Acoustical behavior of Cerium and Thorium Palmitate in non-aqueous binary mixture

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ABSTRACT: Ultrasonic studies of cerium and thorium palmitate in benzene methanol mixture were used to determine the CMC , soap solvent interaction and various acoustic parameters, inter-molecular free-length, adiabatic compressibility, apparent molar compressibility, specific acoustic impedance, molar sound velocity, solvation number, available volume and relative association at different temperatures. The results showed that these soaps behave as weak electrolytes in dilute solutions and the values of the CMC increase with the increasing temperature.

Keywords: Critical micellar concentration; Ultrasonic velocity; Acoustic parameters; Soap-solvent interactions.
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INTRODUCTION

Revival of interest in the study of metal soaps is based on there increasing importance in different industries as well as in academic field. The applications of metal soaps in various fields [1-3] such as softeners, plasticizers, lubricants, chemical thickener in greases, cosmetic gels, catalysts in chemical industries, medicines, emulsifiers, waterproofing agents, dries in paints and coating and processing aid in rubber industry are due to their appreciable solubility in organic solvents, stability and chemical reactivity, together with volatility and availability. Metal soaps are also very interesting for their uses as polymer stabilizers or optical polymer fibers [4], fungicides and pesticides [5] and in the preparation of nanofilms [6]. 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 [7], low melting solids [8], complex formation [9] and non-aqueous solvents [10-12]. Acoustical studies on Uranyl soaps of lower fatty acids have been studied by Varshaet al [13]. Kishore et al. [14] determined the acoustic measurements and compressibility behavior of terbium myristate in benzene-methanol mixture. Acoustical studies, compressibility behavior and Rao formalism of lanthanide soap solutions were carried out by Upadhyaya and Chaturvedi [15].

In continuation with earlier work on metal soaps, we report here results on the ultrasonic measurements of cerium and thorium palmitate in 70/30 benzene-methanol (V/V) of varying concentration and temperature have been measured in order to compute various acoustical parameters. These parameters give clear insight into the formation of micellar aggregates of cerium and thorium palmitate in non-aqueous medium and effect of concentration and size of metal ion on soaps.

MATERIAL AND METHODS

AnalaR grade palmitic acid, benzene, methanol, ethanol, cerium nitrate and thorium chloride (purity 99.9% received from Indian Rare Earth Limited, Kerala) were used for the present investigation. The cerium and thorium palmitate were prepared by the direct metathesis of corresponding potassium soaps by pouring a slight stoichiometric 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 established by determination of their melting points, IR spectra and elemental analysis.

Solutions of cerium and thorium palmitate 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 palmitate 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%. 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[16] (β), intermolecular free length [17] (L$_f$),specific acoustic impedance [18] (Z), apparent molar compressibility(ϕ_k), internal pressure [19] (π_i), primary solvation number [20] (S$_n$), molar sound velocity(R), relative association [21] (R$_a$), available volume [22] (V$_a$) and relaxation strength [23] (r) have been evaluated by the following relationships:

$$\beta = \rho^{-1}v^{-2} \tag{1}$$

$$L_f = K\,(\beta)^{1/2} \tag{2}$$

$$Z = \rho v \tag{3}$$

$$\phi_K = 1000/\,C\rho_o\,(\rho_o\beta-\beta_o\rho) + \beta_o XM_1/\rho_o \tag{4}$$

$$\pi_\square = bRT\,(k\eta/V)^{1/2}\,X\,(\rho^{2/3}/M_{eff}^{7/6}) \tag{5}$$

$$S_n = n_o/n_1\,(1-V\beta/n_o\,V_o\beta_o) \tag{6}$$

$$R = M_{eff}/\rho\,X\,v^{1/3} \tag{7}$$

$$R_a = (\rho/\rho_o)\,(v_o/v)^{1/3} \tag{8}$$

$$V_a = V\,(1-v/v_\alpha) \tag{9}$$

$$r = 1/\,(v/v_\alpha)^2 \tag{10}$$

Where ρ ρ_0, β β_0, v v$_o$are the density, adiabatic compressibility and ultrasonic velocity of solutions and solvent, respectively. The effective molecular weight of the solutions has been calculated by the relationship: M$_{eff}$ = (n$_o$M$_o$ +nM$_1$) / n$_o$+n where n$_o$, M$_o$, n and M$_1$ are the number of moles and molecular weight of solvent and solute, respectively. Where K is Jacobson's constant. C is concentration of (gmol.l$^-$^{1}) of solute, respectively. 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$_\alpha$ is equivalent to 1600 m sec^{-1}.

