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Acoustical Studies on Lithium Laurate in Benzene-Methanol Mixture

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ABSTRACT

Ultrasonic velocity of Lithium laurate has been measured in non-aqueous solvent i.e. 60/40 Benzene-methanol (v/v) mixture at different temperatures (25 and 30°C). The acoustical parameters are discussed in light of different theories of propagation of ultrasonic waves. The effects of soap concentration and temperature on ultrasonic velocity and various acoustic parameters such as adiabatic and molar compressibility, molar sound velocity, salvation number, relative association, relaxation strength and other acoustic parameters have been studied. The results confirm that there is a significant interaction between soap and solvent molecules.

Graphical Abstract

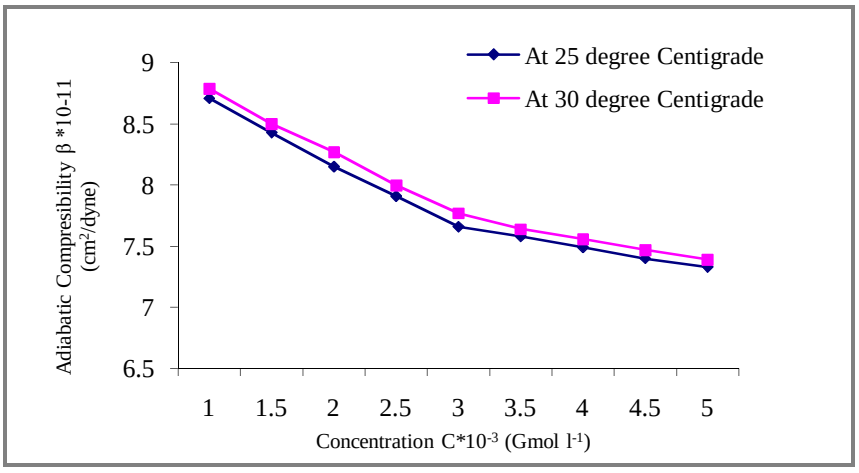

Figure 2. Adiabatic compressibility Vs Concentration of Lithium Laurate in a mixture of 60/40 benzene methanol (v/v).

Keywords: Lithium laurate, Acoustic parameters, Ultrasonic velocity.

INTRODUCTION

Metallic soaps are widely used in industries as detergents, softeners, plasticizers, greases, lubricants, cosmetics and medicines. The study and understanding of acoustical properties are necessary for their applications in industries. Sound velocity is purely a thermodynamic function and with the help of this method [**1**], a number of other thermodynamic properties of electrolyte solutions can be detected. Mehrotra *et al* [**2-4**] determined acoustical parameters of lanthanide soaps in mixed organic solvents. Suleman *et al* [**5, 6**] studied ultrasonic behavior of transition metal soaps in liquor ammonia, whereas acoustical studies, compressibility behaviour and Rao formalism of lanthanide soaps solutions were carried out by Upadhyaya and Chaturvedi [**7**]. Rawat and coworkers investigated molecular interaction and compressibility behaviour of alkaline-earth metal soaps [**8**]. However studies on Lithium soaps in benzene-methanol mixture have not yet been undertaken systematically.

In the work reported here, ultrasonic velocity and density of lithium laurate in 60/40 benzene-methanol (v/v) of varying concentration and temperature have been measured in order to calculate various acoustic parameters. These parameters give a clear insight into micellar aggregate formed by lithium laurate in non-aqueous medium.

MATERIALS AND METHODS

AnalaR grade lauric acid, benzene, methanol, ethanol and lithium acetate (purity 99.9% received from Indian Rare Earth Limited, Kerala) were used for the present investigation. The lithium laurate was prepared by direct metathesis of potassium laurate by pouring a slight stoichiometric excess of aqueous lithum acetate solution into clear potassium laurate dispersion at raised temperature with vigorous stirring. The precipitate was filtered off and washed with hot distilled water and acetone. After initial drying in an air oven 50-60°C, final drying was carried out under reduced pressure. The purity of soap was checked by the elemental analysis and results were found in agreement with theoretically calculated values. He purified soap has the melting point 99°C.

The ultrasonic velocity measurements were recorded on a multi-frequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at 40$\pm$ 0.05°C using a MH_2 frequency. Water maintained at the desired temperature with precision of $\pm$ 0.5°C by a thermostat passed through the jacket of cell before the measurement was actually made. The measured velocities have precision of $\pm$0.5 ms^{-1}. The densities of the solutions were determined at different temperatures with RD bottle calibrated with pure benzene.

