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Ultrasonic Study of Molecular Interactions and Compressibility Behaviour of Samarium Soaps in Benzene-DMSO Mixture

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Abstract: Ultrasonic measurements of samarium soaps (palmitate and myristate) have been carried out in a mixture of benzene and DMSO (70%-30% v/v) to determine the critical micellar concentration(CMC), soap-solvent interaction and various acoustic parameters. The results show that ultrasonic velocity, intermolecular free length, adiabatic compressibility, adiabatic molar volume and apparent molar compressibility decrease while specific acoustic impedance, relative association and solvation number increase with increase in soap concentration. The results of ultrasonic measurements have also been explained in terms of well-known equations.

Keywords: Ultrasonic measurements, molecular interactions, samarium soaps, compressibility, critical micellar concentration(CMC).

I. INTRODUCTION

Metal soaps are widely used in different industries and play an important role in colloid phenomena. The physicochemical characteristics and the structure of these soaps depend largely on the method and conditions of preparation, which have been studied by several reseachers[1-5]. The study of molecular interactions has been a subject of extensive investigations by IR [6-7], NMR[8-9], Raman and ultrasonic absorption[11-13] measurements. The ultrasonic studies can provide interesting information on the specificities of ion-solvent interaction related to the structure of the solute and the reciprocal effects which arise in the solvents. However, ultrasonic studies of the soap solution give more information on the soap-solvent interaction.

The ultrasonic velocity of the solutions of samarium soaps n benzene and DMSO (70%-30% v/v) has been measured and the results have been used to stud the solute-solvent interactions and evaluate the critical micellar concentration (CMC) and various acoustic and thermodynamic parameters.

II. EXPERIMENTAL DETAILS

All chemicals used were of AR/GR (E-Merck) grade. The samarium soaps (palmitate and myristate) were prepared by direct metathesis of corresponding potassium soap with the required amount of aqueous solution of samarium nitrate in the temperature range 50-55°C under vigorous stirring. The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreacted fatty acid. The purity of the soaps was checked by elemental analysis and their IR spectra.

Soap solutions of samarium soaps were prepared by molal basis. The ultrasonic velocity was measured by a multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at 40 ± 0.05°C using a crystal of 1 MHz frequency. The uncertainty of velocity measurements is 0.2%. the densities of the solvent and the solutions were measured by a dilatometer was 15ml and the accuracy of the density results was ± 0.0001 g mol dm^{-3}.

III. RESULTS AND DISCUSSION

The ultrasonic velocity and various acoustical parameters for samarium palmitate and myristate in the mixtures of (70%-30%) benzene-dimethyl sulphoxide (V/V) have been evaluated (Table- I & II) at 40°C temperature. The variation of ultrasonic velocity ν, 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 solutions, 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:

$$\nu = \nu_0 + G_C$$

Where ν and ν_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 ν Vs C, and the magnitude of the G represents the variation of velocity with soap concentration. The plots of ultrasonic velocity, ν Vs. soap concentration, C (Fig-1), are characterized by intersection of two straight lines, where the physical properties of soaps exhibit discontinuity, corresponding to critical micellar concentration, CMC, of samarium palmitate and myristate.

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 of anions 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 model25. 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 parameters.

Table I - Ultrasonic Velocity and Compressibility of Samarium palmitate in a mixture of 70%-30% benzene-DMSO (V/V) at 40°C ± 0.5°.

s.no	concentration C x 10^{-3} (g mole l^{-1})	Density ρ (g ml^{-1}) 40°	Velocity v$x10^{-5}$ (cm/sec)	Adiabatic compressibility β$x10^{11}$ ($cm^2/dyne^{-1}$)	Molar compressibility W x10^{-2}	Apparent molar compressibility $-\Phi_k x10^6$ ($cm^2/dyne^{-1}$)	Relaxation strength r
1	2.0	0.9164	1.132	8.516	28.81	1.2019	0.4994
2	2.4	0.9172	1.136	8.448	28.84	1.4315	0.4959
3	3.0	0.918	1.144	8.323	28.95	1.6778	0.4888
4	3.7	0.9189	1.154	8.172	29.08	1.8866	0.4798
5	4.9	0.9193	1.164	8.029	29.27	1.8151	0.4707
6	5.5	0.9202	1.166	7.993	29.28	1.6773	0.4689
7	6.2	0.9209	1.169	7.946	29.32	1.5731	0.4662
8	7.1	0.9218	1.172	7.898	29.36	1.4458	0.4634
9	7.6	0.9219	1.174	7.870	29.41	1.3936	0.4616
10	8.3	0.9221	1.177	7.828	29.48	1.3423	0.4588
11	9.0	0.9225	1.178	7.812	29.51	1.2589	0.4579
12	10.0	0.9228	1.181	7.769	29.60	1.1846	0.4552