RESULTS AND DISCUSSION

The ultrasonic velocity and various acoustical parameters for cerium and thorium palmitate in the mixtures of 70% benzene + 30% methanol (V/V) have been evaluated (Table-1)with varying concentration and temperatures.

The variation of ultrasonic velocity v, with soap concentration C, can be expressed in terms of concentration derivatives of density ρ and adiabatic compressibility β, by the following relationship:

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

The results indicate that the density increases while the adiabatic compressibility decreases with increasing soap concentration. Therefore, the quantity dρ/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[24]. 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. soap concentration, C (Fig-1), are characterized by intersection of two straight lines, where the physical properties of soaps exhibit discontinuity, corresponding to criticalmicellar concentration, CMC, of cerium and thorium palmitate. 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 much smaller aggregates than in water.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 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 parametersStill, the values of CMC determined at different temperatures are in fair agreement with the values of CMC determined from conductivity measurements.[25]CMC value and Gransey's constant for thorium palmitateis higher than cerium palmitate (Table-2).
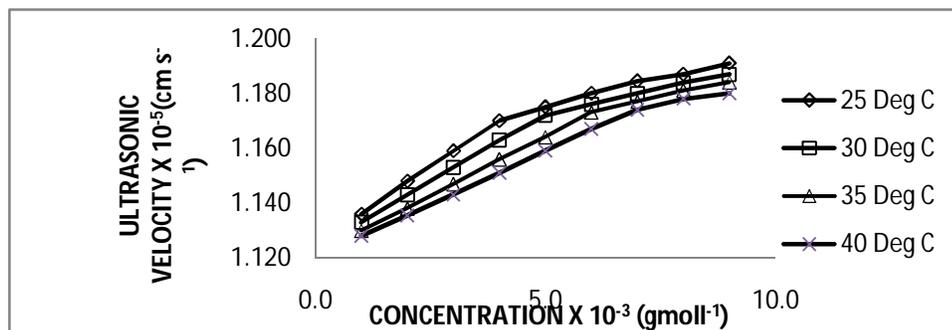

Fig. 1: Ultrasonic velocity Vs. Concentration of Cerium palmitate

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_0 are in fair agreement with the experimental velocity of the solvent mixture, indicating that the molecules of cerium and thorium palmitatedo not aggregate to an appreciable extent below the CMC.

Table1: Ultrasonic velocity and other acoustic parameters of Cerium and Thorium Palmitate in a mixture of 70% Benzene and 30% Methanol (V/V) at $30^0C \pm 0.05$ º C

S.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 Palmitate										
1	1.0	1.135	0.8695	8.928	0.6065	0.9869	1.78	2.0381	552.29	0.4968
2	2.0	1.151	0.8720	8.656	0.5973	1.0037	1.74	2.5103	292.40	0.4825
3	3.0	1.165	0.8741	8.429	0.5894	1.0183	1.71	2.5037	203.93	0.4698
4	4.0	1.172	0.8755	8.316	0.5854	1.0261	1.69	2.1971	156.39	0.4634
5	5.0	1.179	0.8770	8.203	0.5814	1.0340	1.66	2.0151	127.87	0.4570
6	6.0	1.187	0.8780	8.084	0.5772	1.0422	1.63	1.8951	108.88	0.4496
7	7.0	1.194	0.8800	7.971	0.5731	1.0507	1.62	1.8158	95.36	0.4431
8	8.0	1.202	0.8814	7.853	0.5689	1.0594	1.59	1.7547	85.20	0.4356
9	9.0	1.209	0.8836	7.743	0.5649	1.0683	1.57	1.7053	77.29	0.4290
Thorium Palmitate										
1	1.0	1.142	0.8706	8.807	0.6024	0.9942	1.74	2.97	558.81	0.4906
2	2.0	1.159	0.8738	8.520	0.5925	1.0127	1.71	3.79	294.11	0.4753
3	3.0	1.175	0.8770	8.259	0.5834	1.0305	1.68	3.51	205.38	0.4607
4	4.0	1.182	0.8783	8.149	0.5795	1.0382	1.65	2.94	160.76	0.4542
5	5.0	1.190	0.8795	8.029	0.5752	1.0466	1.62	2.62	131.54	0.4468
6	6.0	1.197	0.8806	7.926	0.5715	1.0541	1.60	2.37	111.95	0.4403
7	7.0	1.204	0.8820	7.821	0.5677	1.0619	1.58	2.21	97.92	0.4337
8	8.0	1.212	0.8796	7.708	0.5636	1.0704	1.55	2.09	87.18	0.4262
9	9.0	1.229	0.8809	7.487	0.5554	1.0800	1.52	2.11	78.80	0.4100

