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Ultrasonic Study, Rao Formalism, Compressibility Behaviour and Solvation Number of Magnesium Soaps in Non-Aqueous Medium

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ABSTRACT: Ultrasonic velocity and density of non-aqueous solutions of magnesium myristate and palmitate in 60/40 chloroform-propane 1:2 diol mixture have been measured at four different temperatures. The results are discussed in terms of different theories of ultrasonic wave propagation and Jacobson's model has been used to calculate adiabatic and molar compressibilities, intermolecular free length, solvation number, relative association, relaxation strength, molar sound velocity and other acoustic parameters in non aqueous mixture.

Keywords: Ultrasonic velocity; critical micellar concentration; soap-solvent interaction.

INTRODUCTION

The alkaline-earth metal soaps have been used as corrosion-inhibiting agents[1 & 2], lubricants[3-5], dispersants[6], catalysts[7 & 8] and stabilizers[9]. Ultrasonic technique has been used for studying the ion-solvent interactions in organic liquids[10-12], low melting solids[13], dilute solutions of inorganic acids[14 & 15] and complex formation. Shrivastava et. al[16] reported thermodynamic parameters of organo-metallic compounds in solvents having low dielectric constant. The applications of metallic soaps depend largely on their physical state, stability and their chemical reactivity, together with their volatility and solubility in common organic solvent and their mixtures. The ultrasonic wave is an efficient, powerful and reliable method for various investigations including those of solutions dynamics, molecular interaction, miscibility and compatibility of protein in aqueous solutions[17].

MATERIAL AND METHODS

AnalaR grade myristic acid, palmitic acid, acetone, chloroform and propane 1:2 diol were used. Magnesium soaps were prepared by the interaction of the magnesium sulphate solution in distilled water, with a hot solution of potassium soap, the latter being added drop wise, while stirring at 50-60^0 C. The precipitate was filtered off and washed with hot distilled water and acetone. After an initial drying in air oven (120^{0}C) final drying was carried out under reduced pressure. The purity of the soaps was checked by elemental analysis and results were found in agreement with the theoretically calculated values. The absence of hydroxyl group was confirmed by IR Spectra. The purified soaps have the following melting points:
Magnesium myristate: 175^{0}C
Magnesium palmitate: 192^{0}C
Ultrasonic results were obtained on a multifrequency ultrasonic interferometer (MX–3 Mittal Enterprises, New Delhi) at different temperatures using a crystal of frequency 1 MHz water, maintained at the desired temperature and controlled up to $\pm$0.01^{0}C by a thermostat, was passed through the jacket of the cell before the measurement was actually made. Density of these solutions have been measured in a

thermostat, having thermal stability of $\pm$ 0.01^0 C, using a 10 ml bicapillary pyknometer, with an accuracy of 0.000 5g/ml.

RESULTS AND DISCUSSION

The ultrasonic velocity, v and density, ρ of magnesium myristate and palmitate in a composition of 60% chloroform and 40% propane 1:2 diol (V/V) have been measured at 35^0; 40^0; 45^0 and 50^0C. These results indicated that the ultrasonic velocity and density increase with increasing soap concentration.

The adiabatic compressibility, β_{ad}, molar compressibility, β, have been calculated by the following relationship:

$$\beta_{ad} = \rho^{-1} v^{-2} \qquad \text{-----------(1)}$$

$$\beta = \bar{M} / \rho \, (\beta_{ad})^{-1/7} \qquad \text{-----------(2)}$$

$$\bar{M} = (n_0 M + n M_0) / n_0 + n$$

Where n_0, n, M_0 and M are the number of moles and molecular weight of solvent and soap respectively. Both ultrasonic velocity, v and adiabatic compressibility, β_{ad} when plotted as a function of soap concentration, show an intersection of two straight lines at a definite soap concentration which corresponds to the *CMC* of these metal soaps. The adiabatic compressibility of magnesium myristate and palmitate in 60/40 chloroform propane 1:2 diol mixture decreases with increasing soap concentration (Table 1). The decrease in adiabatic compressibility is attributed to the fact that magnesium soap in dilute solution are considerably ionized into magnesium cations and myristic and palmitic acid anions. These ions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The orientations of solvent molecules around the ions is attributed to the influence of electrostatic field of the ions, increasing the internal pressure, which lowers the compressibility of the soap solutions[18]. The decrease in adiabatic compressibility in post micellization region may be explained on the basis of closed packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and finally internal pressure. The increase in temperature and decrease in chain length of the soap results in the increase of *CMC*. However the *CMC* values were found to be almost independent of the solvent composition.

