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Ultrasonic study of liquid mixtures of aqueous solution of lithium sulphate and lithium hydroxide

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Abstract
The present communication reports the calculated values of the Intermolecular free length (L_f), Relaxation time (t), Molar volume and Molar sound velocity of the various compositions of liquid mixtures of aqueous solutions of Lithium sulphate (Li_2SO_4) and Lithium hydroxide (LiOH) from the measured values of the density, ultrasonic velocity and viscosity at 303,308,313 and 318K.The variations in these parameters have been correlated to derive the intermolecular interactions taking place between the mixtures of present study.

Keywords: intermolecular free length, relaxation time, molar volume and molar sound velocity

Introduction
The properties which may be regarded as useful for the interpretation of molecular interaction and molecular association in binary mixtures are mainly density, refractive index, dielectric constant, sound velocity, compressibility, molar volume, free volume, intermolecular free length, internal pressure, surface tension, space filling factor, Wada's constant, Rao's constant etc. From these parameters we have selected some parameters which are directly related with sound velocity and viscosity of the binary mixtures [1-5]. The aim of present study is to investigate the variation of thermo acoustical parameters of binary liquid mixture of aqueous solutions of Lithium sulphate and Lithium hydroxide with molar concentrations and temperatures. The variation of these parameters with molar concentration may be helpful in pharmaceutical and food industries to prepare various drug dosages, solution, tablets, capsule, gel and injection in solution form [6-9].

Theory
Thermodynamic parameters such as intermolecular free length (L_f), relaxation time (τ), free volume (V_f) and molar sound velocity (R) were calculated from empirical Jacobson's relations [10-14].

Intermolecular Free Length (L_f)
The empirical formula for the intermolecular free length as:

$$L_f = K\sqrt{\beta}$$

Where, b is adiabatic compressibility and K is Jacabson's constant = [98.875+0.375T] $\times 10^{-8}$ and T is the absolute temperature.

Relaxation Time (τ)
Shear's relaxation time evaluated from ultrasonic velocity measurements can give very significant information about the structure and dynamics of solution process. The Shear's relaxation time is a better and more informative parameter then isentropic compressibility as it incorporates the Shear's viscosity effect also. The equation for the evaluation of relaxation time is written as

$$\tau = \frac{4}{3}\eta\beta$$

Where η is viscosity and β is compressibility of liquid.

Molar Volume (V_m)
Molar volume is calculated by following expression:

$$V_m = \frac{M_{eff}}{\rho}$$

Where, M_{eff} is the effective molecular weight given by

$$M_{eff} = X_1M_1 + X_2M_2$$

Where X_1, X_2, and M_1, M_2 are the mole fractions and molecular weights of the components 1 and 2 of the binary mixture.

Molar Sound Velocity(R)
The molar sound velocity is calculated by the following relation

$$R = \frac{M_{eff}}{\rho}(U)^{1/3}$$

Where M_{eff} = $(X_1M_1+X_2M_2)$ is the effective molecular weight, where X_1 and X_2 are the mole fractions of pure component, M_1 and M_2 are their molecular weight respectively.
This relation may also be written as

$$R = V_m (U)^{1/3}$$

Where V_m is molar volume and U is ultrasonic velocity.

Results and Discussion
The calculated values of Intermolecular free length (L_f), relaxation time (t), Molar volume (V_m) and Molar sound

velocity (R) with the varying mole fractions of the binary mixture at different temperature are presented in tables1 to 7 using experimental values of density and ultrasonic velocity reported earlier [15]. The variations of these parameters with varying mole fraction are also presented in figure 1 to 4 for the binary mixtures.

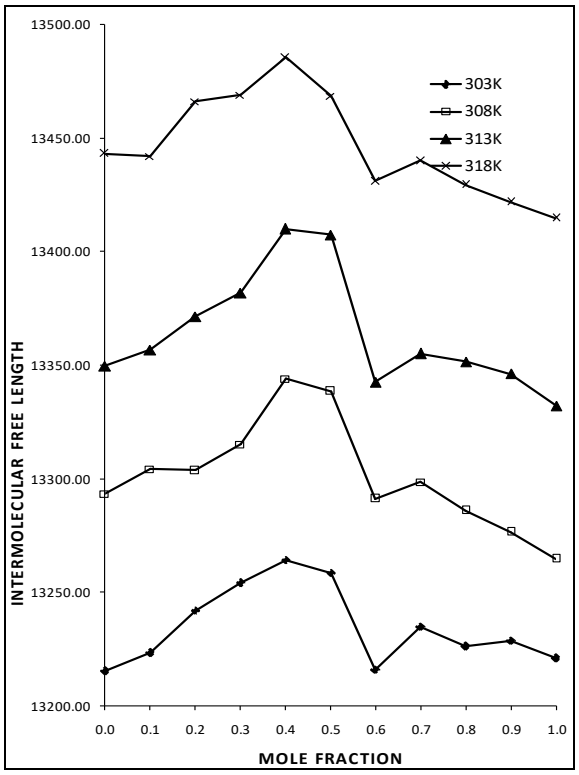

Fig 1: Variation of Inter Molecular Free Length (A°) for the binary mixture of LiOH & Li_2SO_4 with varying mole fraction