Table II - Ultrasonic Velocity and Compressibility of Samarium myristate in a mixture of 70%-30% benzene-DMSO (V/V) at 40°C ± 0.5°.

s.no	concentration $C \times 10^{-3}$ ($g\ mole\ l^{-1}$)	Density ρ ($g\ ml^{-1}$) 40°	Velocity $v\times10^{-5}$ (cm/sec)	Adiabatic compressibility $\beta\times10^{11}$ ($cm^2/dyne^{-1}$)	Molar compressibility $W\ x10^{-2}$	Apparent molar compressibility $-\Phi_k\ x10^{6}$ ($cm^2/dyne^{-1}$)	Relaxation strength r
1	2.0	0.9154	1.124	8.647	28.73	1.4093	0.5065
2	2.4	0.9162	1.128	8.578	28.77	1.5643	0.5030
3	3.0	0.917	1.135	8.465	28.86	1.7751	0.4968
4	3.7	0.9178	1.142	8.354	28.95	1.8669	0.4909
5	4.9	0.9185	1.152	8.204	29.11	1.8466	0.4816
6	5.5	0.9192	1.153	8.183	29.12	1.7027	0.4807
7	6.2	0.9201	1.155	8.147	29.13	1.5886	0.4789
8	7.1	0.9209	1.157	8.112	29.16	1.4662	0.4771
9	7.6	0.9213	1.158	8.094	29.18	1.4062	0.4762
10	8.3	0.9214	1.160	8.066	29.23	1.3445	0.4744
11	9.0	0.9218	1.161	8.048	29.26	1.2791	0.4735
12	10.0	0.9221	1.163	8.018	29.32	1.1153	0.4717

The plots of ultrasonic velocity, v vs. soap concentration, C (Fig.1 & 2) have been extrapolated to zero soap concentration and the extrapolated values of ultrasonic velocity v_0 are in almost in good agreement with the experimental velocity of the solvent mixture, indicating that the molecules of samarium palmitate and stearate do not aggregate to an appreciable extent below the CMC.