The values of molar compressibility, β increase with increasing soap concentration and temperature (Table 1). The plots of β Vs *C* show a point of inflection at *CMC*.

From the Debye – Huckel theory it follows that the apparent molar compressibility, ϕ_k was related to the molar concentration of soap, *C* by the relationship.

$$\phi_k = \phi_k^{\circ} + S_k C^{1/2}, \qquad \text{--------------(3)}$$

The value of standard partial molar compressibility, ϕ_k° and constant S_k have been evaluated from the intercept and slope of the plots of ϕ_k versus $C^{1/2}$ (Table 2). These results show that the values of standard partial molar compressibility, ϕ_k° are higher in 60% chloroform and 40% propane 1:2 diol mixture. The negative values of ϕ_k is probably due to the decreasing internal pressure. The values of S_k are higher in 60% chloroform and 40% propane 1:2 diol mixture indicating that there is significant interaction between soap and solvent molecules.

Table 1: Ultrasonic Velocity, Adiabatic Compressibility, Intermoleculer freelength, Solvation Number and Other allied Parameters of Magnesium myristate in a mixture of 60% Chloroform and 40% Propane 1:2 diol (V/V) at 35 ± 0.050^0 C

S. No.	Concentration (g mol 1^{-1}) C. 10^{-3}	Velocity (cm/sec) v. 10^{-2}	Adiabatic compressibility (cm/dyne) β_{ad} .10^{11}	Specific acoustic impedence Z x 10^{-4}	Inter-molecular free length L_f (A°)	Solvation No. S_n	Relative Association R_A	Relaxation Strength r	Available Volume V_a x 10^7	Apparent molar Compressibilty ϕ_k x 10^7	Apparent molar volume ϕ_v x 10^{-3}	Molar Compressibility β x 10^{-3}
1	4.0	1510.9	4.118	16.215	0.4115	7.157	0.9914	0.5127	0.7990	-4.6208	-1.454	2.4792
2	6.0	1524.1	4.113	16.390	0.4107	7.121	0.9903	0.5110	0.7820	-4.5680	-1.420	2.4898
3	8.0	1536.8	4.107	16.610	0.4095	6.784	0.9881	0.5089	0.7654	-4.4470	-1.375	2.4960
4	10.0	1542.0	4.092	16.716	0,4083	6.790	0.9870	0.5067	0.7540	-4.4392	-1.379	2.5002
5	12.0	1549.0	4.081	16.829	0,4077	6.794	0.9857	0.4997	0.7434	-4.3752	-1.310	2.5060
6	14.0	1566.5	4.075	17.069	0.4061	6.370	0.9840	0.4954	0.7380	-4.0950	-1.271	2.5197
7	16.0	1573.0	4.067	17.189	0.4053	5.871	0.9825	0.4912	0.7298	-3.7532	-1.160	2.5247
8	18.0	1582.1	4.050	17.326	0.4037	5.520	0.9819	0.4871	0.7210	-3.5160	-1.080	2.5343
9	20.0	1588.0	4.045	17.466	0.4027	5.245	0.98.8	0.4841	0.7137	-3.3370	-1.016	2.5453

The intermolecular free length[19] L_f and specific acoustic impedance [20], Z have been evaluated using the following relationship;

$$L_f = K\sqrt{\beta_{ad}} \quad \text{-------------(4)}$$

$$Z = \rho\ v \quad \text{-------------(5)}$$

Where K is the Jacobson's constant. The decrease in the value of L_f ($\pm$ 0.2%) and increase in the value of Z ($\pm$ 2.2%) with increasing soap concentration can be explained on the basis of hydrophobic interaction between soap and solvent molecules which considerably affects the structural arrangement. The value L_f increases with decrease in the chain length of the soap. The plots of L_f versus *C* show a break at *CMC* and the extrapolation of these plots gives the values of pure solvents, indicating that the molecules of magnesium soaps do not show aggregation below the *CMC*.

Table 2: Values of critical micellar concentration (CMC) apparent molar compressibility of Magnesium soaps at infinite dilution and their experimental slope with $\sqrt{c}$ in 60% chloroform and 40% propane 1: 2 diol (V/V) at different temperatures.

