Ultrasonic studies and acoustic behavior of cerium and thorium laurate in benzene–methanol mixture

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ABSTRACT - Ultrasonic velocity of cerium and thorium laurate in benzene-methanol mixture was used to determine the CMC, soap solvent interaction and various acoustic parameters. The results show that ultrasonic velocity, specific acoustic impedance, molar sound velocity increases with increasing soap concentration and decreases with the increase in temperature while intermolecular free length, adiabatic compressibility, apparent molar volume, apparent molar compressibility and solvation number decreases with increase in soap concentration. The internal pressure of the solutions decreases with increase in soap concentration at all temperatures. The results of ultrasonic measurements have been interpreted in the light of well known equations.

Key words - Ultrasonic velocity, CMC, Compressibility behavior, Internal pressure, Acoustic parameters, Soap-solvent interactions

Most striking feature of metal soaps is their increasing importance in different industries as well as in academic fields. The applications of metal soaps is required in various fields[1-4] such as lubricating greases which is intended to improve flow, coating smoothness, finish, printability, antidusting effects, driers in paints, dry cleaning industries, cosmetic gels, heat stabilizers for plastics and in the development of polyvinylchloride as an important commercial polymer and other uses as fungicides and pesticides[5], optical polymer fibers[6], coating pigment in paper industry[7] and in the preparation of nanofilms[8] are due to their appreciable solubility inorganic solvent, stability and chemical reactivity, together with their volatility and availability .The study and understanding of acoustical properties are necessary for their applications in various fields. Ultrasonic methods have been used for providing interesting information on the specificities of ion-solvent interactions related to the structure of solute and solvation of soaps in organic liquids[9], complex formation[10] and in non-aqueous solvents[11,12].

Acoustical studies on Uranyl soaps of lower fatty acids have been studied by Varsha *et al.*[13]. Suleman *et al.*[14, 15] studied ultrasonic behavior of transition metal soap in liquor ammonia. Acoustical studies, compressibility behavior and Rao formalism of lanthanide soap solutions were carried out by Upadhyaya and Chaturvedi[16].

In comparison of earlier studies on metal soaps, we report here results of our studies on ultrasonic velocity of cerium and thorium laurate in 70/30 benzene-methanol (V/V) of varying concentration and temperature in order to compute various acoustical parameters. These parameters give clear insight into the formation of micellar aggregates of cerium and thorium laurate in non-aqueous medium and effect of concentration and size of metal ion on soaps.

EXPERIMENTAL METHODOLOGY

AnalaR grade lauric acid, benzene, methanol, ethanol, cerium nitrate and thorium chloride (purity99.9% received from Indian Rare Earth Limited, Kerala) were used for the present

investigation. The cerium and thorium laurate were prepared by the direct metathesis of corresponding potassium soaps by pouring a slight stochiometric excess of aqueous metal salt solution into the clear dispersion at raised temperature with vigorous stirring. After initial drying in an air oven 50-60^{0}C, final drying was carried out under reduced pressure. The precipitates was filtered off and washed with hot distilled water and acetone. The purity of soaps was checked by determination of their melting points, IR spectra and elemental analysis.

Solutions of cerium and thorium laurate were prepared by dissolving a known amount of soap in mixture of 70/30 benzene-methanol and kept for 2 hrs in a thermostat at desired temperature. The ultrasonic velocity of solutions of cerium and thorium laurate was recorded on a multifrequency ultrasonic interferometer "Model MX-3" (Mittal Enterprises, New Delhi) at different temperatures using a crystal of 1 MH$_z$ frequency. Water maintained at a desired temperature and controlled to $\pm$ 0.5^{0}C by a thermostat passed through the jacket of cell before the measurements was actually made. The uncertainty of velocity measurements was $\pm$ 0.2 per cent. The densities of the solutions were determined at different temperatures with pyknometer calibrated with pure benzene.

Computational method:

The various acoustical parameters namely adiabatic compressibility[17] (β), intermolecular free length[18](L_f), specific acoustic impedance[19] (Z), apparent molar compressibility(ϕ_k), internal pressure[20](π_i), primary solvation number[21] (S_n), molar sound velocity(R), relative association[22](R_a), available volume[23](V_a) and relaxation strength[24] (r) have been evaluated by the following relationships:

$$\beta = r^{-1}v^{-2} \qquad (1)$$
$$L_f = K (\beta)^{1/2} \qquad (2)$$
$$Z = \rho v \qquad (3)$$
$$\phi_K = 1000/ C\rho_o (r_o\beta - \beta_o r) + \beta_o XM_l/\rho_o \qquad (4)$$
$$\pi_i = bRT (k\varsigma/V)^{1/2} X (\rho^{2/3}/M_{eff}^{7/6}) \qquad (5)$$
$$S_n = n_o/n_l (1 - V\beta/n_o V_o \beta_o) \qquad (6)$$
$$R = M_{eff}/\rho . v^{1/3} \qquad (7)$$
$$R_a = (\rho/\rho_o) (\rho_o/\rho)^{1/3} \qquad (8)$$
$$V_a = V (1 - v/v_á) \qquad (9)$$
$$r = 1/ (v/v_á)^2 \qquad (10)$$

where ρ ρ_0, β β_0, v v$_o$ are the density, adiabatic compressibility and ultrasonic velocity of solutions and solvent, respectively. C is concentration (g mol l^{-1})of solute. The effective molecular weight of the solutions has been calculated by the relationship: $M_{eff} = (n_oM_o + nM_l) / n_o + n$ where n$_o$, M$_o$, n and M$_l$ are the number of moles and molecular weight of solvent and solute, respectively. K is Jacobson's constant,

b stands for the cubic packing factor which is assumed to be 2 for all liquids and solutions, k is temperature independent constant (4.28 x10^9), R is gas constant (8.314 kJ.mol^{-1}), T is absolute temperature, V is the molar volume of solution containing n moles of solute, V$_0$ is the molar volume of solvent and v$_á$ is equivalent to 1600 m sec^{-1}.

EXPERIMENTAL FINDINGS AND ANALYSIS

The ultrasonic velocity and various acoustical parameters with change in concentration, at different temperatures (25^0 to 40^{0}C) for cerium and thorium laurate in the mixtures of 70/30 benzene-methanol (V/V) have been evaluated (Table 1).

The ultrasonic velocity, v is related to the density, ñ adiabatic compressibility, β by the relationship:

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

On differentiating this equation with respect to concentration, C one obtains:

$$(dv)/ (dc) = -v/2 [1/\rho \times dr/dc + 1/\beta \times d\beta/dc]$$

The results indicate that the density increases while the adiabatic compressibility decreases with increasing soap concentration. Therefore, the quantity dñ/dc (concentration derivative of density) is positive while the quantity dβ/dc (concentration derivative of compressibility), is negative. Since the values of 1/β. dβ/dc are larger than the values of 1/ρ. dρ/dc for these soap solution, the concentration derivative of velocity, (dv/dc) will be positive and so the velocity increases with increasing soap concentration. The ultrasonic velocity, v varies linearly with soap concentration, C and follows the relationship:

$$v = v_0 + GC$$

where v and v$_0$ are the ultrasonic velocity of the solution and solvent mixture, respectively and G is the Gransey's constant[25]. The values of Gransey's constant can be determined from the slope of the plots of v Vs C, and the magnitude of the G represents the variation of velocity with soap concentration. The plots of ultrasonic velocity, v Vs
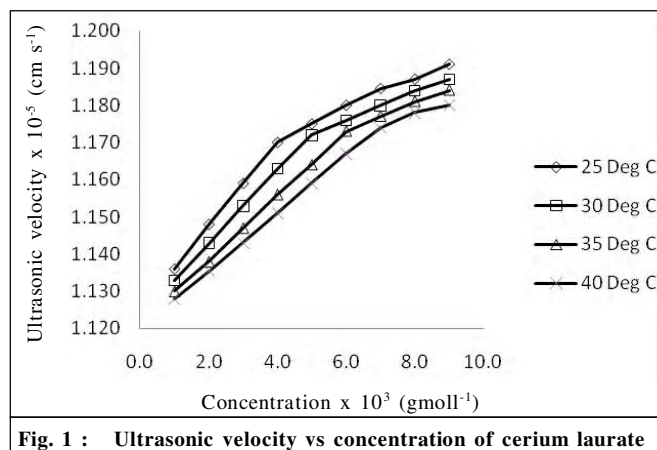

Fig. 1 : Ultrasonic velocity vs concentration of cerium laurate

Table 1 : Ultrasonic velocity and other acoustic parameters of cerium and thorium laurate in a mixture of 70% benzene and 30% methanol (V/V) at $30^0C \pm 0.05^0C$

