

ACOUSTICAL BEHAVIOR OF CERIUM AND THORIUM MYRISTATE IN MIXED ORGANIC SOLVENTS

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Ultrasonic velocity measurements of cerium and thorium myristate have been carried out in a mixture of 70% benzene + 30% methanol (V/V) at different temperatures in order to determine critical micellar concentration (CMC), soap-solvent interactions, and various acoustical 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 an increase in soap concentration. The internal pressure of the solutions decreases with the increase in soap concentration at all temperatures. The results of ultrasonic measurements have been interpreted in the light of well-known equations.

Keywords: ultrasonic velocity, compressibility behavior, CMC, internal pressure, acoustical parameters.

INTRODUCTION

Ion-solvent interactions orient the dipole of the solvent molecules that leads to minimum potential energy. Metal soaps are potentially very useful for applications in various fields,¹⁻⁴ such as lubricating greases, 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. Other uses of metal soaps are as fungicides and pesticides,⁵ optical polymer fibers,⁶ coating pigment in paper industry⁷ and in the preparation of nanofilms.⁸ Ultrasonic methods have been used for providing interesting information on the specificities of ion-solvent interactions related to the structure of the solute and solvation of soaps in organic liquids and has been studied by several researchers. Acoustical studies on uranyl soaps of lower fatty acids have been reported by Varsha *et al.*⁹ Suleman *et al.*^{10,11} studied the 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.¹² Kishore *et al.*¹³ determined the acoustic measurements and compressibility behavior of terbium myristate in benzene-methanol mixture.

In continuation with earlier work on metal soaps, we report here results on the ultrasonic measurement of solutions of cerium and thorium myristate in 70% benzene + 30% methanol (V/V) at different temperatures. These results give a clear insight into the soap-soap and soap-solvent interactions and micellar aggregates formed by cerium and thorium myristate in non-aqueous medium.

EXPERIMENTAL

Materials and methods

Anal R grade myristic acid, benzene, methanol, ethanol, cerium nitrate and thorium chloride (99.9% purity, received from Indian Rare Earth Limited, Kerala) were used for the present investigation. The cerium and thorium myristate 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 high temperature under vigorous stirring. After initial drying in an air-oven at 50-60 °C, final drying was carried out under reduced pressure. The precipitates were filtered off and washed with hot distilled water and acetone. The purity of soaps was established by observing their melting points, IR spectra and elemental analysis.

Solutions of cerium and thorium myristate were prepared by dissolving a known amount of soap in a mixture of 70/30 benzene-methanol and kept for 2 h in

a thermostat at a desired temperature. The ultrasonic velocity of solutions of cerium and thorium myristate was recorded on a multifrequency ultrasonic interferometer Model MX-3 (Mittal Enterprises, New Delhi) at different temperatures, using a crystal frequency of 1 MHz. Water was maintained at a desired temperature and controlled to ± 0.5 °C by a thermostat. The uncertainty of velocity measurements was of $\pm 0.2\%$. The densities of the solutions were determined at different temperatures by a pycnometer calibrated with pure benzene.

Computational methods

Various acoustical parameters, namely adiabatic compressibility (β), molar compressibility (W), intermolecular free length (L_f), specific acoustic impedance (Z), apparent molar volume (ϕ_v), apparent molar compressibility (ϕ_k), internal pressure (π_i), primary solvation number (S_n), molar sound velocity (R), relative association (R_a), available volume (V_a) and relaxation strength (r), have been evaluated by the following relationships:

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

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

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

$$Z = \rho v \quad (4)$$

$$\phi_v = 1000/C\rho_o(\rho_o - \rho) + M/\rho_o \quad (5)$$

$$\phi_k = 1000/C\rho_o(\rho_o\beta - \beta_o\rho) + \beta_o x M/\rho_o \quad (6)$$

$$\pi_i = bRT(k\eta/V)^{1/2} \times (\rho^{2/3}/M_{\text{eff}}^{7/6}) \quad (7)$$

$$S_n = n_o/n(1 - V\beta/n_oV_o\beta_o) \quad (8)$$

$$R = M_{\text{eff}}/\rho \times v^{1/3} \quad (9)$$

$$R_a = (\rho/\rho_o)(v_o/v)^{1/3} \quad (10)$$

$$V_a = V(1 - v/v_a) \quad (11)$$

$$r = 1/(v/v_a)^2 \quad (12)$$

where ρ , ρ_o , β , β_o , v , v_o are the density, adiabatic compressibility and ultrasonic velocity of solutions and solvent, respectively; K is Jacobson's constant; C is concentration (g mol. l^{-1}) of the solute; b stands for the cubic packing factor, which is assumed to be 2 for all liquids and solutions, k is temperature independent constant (4.28×10^9), R is gas constant ($8.314 \text{ KJ.mol}^{-1}$), T is absolute temperature 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_o is the molar volume of solvent; v_a is equivalent to 1600 m s^{-1} .

The effective molecular weight of the solutions has been calculated by the relationship:

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

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 for cerium and thorium myristate in the mixture of 70% benzene + 30% methanol (V/V) have been evaluated (Table 1) with varying concentrations 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 density increases while the adiabatic compressibility decreases, with increasing soap concentration. Therefore, the quantity $d\rho/dc$ (concentration derivative of density) is positive, while the quantity $d\beta/dc$ (concentration derivative of compressibility), is negative. Since the values of $1/\beta \cdot d\beta/dc$ are larger than the values of $1/\rho \cdot d\rho/dc$ for the soap solution, the concentration derivative of velocity (dv/dc) will be positive and so velocity increases with an increasing concentration of soap, which is in fair agreement with the results of other workers reported for different electrolytic solutions.^{14,15} The variation in ultrasonic velocity v , with the concentration of soap solutions C , follows the relationship:

$$v = v_o + GC$$

where v and v_o are the ultrasonic velocity of the solution and solvent mixture, respectively, and G is Gransey's constant.¹⁶

The plots of ultrasonic velocity v vs soap concentration C (Fig. 1) are characterized by an intersection of two straight lines at a definite soap concentration, where the physical properties of the soaps exhibit discontinuity, corresponding to critical micelles formation (CMC) of cerium and thorium myristate. CMC value and Gransey's constant of thorium myristate are higher than those of cerium myristate. The value of Gransey's constant decreases, whereas the CMC values increase with the increase in temperature for cerium and thorium myristate (Table 2). 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 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 center of the micelles with the hydrocarbon chains extending outwards into the solvent.

Table 1
Experimental ultrasonic velocity and other acoustic parameters of cerium and thorium myristate
in a mixture of 70% benzene and 30% methanol (V/V) at 30 °C ± 0.05 °C