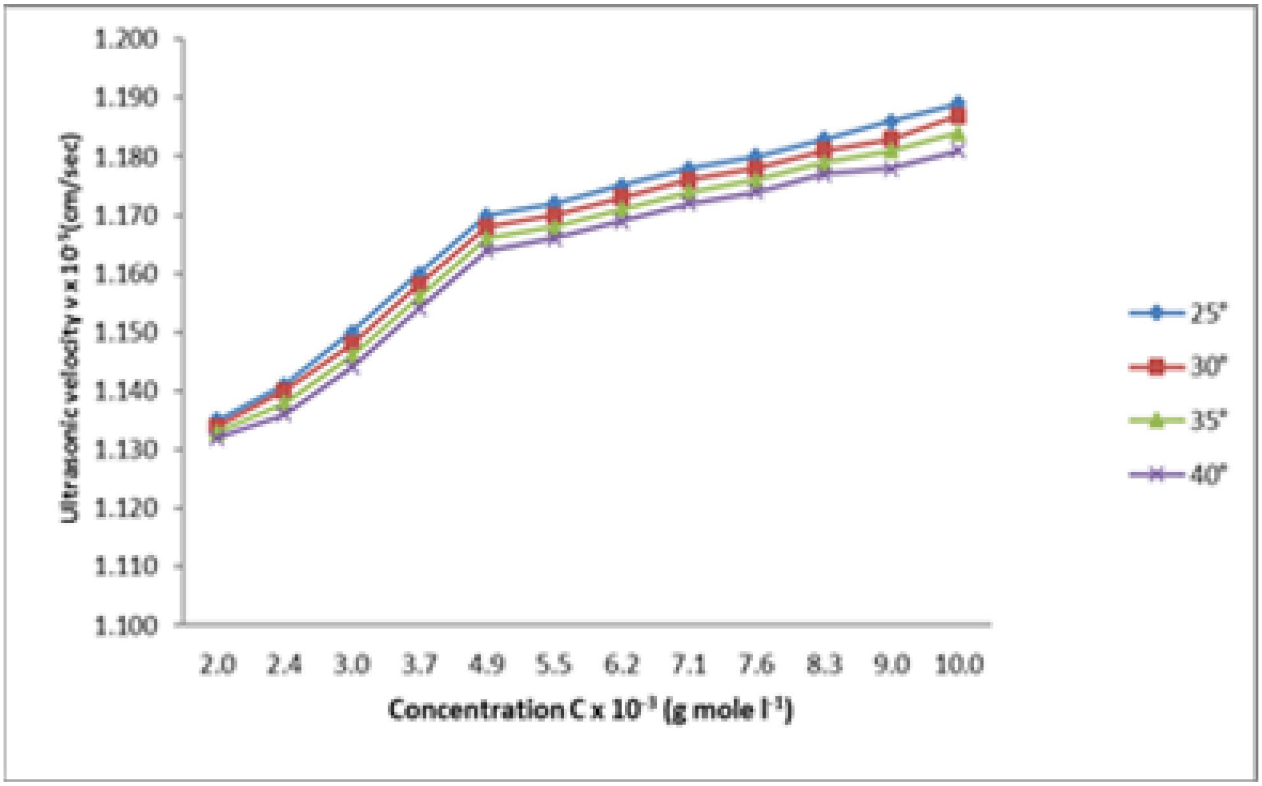

Fig:1 Ultrasonic velocity, v versus concentration C of samarium palmitate.

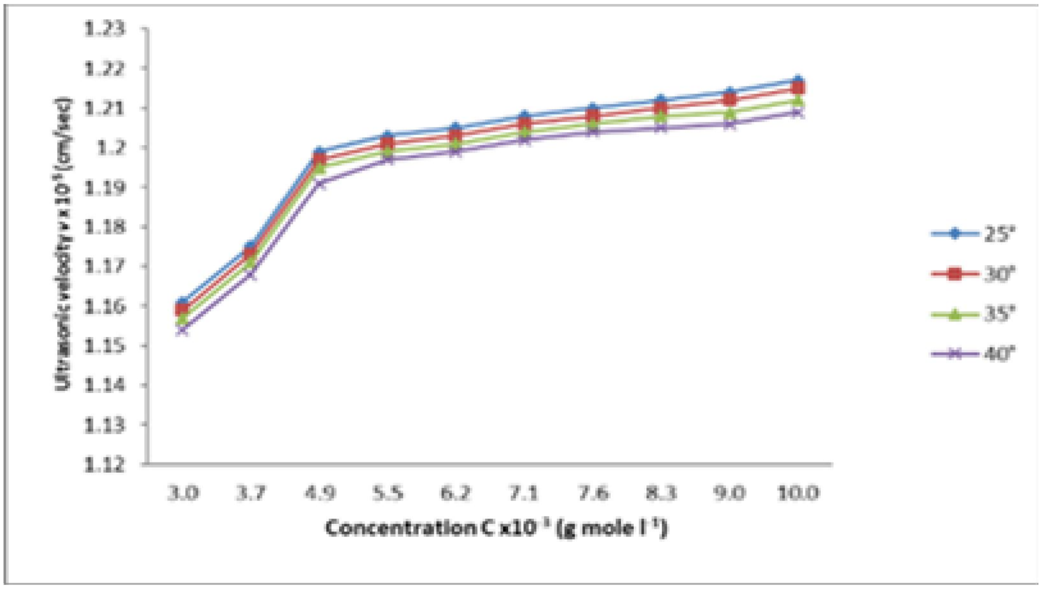

Fig:1 Ultrasonic velocity, v versus concentration C of samarium Myristate.

The nature of adiabatic compressibility variation is found to be the reverse to that of ultrasonic velocity. The adiabatic compressibility of samarium palmitate and myristate in (70%-30%) benzene-DMSO 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 cations and anions. 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

The results of adiabatic compressibility, β of the solutions of samarium palmitate and myristate have been expressed in terms of 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 β0 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. √C and the magnitude of A and B depend upon the nature of solute and solvent used. A perusal of data collected in Table III shows that the values of constants A and B are higher for samarium palmitate and myristate. By following Gucker’s [27] limiting law apparent molar compressibility, ϕk is related to concentration, C by relationship.

$\phi k = \phi k° + Sk\, C^{1/2}$

Where ϕk° is the limiting apparent molar compressibility and Sk is constant. The values of constant, Sk and limiting apparent molar compressibility ϕk° have been obtained from the slope and intercept of plots ϕk vs. $C^{1/2}$ (Table-III). The negative values of ϕk of decreases sharply up to the CMC and again it increases with square root of soap concentration. The decrease in the negative value of apparent molar compressibility ϕk may be attributed to the fact that the solvent becomes less compressible in dilute solutions. The increase in values of ϕk in the post micellization region indicates the incompressible nature of samarium soaps in higher concentration region.

Table III: Values of various constants at 40^0C + 0.050C

Soaps	CMC x 10^{-3} (g mol l^{-1})	Gransey’s constant G x 10^{-5}	Bachem’s relationship		Limiting apparent molar compressibility	
			A x 10^{-9}	B x 10-9	Φk^0 x 10^6	Sk x 10^6
Samarium palmitate	4.87	4.00	6.18	11.09	5.80	26.9
Samarium myristate	5.55	3.43	5.62	9.23	5.10	27.4

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 [28].