Acoustic parameters such as adiabatic compressibility β, molar compressibility W, intermolecular free length L_f [**9**], apparent molar compressibility Φ_k [**10**], specific acoustic impedance Z [**10**], available volume V_a [**11**], molar sound velocity R [**12**], relative association R_A [**13**], primary salvation number S_n and relaxation strength r [**14**] were calculated using the following relationships.

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

$$\bar{W} = (M/\rho)(\beta)^{-1/7} \quad \text{..(ii)}$$

$$\Phi = \frac{1000(\rho\beta - \beta_0\rho)}{C\rho} + \frac{\beta_0 M}{\rho_0} \quad \text{..(iii)}$$

$$L = K\sqrt{\beta} \quad \text{..(iv)}$$

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

$$V_a = V\,(1\text{-}v/v\alpha) \qquad ..(vi)$$

$$R = (\bar{M}/\rho)\,(v)^{1/3} \qquad ..(vii)$$

Where

$$M = \frac{n_0\bar{M}_0 + nM}{n_0 + n}$$

$$R_A = (\rho / \rho_0)\,(v_0 / v)^{1/3} \qquad ..(viii)$$

$$S_n = n_0/n\,[1\text{-}\,V\,\bar{\beta} / n_0\beta_0\,\bar{V}_0) \qquad ..(ix)$$

and

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

Here ρ_0, ρ, β_0, p, vo, v, V_0 and V are the density, adiabatic compressibility, ultrasonic velocity and molar volume of solvent and solutions, respectively and n_0, M_0, n and M are the number of moles and molecular weight of solvent and solute, respectively and K and M are the temperature dependent Jacobson's constant and effective molecular weight of solution, v_α is equivalent to 1600 m sec^{-1} Φ_k is apparent molar compressibility.

RESULTS AND DISCUSSION

The various acoustic parameters of lithium laurate were measured at 25 and 30°C in a mixture of 60/40 benzene-methanol (v/v) (table 1 and table 2). The results show that ultrasonic velocity and density increase with increasing soap concentration. However, these values decrease with increase in temperature. The relation between ultrasonic velocity v and soap concentration C for dilute solution is given by following equation

$$v = v_0 + GC \qquad .. (xi)$$

Where, v_0 is ultrasonic velocity of pure solvent and G is Garney's constant [**15**].

Table 1. Ultrasonic velocity, compressibility and other acoustical parameters of Lithium laurate in 60/40 benzene-methanol (v/v) mixture at 25°C ± 0.5°C.

S. No	Cx10^3 (g mol l^{-1})	P (g ml^{-1})	Vx10^{-5} (cm sec^{-1})	βx10^{11} (cm^2 $dyne^{-1}$)	W 10^{-2}	-Φk x 10^6(cm^2 $dyne^{-1}$)	L_f (A)	Zx10^{-5}	S_n	R	Va	R_A	r
1	1.0	0.8479	1.164	8.71	16.38	6.35	0.5993	0.986	165.85	2923	16.31	0.994	0.471
2	1.5	0.8480	1.183	8.43	16.45	6.20	0.5893	1.003	131.16	2937	15.59	0.990	0.453
3	2.0	0.8489	1.202	8.15	16.51	6.04	0.5797	1.020	113.01	2950	14.87	0.985	0.436
4	2.5	0.8498	1.220	7.91	16.58	5.85	0.5708	1.037	101.01	2964	14.19	0.982	0.419
5	3.0	0.8506	1.239	7.66	16.64	5.71	0.5618	1.054	93.04	2977	13.47	0.977	0.400
6	3.5	0.8512	1.245	7.58	16.66	5.13	0.5589	1.060	82.17	2982	13.25	0.977	0.394
7	4.0	0.8519	1.252	7.49	16.68	4.72	0.5556	1.067	74.31	2986	12.98	0.976	0.388
8	4.5	0.8524	1.259	7.40	16.71	4.40	0.5523	1.073	68.16	2990	12.72	0.974	0.381
9	5.0	0.8530	1.265	7.33	16.73	4.11	0.5495	1.079	62.95	2994	12.49	0.973	0.375

Ultrasonic velocity v and adiabatic compressibility β when plotted against concentration C (Figure 1 and Figure 2) show an intersection of two straight lines at a definite soap concentration, the critical micellar concentration (CMC) of the metal soap. The increase in the temperature of soap solution results in the increase in critical micellar concentration (CMC). The values of Gernsey's constant obtained from the plots of ultrasonic velocity v versus concentration C decrease with increasing temperature.