Sr. No.	Concentration $C \times 10^3$ (g.mol l^{-1})	Ultrasonic velocity $v \times 10^{-5}$ (cm/sec.)	Density ρ (g.ml $^{-1}$)	Adiabatic compressibility $\beta \times 10^{11}$ (cm^2 dyne^{-1})	Intermolecular free-length L_f (Å)	Specific acoustic impedance $Z \times 10^{-5}$	Internal pressure $\pi_i \times 10^5$	Apparent molar compressibility - $(\phi_K) \times 10^6$ (cm^2 dyne^{-1})	Solvation number S_n	Relaxation strength r
Cerium laurate										
1.	1.0	1.133	0.8674	8.981	0.6084	0.9828	1.79	1.4000	546.48	0.4986
2.	2.0	1.143	0.8695	8.803	0.6023	0.9938	1.76	1.7500	284.15	0.4897
3.	3.0	1.153	0.8716	8.630	0.5964	1.0050	1.73	1.8190	196.49	0.4807
4.	4.0	1.163	0.8736	8.463	0.5906	1.0160	1.71	1.8344	152.45	0.4717
5.	5.0	1.172	0.8751	8.319	0.5855	1.0256	1.69	1.7871	125.40	0.4634
6.	6.0	1.176	0.8762	8.252	0.5832	1.0304	1.67	1.6202	105.90	0.4598
7.	7.0	1.180	0.8775	8.184	0.5808	1.0355	1.65	1.5054	92.01	0.4561
8.	8.0	1.184	0.8787	8.118	0.5784	1.0404	1.63	1.4155	81.55	0.4524
9.	9.0	1.187	0.8799	8.066	0.5765	1.0444	1.62	1.3301	73.25	0.4496
Thorium laurate										
1.	1.0	1.136	0.8676	8.931	0.6067	0.9856	1.78	1.6000	552.77	0.4959
2.	2.0	1.146	0.8696	8.756	0.6007	0.9966	1.75	1.9932	287.34	0.4870
3.	3.0	1.155	0.8718	8.598	0.5953	1.0069	1.72	2.1000	198.64	0.4789
4.	4.0	1.162	0.8738	8.476	0.5918	1.0140	1.70	1.7521	154.02	0.4739
5.	5.0	1.170	0.8756	8.343	0.5864	1.0245	1.68	1.7496	126.74	0.4653
6.	6.0	1.176	0.8770	8.245	0.5818	1.0333	1.66	1.6992	107.11	0.4577
7.	7.0	1.180	0.8782	8.178	0.5773	1.0420	1.64	1.6517	93.01	0.4501
8.	8.0	1.185	0.8796	8.096	0.5729	1.0509	1.62	1.6186	82.35	0.4424
9.	9.0	1.190	0.8809	8.016	0.5685	1.0597	1.60	1.5884	74.08	0.4347

soap concentration, C (Fig. 1), show a characteristic transition which is generally related to the formation of aggregates arising from the intrinsic amphiphlic nature of soap molecules and has been used to determine the critical micellar concentration, CMC, above which the multimolecular aggregates are formed *i.e.* micelles of cerium and thorium laurate. The main cause of micellization in organic solvent is the energy change due to 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 very 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 visualized as Hartley's Inverted micelles in which polar head groups are present in the center of the micelles with the hydrocarbon chains extending outwards into the solvent. The determination of CMC in organic solvent cannot be carried out by the methods commonly used for aqueous solutions as the association starts at very low concentrations. Therefore the ultrasonic velocity and density measurements have been used to determine the CMC value and various other acoustical parameters.

On comparison CMC value and Gransey's constant for thorium laurate is higher than cerium laurate (Table 2).

The plots of ultrasonic velocity, v vs soap concentration, C (Fig.1) have been extrapolated to zero soap concentration and the extrapolated values of ultrasonic velocity v_o are in fair agreement with the experimental velocity of the solvent mixture, indicating that the molecules of cerium and thorium laurate do not aggregate to an appreciable extent below the CMC.

The nature of adiabatic compressibility variation is found to be the reverse to that of ultrasonic velocity. The adiabatic compressibility of cerium and thorium laurate in 70/30 benzene-

Table 2 : Values of various constants at $30^0C \pm 0.05^0C$

Soaps	CMC $X 10^{-3}$ (g mol l^{-1})	Gransey's constant $GX10^{-5}$	Bachem's relationship		Limiting apparent molar compressibility	
			$A \times 10^{-9}$	$B \times 10^{-8}$	$-\phi_k \times 10^{-6}$	$S_K \times 10^{-4}$
Cerium laurate	4.25	9.50	-0.194	0.90	0.62	0.27
Thorium laurate	4.85	10.00	-0.127	1.05	0.98	0.30