The nature of adiabatic compressibility variation is found to be the reverse to that of ultrasonic velocity. The adiabatic compressibility of cerium and thorium palmitate in 70/30 benzene-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 comparison of the results showed that the adiabatic compressibility of thorium palmitate is lower than the cerium palmitate. 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.
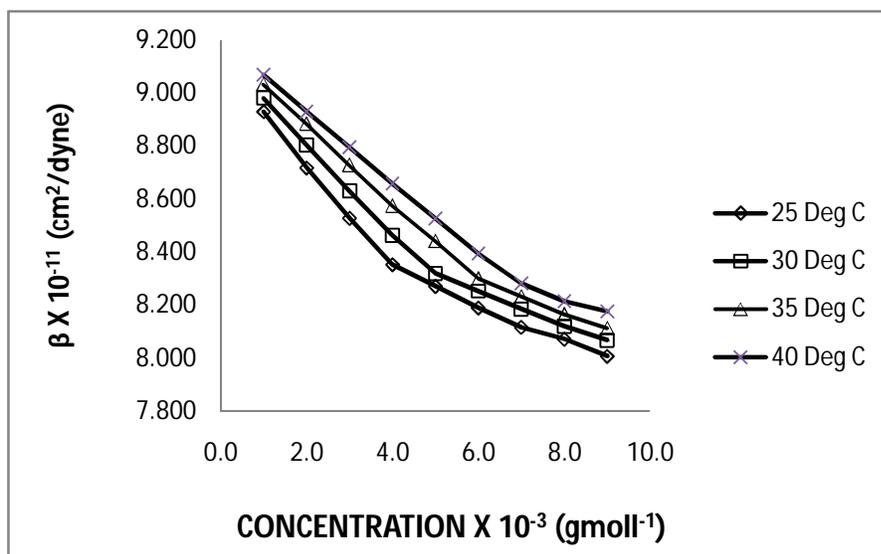

Fig.2: Adiabatic Compressibility Vs Concentration of Cerium palmitate

The results of adiabatic compressibility, β of the solutions of cerium and thorium palmitatecan 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 palmitate as compared to cerium palmitate.

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

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

Where ϕ_k is the limiting apparent molar compressibility and S_k is constant. The values of constant, S_k and limiting apparent molar compressibility ϕ_k^0 have been obtained from the slope and intercept of plots ϕ_k vs. $C^{1/2}$(Table-2). The negative values of $\phi_k$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 $\phi_k$may be attributed to the fact that the solvent becomes less compressible in dilute solutions[28]. The increase in values of ϕ_k in the post micellization region indicates the incompressible nature of the concentrated solutions.

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 x10^{-9} 10^{-8}	B X	$-\phi_k^0\phi$ X10^{-6} 10^-	S_K X
Cerium palmitate	3.10	14.50	-0.105	1.38	0.90	0.36
Thorium palmitate	4.05	15.50	-0.060	2.10	1.40	0.39

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 impedance, 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 affecting structural arrangements.

The values of relaxation strength r, available volume, V_a solvation number, S_n decrease with increase in concentration for cerium and thorium palmitate, 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 palmitate than for thorium palmitate at all concentrations.

CONCLUSION

It is concluded that there is a significant interaction between the solute-solvent molecules in dilute solution and soap molecules do not aggregate appreciably below the CMC.cerium and thorium palmitate behave as weak electrolytes in 70% benzene + 30% methanol mixture(v/v). The values of CMC increase with the cation size and the values of various acoustic parameters are in good agreement.

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