S.No	Concentration $C \times 10^3$ (g.mol l ⁻¹)	Ultrasonic velocity $v \times 10^{-5}$ (cm/s)	Density ρ (g.ml ⁻¹)	Adiabatic compressibility $\beta \times 10^{11}$ (cm ² dyne ⁻¹)	Intermolecular freelength 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	Relative association R_a
Cerium Myristate										
1	1.0	1.135	0.8670	8.953	0.6069	0.9849	1.78	1.6128	548.04	0.9984
2	2.0	1.146	0.8705	8.747	0.5983	1.0011	1.75	2.0204	287.24	0.9981
3	3.0	1.157	0.8737	8.557	0.5905	1.0161	1.72	2.0924	199.56	0.9979
4	4.0	1.167	0.8757	8.385	0.5843	1.0281	1.70	2.0519	154.87	0.9978
5	5.0	1.176	0.8767	8.255	0.5810	1.0345	1.68	1.9225	126.92	0.9976
6	6.0	1.182	0.8777	8.162	0.5777	1.0410	1.65	1.7746	107.62	0.9972
7	7.0	1.188	0.8787	8.070	0.5745	1.0474	1.63	1.6675	93.81	0.9966
8	8.0	1.194	0.8798	7.979	0.5713	1.0540	1.61	1.5873	83.45	0.9962
9	9.0	1.200	0.8809	7.890	0.5685	1.0597	1.59	1.5227	75.36	0.9958
Thorium Myristate										
1	1.0	1.136	0.8680	8.927	0.6065	0.9860	1.77	2.0130	555.62	1.0004
2	2.0	1.150	0.8704	8.687	0.5983	1.0010	1.74	2.4327	289.75	0.9995
3	3.0	1.163	0.8728	8.471	0.5908	1.0151	1.71	2.3593	200.61	0.9994
4	4.0	1.174	0.8753	8.289	0.5845	1.0276	1.69	2.2902	155.90	0.9993
5	5.0	1.180	0.8772	8.187	0.5809	1.0351	1.66	2.0761	128.11	0.9991
6	6.0	1.186	0.8786	8.092	0.5775	1.0420	1.64	1.9130	108.73	0.9989
7	7.0	1.192	0.8799	7.999	0.5741	1.0488	1.62	1.7921	94.83	0.9987
8	8.0	1.198	0.8812	7.907	0.5708	1.0557	1.60	1.7001	84.37	0.9984
9	9.0	1.203	0.8825	7.830	0.5680	1.0616	1.58	1.6120	76.22	0.9979

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. Still, the values of CMC determined at different temperatures are in fair agreement with the values of CMC determined from conductivity measurements.¹⁷ The plots of ultrasonic velocity 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 myristate 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 myristate in 70% benzene + 30% methanol mixture (V/V) decreases with increasing concentration of the soap solutions and increases with increasing temperature. The decrease in adiabatic compressibility is attributed to the fact that the soap molecules ionise in dilute solutions. These ions are surrounded in solution 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 the 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 are extrapolated to zero soap concentration and the extrapolated values of adiabatic compressibility β_0 (Fig. 2) are in fair agreement with the experimental values of adiabatic compressibility for the solvent.

The results of adiabatic compressibility β of the solutions of cerium and thorium myristate can be explained, in the light of Bachem's¹⁸ 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} . A perusal of the data collected in Table 2 shows that the values of constants A and B are higher for thorium myristate, as compared to cerium myristate.

Following Gucker's limiting law,¹⁹ apparent molar compressibility ϕ_k is related to concentration C by the following relationship:

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

where ϕ_k^0 is the limiting apparent molar compressibility and S_k is a constant. The values of the constant S_k and limiting apparent molar compressibility ϕ_k^0 have been obtained from the slope and intercept of the plots ϕ_k vs $C^{1/2}$. The negative values of ϕ_k decrease sharply upto CMC and then increase again with the 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.²⁰ The increase in ϕ_k values in the post-micellization region indicates the incompressible nature of the concentrated solutions. The comparison of the results shows that the values of $-\phi_k$ and S_k decrease with temperature and are higher for thorium myristate than for cerium myristate. The internal pressure²¹ of the solutions decreases with the increase in concentration. The decrease in internal pressure of the solutions indicates that the addition of solute decreases the cohesive forces of the solvent at all temperatures.

The decrease in intermolecular free length L_f ²² and the increase in specific acoustic impedance Z ,²³ with increasing soap concentration, are an indicative of the increase in intermolecular forces with the addition of soap-forming aggregates of solvent molecules around solute ions, supporting the strong solute-solvent interactions affecting structural arrangements.²⁴

The plots of intermolecular free length L_f vs concentration C and specific acoustic impedance Z vs concentration C are also characterized by the intersection of two straight lines at the CMC, indicating that the molecules of cerium and

thorium myristates do not aggregate to an appreciable extent below the CMC. The value of intermolecular free length increases, whereas the value of specific acoustic impedance decreases with the increase of temperature. The values of relaxation strength r_s ,²⁵ available volume V_a ,²⁶ solvation number S_n ,²⁷ decrease with increasing concentration for cerium and thorium myristate, however the values of relaxation strength and available volume increase, whereas the values of solvation number decrease with increasing temperature. The solvation number corresponds to the number of solvent molecules in the solvation sheath of the ions. On primary account of electrostriction, the molecules in the primary solvation sheath will be highly compressed, so

that they will be less compressible than those in the bulk of the solution when an external pressure is applied. The compressibility of the solvent molecules 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 the post-micellization region, which may be attributed to greater intake of solvent molecules in this 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 the values of solvation number are lower for cerium myristate than for thorium myristate.