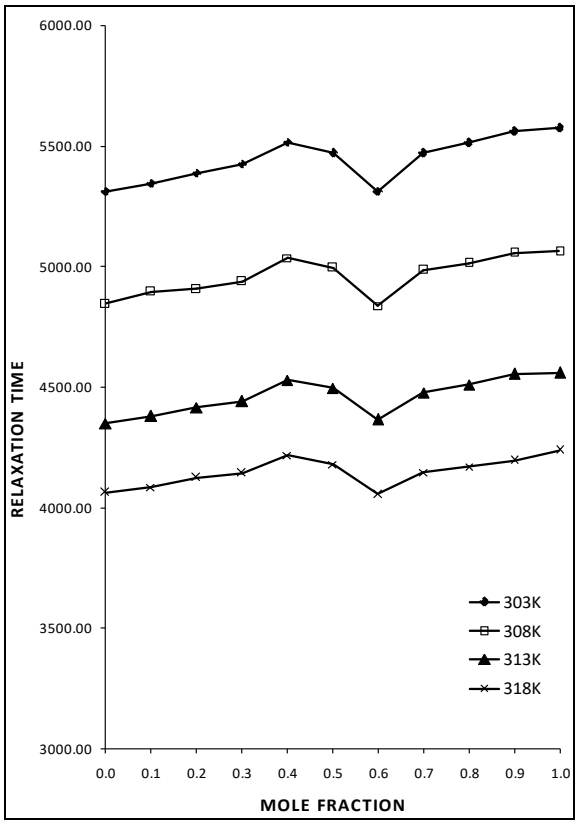

Fig 2: Variation of Relaxation Time ($\times 10^{-10}$sec.) for the binary mixture of LiOH & Li_2SO_4 with varying mole fraction

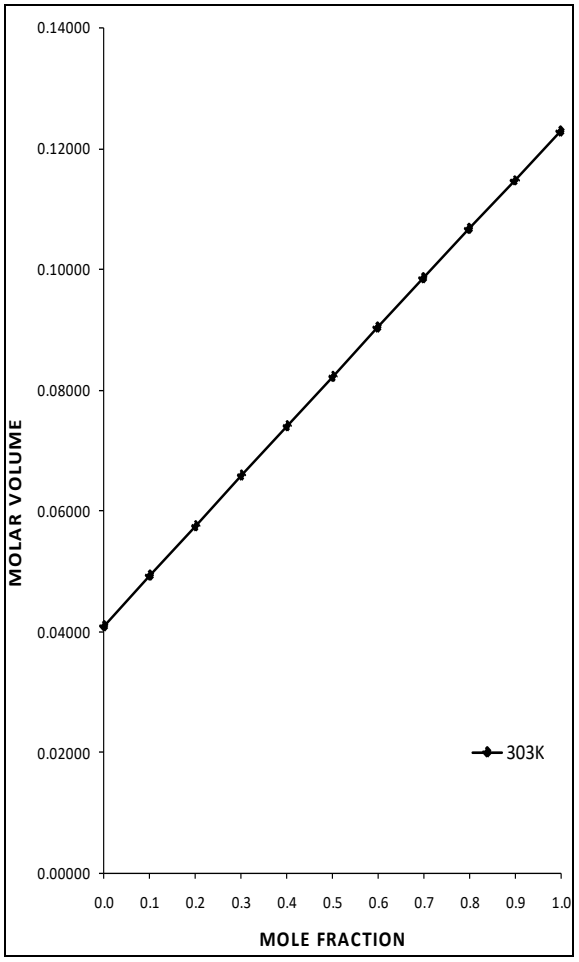

Fig 3: Variation of Molar Volume (m^3/mole) for the binary mixture of LiOH & Li_2SO_4 with varying mole fraction

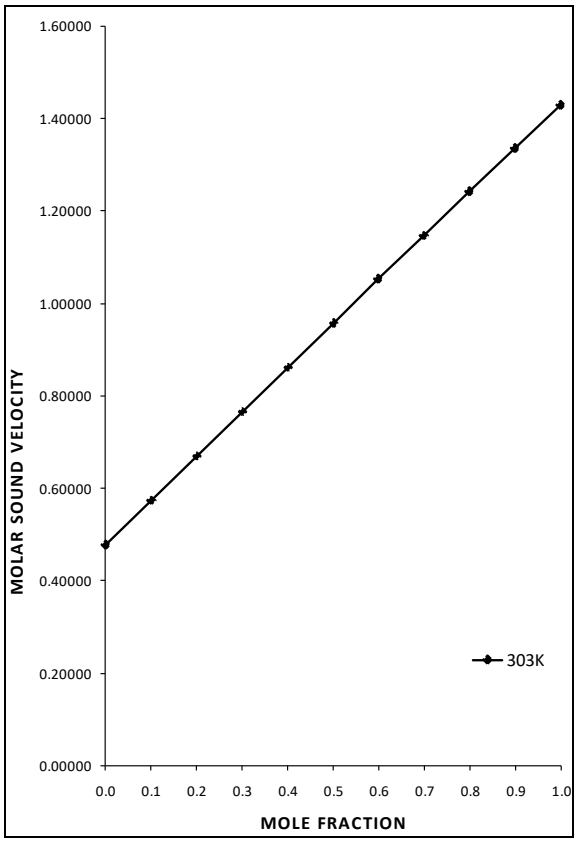

Fig 4: Variation of Molar Sound Velocity for the binary mixture of LiOH & Li_2SO_4 with varying mole fraction