The values of relaxation strength r, available volume, Va solvation number, Sn decrease with increase in concentration. The value of solvation number corresponds to the number of solvent molecules in the primary solvation sheath of the ions. On 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.

IV. CONCLUSIONS

The ultrasonic velocity throws light on evaluation of various acoustical parameters of samarium palmitate and myristate in benzene-dimethylsulphoxide mixture. These results confirm that there is a significant interaction between samarium soaps and solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably below the CMC. The values of CMC for samarium soaps (palmitate and myristate) increase with increasing temperature

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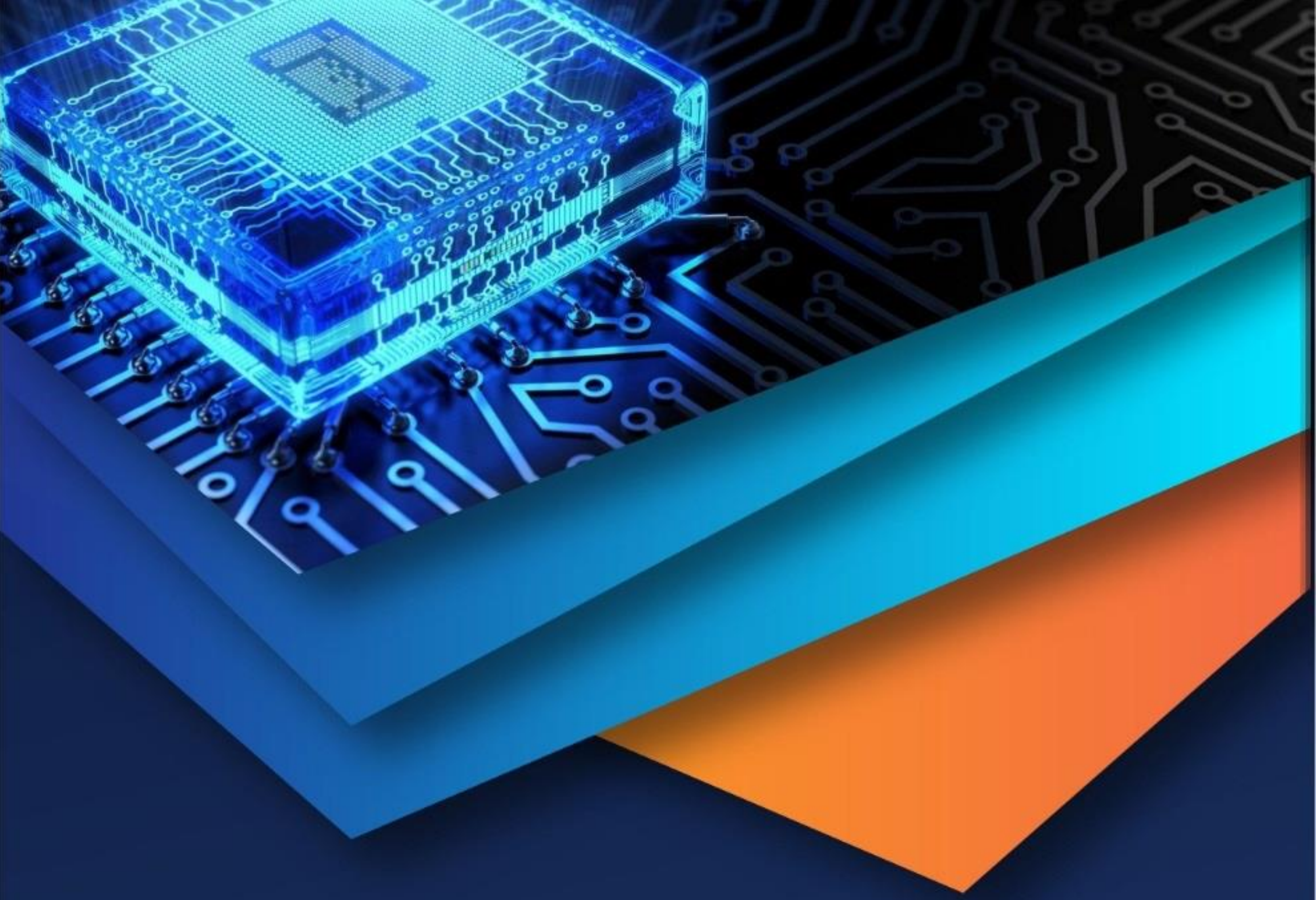

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