Table 2
Values of various constants for cerium and thorium myristate in 70% methanol + 30% benzene (V/V) at different temperatures

S. No	Name of constant	Cerium myristate		Thorium myristate	
		30 °C	40 °C	30 °C	40 °C
1	CMC $\times 10^{-3}$ (g mol l ⁻¹)	3.50	5.50	4.51	6.50
2	Gransey's constant (G $\times 10^{-5}$)	11.00	8.50	9.50	9.00
3	A $\times 10^{-9}$	-0.11	-0.05	-0.12	-0.09
4	B $\times 10^{-8}$	1.27	1.50	1.40	1.60
5	$-\phi_K \times 10^{-6}$	0.70	0.10	1.00	0.68
6	$S_k \times 10^{-4}$	0.31	0.25	0.32	0.28

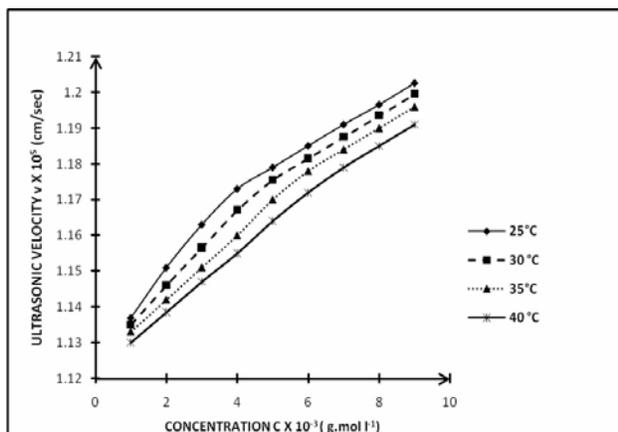


Figure 1: Ultrasonic velocity vs concentration of cerium myristate

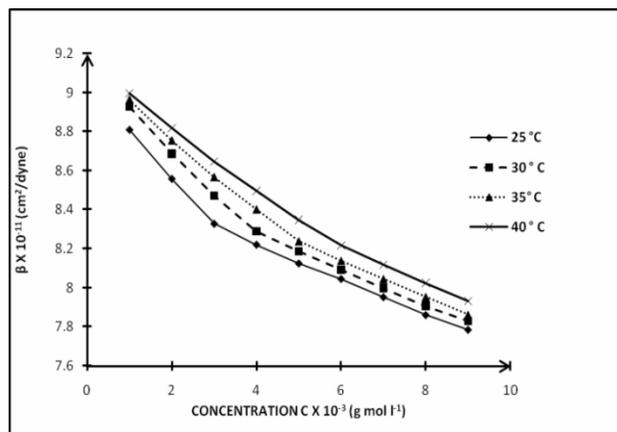


Figure 2: Adiabatic compressibility vs concentration of cerium myristate

The decrease in 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 to increased solvation of ions. The values of relative association increase with increasing temperature, being higher for thorium myristate than for cerium myristate. The values

of various acoustic parameters are in good agreement.

CONCLUSION

The results confirm that there is a significant interaction between the soap and solvent molecules in dilute solutions, and soap molecules do not aggregate appreciably below the CMC, while cerium and thorium myristate behave as weak electrolytes in 70% benzene + 30% methanol mixture(v/v). The values of CMC increase with the cation size and are in agreement with those obtained for other physical parameters.

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