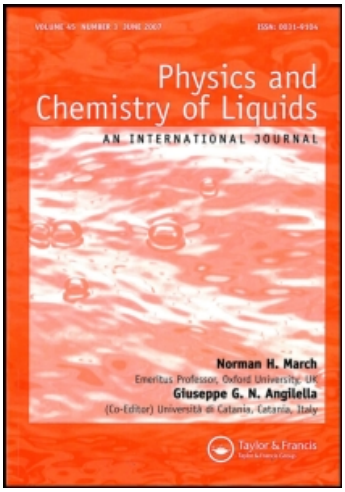

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Studies on Acoustic Behaviour of Samarium Caproate in Alkanols

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The effects of soap concentration and chainlength of the solvent (alkanols) on the ultrasonic velocity and various acoustic parameters (intermolecular free length, adiabatic compressibility, apparent molal compressibility, specific acoustic impedance, apparent molal volume, molar sound velocity and solvation number) for the solutions of samarium caproate have been investigated. The results have been used to determine the CMC, soap-solvent interaction and solvation number.

Key Words: Ultrasound, solvation number.

INTRODUCTION

The ultrasonic technique has been used for studying the solute-solvent interaction in a number of systems including organic liquids,[1–3] low melting solids,[4] dilute solutions of inorganic acids[5,6] and complex formation.[7–9] The propagation of ultrasound wave and the measurement of its velocity[10–14] and absorption[15,16] in inorganic, organic and organometallic binary systems have been used to determine the nature of molecular interactions in these systems. The variation of ultrasonic velocity and various acoustic parameters with temperature has been studied by several workers[17–21] using diffraction[22] and pulse technique.[23]

The present work deals with the ultrasonic measurements of the solutions of samarium caproate in various alkanols. The results have been used to determine the CMC, soap-solvent interaction and various

Table 1 Percentage of elements in samarium caproate.

Element	Found	Calculated
Carbon	14.51	14.52
Hydrogen	2.22	2.22
Samarium	30.33	30.32

acoustic parameters. The effect of the soap concentration and chain-length of the solvent on the various acoustic parameters have also been studied.

EXPERIMENTAL

Chemicals used were AR/GR (E Merck) grade reagents. The solvent (alcohols) were purified by standard methods. Samarium caproate was prepared by direct metathesis of potassium caproate with required amount of aqueous solution of samarium nitrate at 50–55°C under vigorous stirring. The precipitated soap was washed several times with distilled water and finally with methanol. The soap was recrystallised with benzene-methanol mixture, dried under reduced pressure and stored over calcium chloride. The absence of hydroxyl group in the soap was confirmed by studying its infrared (IR) spectrum. The purity of the soap was checked by elemental analysis and the results (Table 1) were in agreement with the theoretically calculated values. The melting point of the purified samarium caproate was 95.0°C.

The ultrasonic velocity of the solution of samarium caproate was measured by a multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at a frequency of 6 MHz at constant temperature, (40 ± 0.05°C). The densities of the solvents and solutions were measured by a pyknometer at constant temperature. The pyknometer was calibrated with distilled water and the buoyancy corrections were applied.

CALCULATIONS

The adiabatic compressibility, β, specific acoustic impedance, Z, intermolecular freelength, L_f, apparent molal compressibility, ϕ_k, apparent

molal volume, ϕ_v, molar sound velocity, R, and solvation number, S_n, were calculated by using the equations:

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

$$Z = v\rho \tag{2}$$

$$L_f = k\beta^{1/2} \tag{3}$$

$$\phi_k = \frac{1000}{C\rho_0}[\beta\rho_0 - \beta_0\rho] + \frac{\beta_0 M}{\rho_0} \tag{4}$$

$$\phi_v = \frac{1000}{C\rho_0}[\rho_0 - \rho] + \frac{M}{\rho_0} \tag{5}$$

$$R = \frac{\bar{M}}{\rho} v^{1/3} \tag{6}$$

$$\bar{M} = \frac{n_0 M_0 + nM}{n_0 + n}$$

$$S_n = \frac{n_0}{n}\left[1 - \frac{\bar{V}\beta}{n_0 \bar{V}_0 \beta_0}\right] \tag{7}$$

where ρ_0, ρ; β_0, β; n_0, n; M_0, M and $\bar{V}_0$, $\bar{V}$ are the density, adiabatic compressibility, number of moles, molecular weight and molar volume of solvents and solutions respectively, k, C and v are the temperature dependent Jacobson's constant, concentration in $g \cdot mol \cdot l^{-1}$ and ultrasonic velocity, respectively.