methanol mixture (V/V) decreases with increases in concentration of the soap solutions and increases with increase in temperature. The decrease in adiabatic compressibility is attributed to the fact that the soap molecules in dilute solutions ionize in dilute solutions. These ions in solution are surrounded by a layer of solvent molecules, firmly bound, and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of ions which affects the internal pressure and lowers the compressibility of the solution *i.e.* the solutions become harder to compress. The plots of β Vs C (Fig. 2) are extrapolated to zero soap concentration and the extrapolated values of adiabatic compressibility, β_0 are in fair agreement with the experimental values of adiabatic compressibility for the solvent
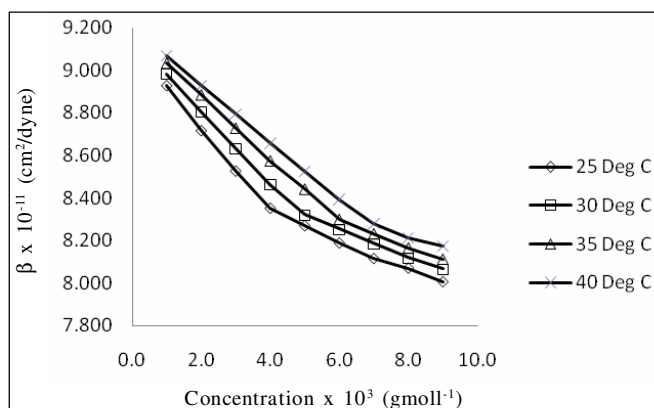

Fig. 2 : Adiabatic compressibility Vs concentration of cerium laurate

The adiabatic compressibility, β of the solutions of cerium and thorium laurate can be expressed in terms of that of solvent β_0 and molar concentration, C by Bachem's[26] empirical relationship

$$\beta = \beta_0 + AC + BC^{3/2}$$

Where A and B are constants, C is molar concentration of soap solutions and β and β_0 are the adiabatic compressibility of the solution and solvent, respectively. The constants A and B have been determined from the intercept and slope of the plots of $(\beta - \beta_0)/C$ Vs. $\sqrt{C}$ and the magnitude of A and B depend upon the nature of solute and solvent. A perusal of data collected in Table 2 shows that the values of constants A and B are higher for thorium laurate as compared to cerium myristate.

By following Gucker's limiting law[27] apparent molar compressibility, f_k is related to concentration, C by relationship.

$$\phi_k = \phi_k^0 + S_k \ C^{1/2}$$

where f_k is the limiting apparent molar compressibility and S_k is constant. The values of constant, S_k and limiting apparent molar compressibility ($_lk^{+0}$) have been obtained from the slope and intercept of plots ϕ_k vs. $C^{1/2}$(Table 2). The negative values of ϕ_k decreases sharply upto the CMC and again it increases with square root of soap concentration. The decrease in the negative value of apparent molar compressibility ϕ_k may be attributed to the fact that the solvent becomes less compressible in dilute solutions[28]. The increase in values of $_k$ in the post micellization region indicates the incompressible nature of the concentrated solutions. The comparison of the result shows that the values of $-\phi_k$ and S_k decreases with temperature and these values are higher for thorium laurate than for cerium laurate.

The internal pressure of the solution decreases with increase in concentration. The decrease in internal pressure of the solutions indicates that addition of solute decreases the cohesive forces of the solvent at all temperatures. The decrease in value of intermolecular free length, L_f and increase in value of specific acoustic impedence, Z with increase in soap concentration is an indicative of the increase in intermolecular forces with the addition of soap forming aggregates of solvent molecules around solute ions, supports the strong solute-solvent interactions due to which structural arrangements is affected[29].

The plots of intermolecular free length, L_f Vs concentration, C and specific acoustic impedance, Z, Vs concentration, C show a break at the CMC, indicating that the molecules of cerium and thorium laurate do not aggregate to an appreciable extent below the CMC. The values of intermolecular free length increase whereas the value of specific acoustic impedance decreases with the increase of temperature. The values of relaxation strength r, available volume, V_a solvation number, S_n decrease with increase in concentration for cerium and thorium laurate, however the values of relaxation strength and available volume increases whereas the values of solvation number decreases with the increase of temperature. The value of solvation number corresponds to the number of solvent molecules in the primary solvation sheath of the ions. On primary account of electrostriction, molecules in the primary solvation sheath will be highly compressed so that these molecules will be less compressible than those in the bulk of solution when an external pressure is applied. The compressibility of solvent molecules is near but not in the primary solvation sheath is the 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. On comparison the values of relaxation strength and available volume are higher and a value of solvation number is lower for cerium laurate

than for thorium laurate.

The decrease in values of relative association, R_A with concentration has been attributed either to the decreased association between soap and mixed organic solvent molecules at higher concentration or increasing solvation of ions. The values of relative association increase with increase of temperature. The value of relative association is higher for thorium laurate than for cerium laurate.

It is concluded that there is a significant interaction between the solute-solvent molecules in dilute solution and value of CMC is higher for thorium laurate than for cerium laurate.

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