM/\rho_o \quad \text{.....(6)}$$

$$R = M\ eff/\rho\ x\ v^{1/3} \quad \text{.....(7)}$$

$$R_a = (\rho/\rho_o)\ (v_o/v)^{1/3} \quad \text{.....(8)}$$

$$S_n = n_o/n\ (1-V\beta/n_oV_o\beta_o) \quad \text{.....(9)}$$

$$V_a = V\ (1-v/v_\alpha) \quad \text{.....(10)}$$

$$r = 1/(v/v_\alpha)^2 \quad \text{.....(11)}$$

where ρ, ρ_0, β, β_0, v, v_o, V and V_o are the density, adiabatic compressibility , ultrasonic velocity and molar volume of neodymium soap solutions and mixed organic solvent, respectively ;K is Jacobson's constant; C is concentration (g mol. l^{-1}) of the solute, and M_{eff} is effective molecular weight of the soap solution; V is the molar volume of the solution containing n moles of solute and V_0 is the molar volume of solvent; v_α is equivalent to 1600 m s^{-1}. The effective molecular weight of the solutions has been calculated by the relationship:

$$M_{eff} = (n_oM_o+nM)/n_o+n$$

Where; n_o, M_o, n and M are the number of moles and molecular weight of solvent and solute, respectively.

RESULTS AND DISCUSSION: The ultrasonic velocity and various acoustical parameters of neodymium caprylate and laurate at 25°C, 30°C, 35°C, 40°C in a mixture of 60/40 benzene-dimethylsulphoxide mixture(V/V) is measured at different concentrations.

The variation of ultrasonic velocity v, with soap concentration C depends upon the concentration derivatives of density ρ and adiabatic compressibility β by the relationship:

$$\left(\frac{dv}{dc}\right) = -\frac{v}{2}\left[\frac{1}{\rho}\left(\frac{d\rho}{dc}\right) + \frac{1}{\beta}\left(\frac{d\beta}{dc}\right)\right]$$

The concentration derivative of density (dρ/dc) is positive while the quantity (dβ/dc) is negative and since the value of 1/β (dβ/dc) larger than the values of 1/ρ (dρ/dc) for neodymium soap solutions dv/dc will be positive therefore the velocity increases with increasing concentration of neodymium soaps, which is in accordance with the results of other workers reported for different electrolytic solutions[8 & 9].

The equation for variation of ultrasonic velocity, v with neodymium soap concentration, C for dilute solution is as follows:

$$v = v_o + GC$$

Where; v_o is the ultrasonic velocity of solvent mixture and G is Gransey's constant[10].

The plots of ultrasonic velocity (v) versus soap concentration C (Figure 1) are characterized by an intersection of two straight lines at a definite soap concentration where the physical properties of the neodymium soap exhibit discontinuity, which corresponds to the CMC of these soaps (Table 1). The main cause of micellization at particular concentration in mixed organic solvent is the change of energy between the polar ionic groups of soap molecules due to the dipole-dipole interaction between the polar head groups of soap molecules. The aggregation begins at very low concentration in organic solvents and results in the formation of much smaller aggregates than in H_2O.The association in organic solvents can be described in terms of a stepwise association model. The molecules of soap are characterized by the presence of both lyophilic and lyophobic moieties in the same molecules, and micelles in organic solvents can be regarded as Hartley's "inverted" micelles, in which polar head groups are present in the centre of the micelles with the hydrocarbon chains extending outwards into the solvent.

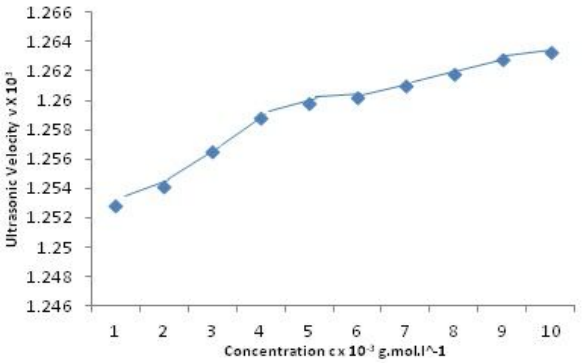

Figure 1: Ultrasonic Velocity vs. Concentration of Neodymium soap in 60/40 benzene-dimethyl sulphoxide mixture (V/V).

The nature of adiabatic compressibility β is found to be opposite to that of ultrasonic velocity v. This decrease in adiabatic compressibility with increasing concentration of the soap solutions is due to ionization of soap molecules into metal cation and fatty acid anions. The adiabatic compressibility of neodymium soaps (caprylate and laurate) in 60/40 benzene-dimethylsulphoxide mixture (V/V) decreases with increasing soap concentration and increases with increasing temperature. The decrease in adiabatic compressibility is attributed to the fact that the soap molecules get ionized in dilute solutions into neodymium metal cations and fatty acid anions. These ions are surrounded by a layer of solvent molecules firmly bounded and oriented towards ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of the ions, which affects the internal pressure, lowering the compressibility of the neodymium soap solutions[11].