RESULTS AND DISCUSSION

The ultrasonic velocity, v, specific acoustic impedance, Z, apparent molal volume, ϕ_v and molar sound velocity, R, of the solutions of samarium caproate increase while the intermolecular free length, L_f, adiabatic compressibility, β, and apparent molal compressibility, ϕ_k decrease with increasing concentration of soap and chainlength of alkanols. The variation of ultrasonic velocity with concentration depends upon the concentration derivatives of density and compressibility and can be expressed as:

$$\frac{dv}{dc} = -\frac{v}{2}\left(\frac{1}{\rho}\cdot\frac{d\rho}{dc} + \frac{1}{\beta}\cdot\frac{d\beta}{dc}\right) \tag{1}$$

The results indicate that the density increases while the adiabatic compressibilty decreases with increasing soap concentrations. Thus the

concentration derivative of density, $(d\rho/dc)$, is positive while the concentration derivative of compressibility, $(d\beta/dc)$, is negative. Since the values of $1/\beta\,(d\beta/dc)$ are larger than of $1/\rho\,(d\rho/dc)$ for these soap solution, the concentration derivative of velocity, dv/dc is positive which is in close agreement with the results of other workers[24,25] reported for electrolytic solutions. The decrease in adiabatic compressibility may be due to the fact that the soaps behave as simple electrolyte in solutions and ionise into simple cations, Sm^{3+} and fatty acid anions, $RCOO^-$. The ions in solutions 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 the ions. The internal pressure increases and which results in the lowering of the compressibility of the soap solutions.

The plots of ultrasonic velocity, (Figure 1), adiabatic compressibilty, intermolecular freelength and specific acoustic impedance vs. concentration of samarium caproate show a break at a definite soap concentration which corresponds to the CMC of samarium caproate. The CMC increase with decreasing dielectric constant of alkanols (Table 1). This may be due to the fact that the high dielectric constant of the solvent reduces the electrostatic attractive forces between the positive and negative ions and thus favours the dissociation of the soap molecules which ultimately results in the micellization. The results show that the micelle formation occurs more easily in methanol than in other higher alcohols showing the following trend:

Methanol > Ethanol > Propanol-1 > Butanol-1 > Pentanol-1.

The plots of ultrasonic velocity vs. concentration have been extrapolated to zero soap concentration and the extrapolated values of the ultrasonic velocity, v_0 are in agreement with the calculated values of the ultrasonic velocity for the solvent (Table 1). The variation in ultrasonic velocity, v, with soap concentration, C, for dilute solutions below the CMC follows the relationship:

$$v = v_0 + GC \tag{2}$$

where, G is the Garnsey's constant. The calculated values of Garnsey's constant, G for samarium caproate in alkanols increase with decreasing dielectric constant of the solvent (Table 2).

The adiabatic compressibility, β, of the dilute solutions of samarium caproate in alkanols obeys Bachem's relationship:[26]

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

Table 2 Various parameters for samarium caproate in alkanols.