Temperature (°C)	CMC x 10^3 (g mole l^{-1})	- $Ø°_k$ x 10^7	- S_k x 10^7 slope of $Ø_k$ versus $\sqrt{c}$
Magnesium myristate			
35	12.0	5.80	37.50
40	13.0	5.19	32.40
45	14.4	4.70	30.00
50	13.0	4.22	29.30
Magnesium palmitate			
35	10.1	6.60	55.65
40	10.6	6.37	40.00
45	11.2	6.10	37.88
50	11.9	5.90	33.30

The solvation number[21], S_n and relative association[22], R_A of magnesium soaps were determined by the relationships:

$$S_n = \frac{n_0}{n}\left(1 - \frac{\beta_{ad}}{\beta_{ad^0}}\right) \quad \text{------------(6)}$$

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{v_0}{v}\right) \quad \text{-------------(7)}$$

Where, n_o, n, ρ_o, ρ, $\beta_{ad}{}^0$, β_{ad}, v_o and v are the number of moles, density, adiabatic compressibility and ultrasonic velocity of the solvent and soap solution respectively. The values of solvation number S_n and relative association, R_A decrease with increasing soap concentration. The positive value of S_n suggests appreciable solvation of ions. The value of S_n corresponds to the number of solvent molecules in the primary solvation sheath of the ions. On account of electrostriction molecules in the solvation sheath will be highly compressed, So that these molecules will be less compressible then those in the bulk of the solution when an external pressure is applied. The compressibility of solvent molecules in the primary solvation sheaths is the same as that of the pure solvent. The decrease in the values of R_A has been attributed either to decreased association between soap and organic solvent molecules at higher concentration, or decreasing solvation of ions.

The relaxation strength, r and molar sound velocity [23] R_n of magnesium soaps were determined by the relationships.

$$r = 1 - (v / v_\alpha)^2 \quad \text{--------------(8)}$$

$$R_n = \bar{M}/p(v)^{\frac{1}{3}} \quad \text{--------------(9)}$$

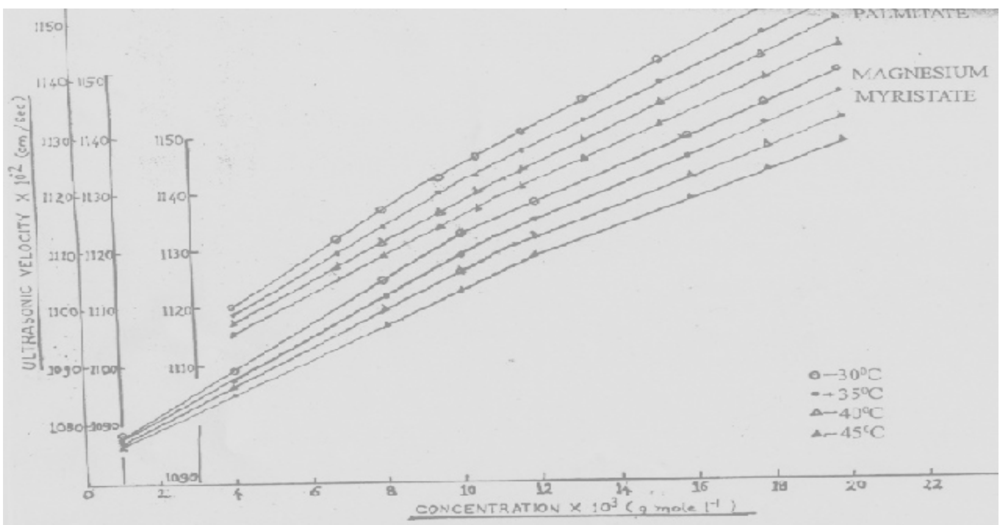

Figure 1: Ultrasonic velocity Vs concentration of magnesium myristate and magnesium palmitate in 60% chloroform and 40% propylene glycol (v/v) at different temperatures

Where, v_α is equivalent to 1600 ms^{-1}. The values of relaxation strength, r decrease while the molar sound velocity [24], R_n increases with increasing soap concentration (Tables1&2). The values of r and R_n increase with rise in temperature.

The values of apparent molar volume increase while the values of available volume[24], V_a decrease with increasing soap concentration. The plots of apparent molar volume versus $C^{1/2}$ and available volume against C, are characterized by the break at the *CMC*.

Data on ultrasonic velocity show that the values of *CMC* of magnesium myristate and palmitate increase with increasing temperature in non-aqueous solutions (chloroform- propane 1:2 diol mixture). These results also confirm that there is a significant interaction[25, 26 & 28] between magnesium soaps and solvent molecules and the values of the various acoustic parameters are in agreement with the results of other worker[27].

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