Table 2. Ultrasonic velocity, compressibility and other acoustical parameters of Lithium laurate in 60/40 benzene-methanol (v/v) mixture at 30°C ± 0.5°C

S.No.	$Cx10^3$ (g mol l^{-1})	ρ (g ml^{-1})	$Vx10^{-5}$ (cm/sec)	β x 10^{11} (cm^2 $dyne^{-1}$)	$Wx10^{-2}$	$-\Phi_k$ x 10^6 (cm^2 $dyne^{-1}$)	L_f (A)	$Zx10^{-5}$	S_n	R	Va	R_A	r
1	1.0	0.8468	1.159	8.79	16.36	5.94	0.6019	0.981	160.34	2920	16.50	0.995	0.475
2	1.5	0.8477	1.178	8.50	16.43	5.93	0.5919	0.999	127.52	2933	15.78	0.990	0.458
3	2.0	0.8486	1.194	8.27	16.48	5.66	0.5837	1.013	108.24	2945	15.17	0.987	0.443
4	2.5	0.8494	1.213	8.00	16.56	5.60	0.5743	1.030	97.93	2959	14.46	0.983	0.425
5	3.0	0.8502	1.230	7.77	16.62	5.44	0.5660	1.046	89.70	2971	13.82	0.979	0.409
6	3.5	0.8509	1.240	7.64	16.65	5.05	0.5613	1.055	80.89	2978	13.44	0.977	0.399
7	4.0	0.8514	1.246	7.56	16.67	4.67	0.5584	1.061	72.87	2982	13.36	0.976	0.393
8	4.5	0.8521	1.253	7.47	16.69	4.31	0.5551	1.068	66.91	2987	12.94	0.975	0.387
9	5.0	0.8526	1.260	7.39	16.72	4.06	0.5518	1.074	62.08	2992	12.68	0.974	0.380

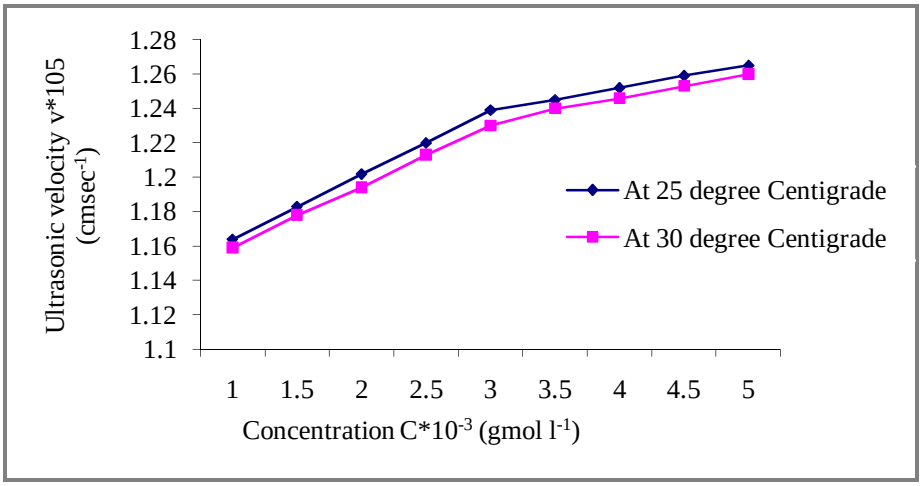

Figure 1. Ultrasonic velocity Vs Concentration of Lithium Laurate in a mixture of 60/40 benzene-methanol (v/v).