Intermolecular free length (L_f)

The values of intermolecular free length (L_f) for binary mixture at temperature 303K, 308K, 313K and 318K are presented in table 2. Intermolecular free length in binary liquid mixtures can be used to access the attraction between the component molecules. It denotes the magnitude of either the ion-ion interaction or the ion solvent interaction or both in a binary mixture. Intermolecular free length depends upon the adiabatic compressibility and show a behavior similar to that of the compressibility and inverse to the ultrasonic velocity.

The graphical representation of intermolecular free length is shown in fig. 1 where the free length decreases with increasing mole fraction of Li_2SO_4. The reason is that increasing the number of larger sulphate ions in a given volume leads to decrease in gap between the molecules of two species (solute-solvent). The decreasing free length shows a sudden decrease at a specific mole fraction (0.6) of $Li_2SO_4$and on further increasing the mole fraction the intermolecular free length again decreases non linearly, there by indicating that there is a significant interaction present between solute and solvent molecules, due to which structural arrangements are considerably affected. A number of other workers also indicated the similar trends about intermolecular free length as indicated in present study [16, 17].

Relaxation time (τ)

When we pass ultrasonic waves in any liquid some energy is transferred to the molecules of solution as the finite acoustic impedance of liquid restricts the free movement of ultrasonic wave through it. The amount of energy passed to a given volume of liquid grows exponentially with time to its final value and is characterized by a finite time constant which is known as the relaxation time (τ). The Shear's relaxation time is a better and more informative parameter than the compressibility (β) as it incorporates Sear's viscosity effect also.

The values of relaxation time (τ) for all possible mole fractions of binary mixture are presented in table 3 at temperature 303K, 308K, 313K and 318K and the variation of relaxation time with increasing mole fraction of Li_2SO_4shown graphically in fig. 3 On increasing mole fraction of Li_2SO_4relaxation time increases non linearly and at a specific mole fraction (0.6) it shows a sudden decrease and on further increasing the mole fraction, the relaxation time again starts increasing. This specific mole fraction is exactly same as that observed in case of velocity, adiabatic compressibility, acoustic impedance and intermolecular free length which confirm the complex formation and strong ion solvent interactions in binary mixture at 0.6 mole fraction of Li_2SO_4. Dange [13] has reported the increase in relaxation time with increasing mole fraction in binary mixtures of Nicotinic acid in methanol solutions at 288, 298 and 308 K and indicated the presence of molecular interactions by addition of solute concentration at given temperature. He also reported decrease in relaxation time with increase in temperature at all mole fractions. Similar results are shown in fig. 3 in our present study.

Molar Volume

For the binary mixture the values of molar volume (V_m) are presented in table 4 for all mole fractions at temperature 303K, 308K, 313 and 318K. Since in a binary mixture two components are mixed in varying proportions thus to calculate the molar volume, we have first calculated the effective mass (M_{eff}) of all combination of binary mixture. Then dividing the effective mass of binary mixture of any specific mole fraction by its density (determined experimentally) we have calculated the molar volume of binary mixture for every mole fraction under consideration. Graphical representation of molar volume is shown in fig. 4 where molar volume increases linearly with increasing mole fraction and with increasing temperature the molar volume gets decreased for every mole fraction. As for any specific mole fraction M_{eff} remains the same at all temperature and density increases with increasing temperature thus molar volume gets decreased with increase in temperature.

Molar sound velocity

Using the values of molar volume, we have calculated the values of an important parameter called molar sound velocity or Rao's molar sound function (R). The values of molar sound velocity are presented in table 5 and their graphical representation is shown in fig.5 for binary mixture at temperature 303K, 308K, 313K and 318K. On increasing the mole fraction of Li_2SO_4 molar sound velocity increases linearly at all temperatures which again supports the existence of ion solvent interactions and complex formation. Similar behavior of molar sound velocity is reported earlier by Thorat [18]. The molar sound velocity depends directly on cube root of ultrasonic velocity thus it shows the behavior quite similar to that shown by ultrasonic velocity. The molar sound velocity also increases on increasing the temperature for all mole fractions.

Conclusion

From the above discussion it is quite clear that the variation of acoustic and thermodynamic parameters with concentration and temperature strongly supports the existence of molecular interactions in the binary mixture. Further the sudden rise or fall in various parameter at the same specific mole fraction (0.5) of Li_2SO_4confirm the complex formation at this mole fraction.

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