Solvent	CMC	$G \times 10^5$	$A \times 10^{11}$	$B \times 10^{11}$	$\phi_k^0 \times 10^7$	ϕ_v^0	$v_0 \times 10^{-5}$ extrapolated	$v_0 \times 10^{-5}$ experimental
Methanol	0.015	2.50	12	+208	−0.5	640	1.108	1.115
Ethanol	0.020	2.81	38	+83	−3.7	478	1.115	1.117
Propanol-1	0.024	3.41	55	−25	−5.1	284	1.130	1.132
Butanol-1	0.028	3.46	68	−100	−6.4	170	1.140	1.139
Pentanol-1	0.032	3.33	79	−133	−7.7	115	1.146	1.143

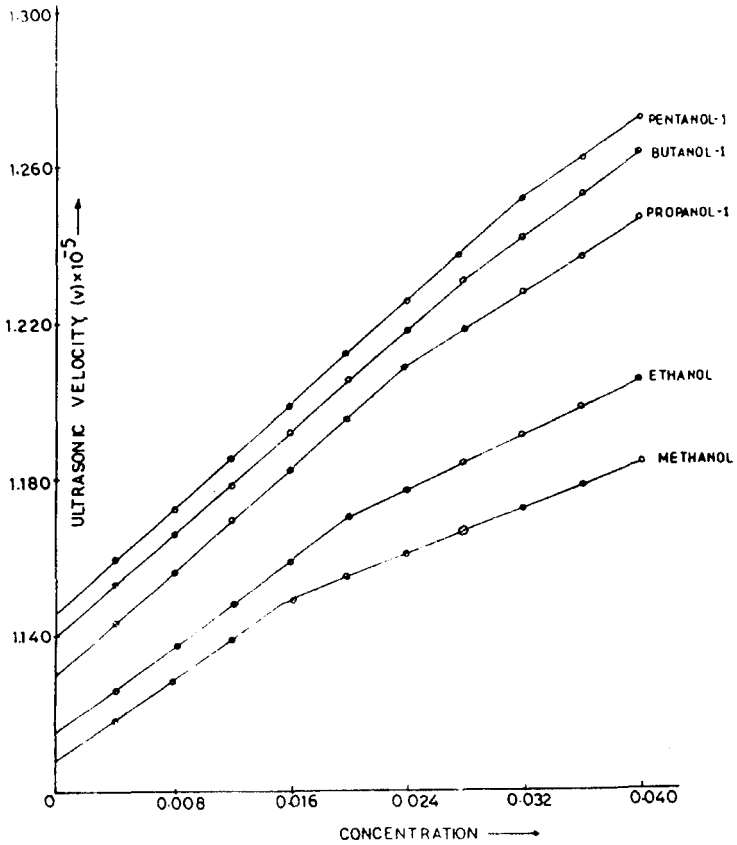

Figure 1 Ultrasonic velocity, (v) vs. concentration, (C).

where, A and B are constants and C is the concentration of soap in $g \cdot mol \cdot l^{-1}$. The constants A and B have been determined from the intercept and slope of linear plots of $(\beta - \beta_0)/C$ vs. $C^{1/2}$ and are recorded in Table 2. The values of A increrase while of B decrease with decreasing dielectric constant of alkanols.

The increase in the values of specific acoustic impedance, Z, with soap concentration, C, can be explained on the basis of hydrophobic interaction between the soap and solvent molecules which increases with intermolecular distance making relatively wider gaps between the molecules and becoming the main cause of impedient in propagation of ultrasonic waves.

The plots of apparent molal compressibility, ϕ_k, vs. square root of soap concentration, $C^{1/2}$ and of apparent molal volume, ϕ_v vs. $C^{1/2}$

exhibit a break at a concentration which corresponds to CMC of samarium caproate in alkanols. The values of ϕ_k^0 and ϕ_v^0 have been obtained by extrapolation of the plots below the CMC to zero soap concentration (Table 2). The extrapolated values of ϕ_k and ϕ_v decrease with decreasing dielectric constant of the solvent. The results are in agreement with the results reported by Masson[27] for electrolytic solutions.

The solvation number, S_n of dilute solutions of samarium caproate in alkanols varies linearly with the concentration of soap.

The values of molal sound velocity, R, increase linearly with increasing soap concentration and chainlength of alkanols.

The results of ultrasonic velocity show that the adiabatic compressibility, intermolecular freelength decrease while specific acoustic impedance, apparent molal compressibility, apparent molal volume and solvation number increase with increasing soap concentration.

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