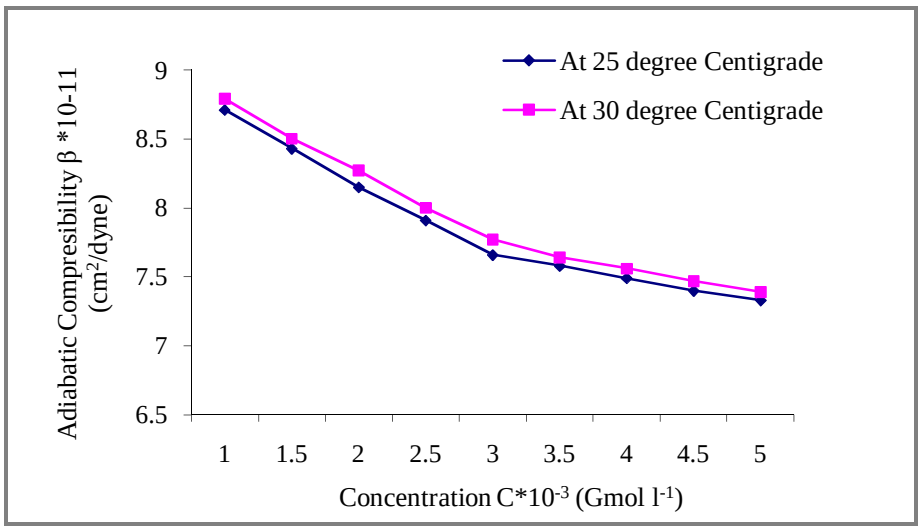

Figure 2. Adiabatic compressibility Vs Concentration of Lithium Laurate in a mixture of 60/40 benzene methanol (v/v).

The nature of adiabatic compressibility β is reverse to that of ultrasonic velocity v. Increase in soap concentration causes decrease in the values of adiabatic compressibility at both temperatures.

However adiabatic compressibility increases with rise in temperature. The decrease in adiabatic compressibility after critical micellar concentration may be due to the closed packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and finally internal pressure.

The Bachem's relationship [16] for adiabatic compressibility b of solutions of terbium soap is presented by following equation

$$\beta = \beta_0 + AC + BC^{3/2} \qquad \text{..... (xii)}$$

Where, A and B are constants, C is molar concentration of soap solutions. The values of constants have obtained

From the intercept and slope of plots of β-β_0/C Vs $\sqrt{C}$. The plots of β-β_0/C vs $\sqrt{C}$ show a break at the critical micellar concentration.

The apparent molar compressibility β_k is related to concentration C by Gucker's limiting law [17-21],

$$\Phi_k = \Phi_k^0 + S_k C^{1/2} \qquad \text{..... (xiii)}$$

where Φ_k^0 is limiting partial molar compressibility and S_k is constant. Φ_k^0 and S_k have obtained from intercept and slope of plots Φ_k Vs $\sqrt{C}$ below the critical micellar concentration. The positive value of S_k signifies a considerable soap-solvent interaction below CMC. Increase in the values of Φ_k after post micellization region indicates the incompressible nature of the concentrated solutions. Values of various constants for lithium laurate have mentioned in table 3.

Table 3. Values of various constants for Lithium laurate in a mixture of 60/40 benzene-methanol (v/v) at different temperatures

S.No.	Temperature (°C)	CMC x 10^3 (g mol l^{-1})	Garnsey's constant (G x 10^{-6})	-A x 10^9	B x 10^9	$-\Phi^0_k$ x 10^6	S_k x 10^6
1	25	3.00	3.78	6.20	15.01	6.82	30.00
2	30	3.17	3.60	5.82	16.01	6.52	33.03

The values of specific acoustic impedance Z and intermolecular free length L_f for lithium laurate in a mixture of 60/40, benzene-methanol (v/v) at different temperatures suggest that the increase in specific acoustic impedance Z and decrease in the intermolecular free length L_f with increase in soap concentration can be explained on the basis of lyophobic interactions between soap and solvent molecules.

The L_f increases with increasing temperature. However specific acoustic impedance has shown the reverse trend to that of intermolecular free length.

The solvation number S_n decreases with increase in soap concentration and temperature. The value of S_n corresponds to the number of solvent molecules in the primary salvation sheath of ions. The positive value of S_n suggests appreciable solvation of ions. The molar sound velocity R increases with increasing soap concentration. However, there is decrease in molar sound velocity R with rise in temperature. A rise in temperature increases the molar volume, probably due to decrease in the density of these solutions. The molar sound velocity is, however independent of temperature.

The increase in relative association R_A with increasing temperature is due to decreasing in solvation. R_A decreases with increasing concentration due to increasing solvation of ions. The values of available volume V_a decrease with increasing soap concentration while rise in temperature results,

increases of available volume V_a. The relaxation strength r increases with the rise in temperature, however increase in soap concentration decreases the relaxation strength.

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