The results of adiabatic compressibility β of the solutions of neodymium caprylate and laurate can be explained in terms of Bachem's relationship[12]:

$$\beta = \beta_o + AC + BC^{3/2}$$

Where; A and B are constants, C is the molar concentration of soap solution and β and β_o are the adiabatic compressibility of the solution and solvent mixture respectively. The values of constants A and B are obtained from the intercept and slope of the plots of [β-β_o/C] versus √C below the CMC. The plots of β-β_o/C versus √C shows a break at the CMC.

Table 1: Values of critical Micellar concentration of Neodymium soaps in 60/40 benzene dimethyl sulphoxide mixture V/V.

S. No.	Name of the Soap	Temperature °C			
		25°C	30°C	35°C	40°C
1	Neodymium Caprylate	4.50	4.70	4.80	5.10
2	Neodymium Laurate	4.0	4.15	4.50	4.80

Table 2: Ultrasonic velocity and other acoustical parameters of neodymium caprylate in 60/40 benzene dimethyl sulphoxide mixture V/V at 25°C±0.05°C.

S. No.	Concentration C x 10^3 (g.mol l^{-1})	Ultrasonic velocity *v* x 10^{-3} (m/s)	Density ρ (kg.m^{-3})	Adiabatic compressibility β x 10^{10} (m^2N^{-1})	Intermolecular Free length Lf (Å)	Specific acoustic impedance Z x 10^{-5} $Kgm^{-2}s^{-1}$	Apparent molar compressibility -(φK) x 10^6 M^3N^{-1} (K mol)$^{-1}$	Solvation number Sn
1	1	1.2528	991.2	6.4280	0.5071	12.418	1.889	270.3
2	2	1.2541	991.6	6.4121	0.5064	12.436	1.902	136.1
3	3	1.2565	991.7	6.3870	0.5054	12.461	1.952	91.9
4	4	1.2588	991.8	6.3630	0.5045	12.485	1.998	70.0
5	5	1.2598	991.9	6.3523	0.5041	12.496	1.844	56.4
6	6	1.2602	992.0	6.3476	0.5039	12.501	1.663	46.8
7	7	1.261	992.1	6.3389	0.5035	12.510	1.552	40.3
8	8	1.2618	992.2	6.3302	0.5032	12.520	1.473	35.6
9	9	1.2628	992.4	6.3189	0.5027	12.532	1.419	31.9
10	10	1.2633	992.5	6.3133	0.5025	12.538	1.408	28.7

The molar compressibility (W) of neodymium soaps increases with increasing soap concentration and chain length of soap molecules. However, molar compressibility decreases with rise in temperature. The apparent molar compressibility ϕ_k of these soaps is related to concentration by Gucker's limiting law[13].

$$\Phi_k = \phi^o_k + S_kC^{1/2}$$

Where; ϕ^0k is limiting apparent molar compressibility and Sk is constant. The values of the constant Sk and limiting apparent molar compressibility ϕ^o_k have been obtained from the slope and intercept of the plots ϕk vs $C^{1/2}$. The positive value of Sk indicates a considerable soap -solvent interactions below the CMC. The decrease in intermolecular free length L_f[14] and the increase in specific acoustic impedance Z[15] with increasing soap concentration, is an indicative of the increase in intermolecular forces with the addition of soap forming aggregates of solvent molecules around soap ions, supports the strong soap-solvent interactions due to which structural arrangements is affected[16].

The values of solvation number Sn[17] decreases with increase in concentration of neodymium soap (Table 2). The value of Sn corresponds to the number of solvent molecules in the primary solvation sheaths of ions. On account of electrostriction, molecules in the primary solvation sheath are same as that of pure solvent. The values of solvation number exhibit a change in post micellization region which may be attributed to greater intake of solvent molecules in post micellization region to reduce the repulsive forces acting between polar heads of ionic micelles. The values of available volume Va[18] increases with the rise in temperature and decreases with increasing soap concentration. The values of relaxation strength r[19] decrease with increase in neodymium soap concentration however these values increase with the rise in temperature. The results of neodymium soaps are in agreement with the work reported earlier[20-32] by other workers for different lanthanide soaps in organic solvents.

CONCLUSION: The ultrasonic velocity throws light on evaluation of various acoustical parameters of neodymium caprylate and laurate in benzene-dimethylsulphoxide mixture. The results confirm that there is a significant interaction between neodymium soaps and soap molecules in dilute solutions, and soap molecules do not aggregate appreciably below the CMC and neodymium caprylate and laurate behave as weak electrolyte in 60/40 benzene-DMSO mixture (V/V). The values of CMC increase with the increasing temperature and are in agreement with those obtained from other physical properties.

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