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Ultrasonic Study Of L-Valine In Aqueous Magnesium Nitrate Solutions At 303.15K

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ABSTRACT:

Molecular interaction studies using ultrasonic technique in the binary liquid mixture of amino acid in aqueous solutions of electrolyte has been carried out at 303.15 K. Using measured values of Density (ρ), Ultrasonic Velocity (U), Viscosity (η) and acoustical parameters such as Adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A) evaluated. From the properties of these parameters, the nature and the strength of molecular interactions in this binary system are discussed. The results are interpreted in terms of molecular interaction between the component of the mixtures.

KEYWORDS: Velocity, Acoustical parameters, Amino acid, Magnesium Nitrate

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INTRODUCTION:

The study of molecular interaction in binary and ternary liquid mixtures plays an important role in the development of molecular sciences. A large number of studies have been made on the intermolecular interaction in liquid system by various methods like Ultraviolet, Dielectric constant, Infrared, Raman Effect, Nuclear magnetic resonance and Ultrasonic method. In recent years Ultrasonic method has become a powerful tool in providing information regarding the physico-chemical properties of liquid system. The study of L-Valine in aqueous MgNo₃ at 303.15 K. Ultrasonic and thermodynamic properties of these model compounds (amino acid) in aqueous electrolytes media provide information of solute–solvent and solute–solute interactions¹⁻⁴. Metal ions have been reported⁵⁻⁸ The amino acid is selected as a solvent in the present work since it finds a variety of applications. The ultrasonic study of liquids is very important in understanding the nature and strength of molecular interactions. The biological activity of drug molecules and the activation energy of the metabolic process basically depend on the type and strength of the intermolecular interactions. Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality. The ultrasonic velocity (U), density (ρ) and viscosity (η) can be used to study the physicochemical behavior and molecular interactions such as ion-solvent interaction and solvent-solvent in pure liquids, liquid mixtures and solutions.

In view of growing interest, the result of an ultrasonic velocity, density and viscosity to study the related acoustical parameters for the binary system of aqueous MgNo₃+amino acid at the temperature 303.15K have been reported in the present paper.

EXPERIMENTAL DETAILS:

Analytical reagent (AR) grade and spectroscopic reagent (SR) grade with minimum assay of 99.9% of L-Valine and Magnesium Nitrate were obtained from SISCO Research Laboratories and Sd Fine chemicals, India which is used as such without further purification. Water used in the experiment was deionised, distilled and degassed prior to making solutions. The required quantity of L-Valine for given molality was dissolved and similar procedure has been adopted for different molalities of L-valine with a precision of 0.1 mg an electronic digital balance (Model: SHIMADZU AX-200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kg}\times\text{m}^{-3}$. An ultrasonic interferometer having the frequency 3MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F-81) with an overall accuracy of 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell

made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K. The various acoustical parameters such as Adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A), have been calculated from the measured data using the following standard expressions⁹.

The adiabatic compressibility β , were calculated using the following relation:

$$\beta = 1/\rho u^2 \quad \dots(1)$$

where ρ is the density of the mixture and u is the ultrasonic velocity.

Inter molecular free length

$$L_f = K_T \beta^{1/2} \quad \dots(2)$$

Where K_T is the temperature dependent constant.

The acoustic impedance is given by the product of ultrasonic velocity and density as shown below:

$$Z = U \times \rho \quad \dots(3)$$

$$\text{Relative association } R_A = (\rho_0/\rho)X(U_0/U)^{1/2} \quad \dots(4)$$

Density of the solute = ρ , u = Velocity of the solute

Density of the Solvent = ρ_0 , U_0 = Velocity of solvent

RESULTS AND DISCUSSION:

The experimentally measured values of Density (ρ), Ultrasonic velocity (U), Viscosity (η) and thermodynamic parameters such as Adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A) of the system at temperature 303.15 K at frequency 3MHz are presented in Table-1

Table 1. The experimentally measured values of Density (ρ), Ultrasonic velocity (U), Viscosity (η) and the calculated values of Adiabatic compressibility (β_a), Intermolecular free length (L_f), specific acoustical impedance (Z) and) and Relative association (R_A) with respect to mole fractions of amino acid in electrolyte at temperature 303.15K.

| Molality | (ρ) Density | (η) Viscosity | (U) Velocity | (β) Adiabatic compressibility | (L_f) Intermolecular free length | (Z) Acoustic Impedance | (R) Relative association |
|----------|-----------------------|-------------------------|---------------------|---|--|----------------------------------|------------------------------------|
| 0.0 | 1014.3 | 0.8554 | 1526.7 | 4.286 | 0.132115 | 0.6668 | 0.99502 |
| 0.1 | 1017.5 | 0.8733 | 1534.2 | 4.230 | 0.131626 | 0.6670 | 0.99608 |
| 0.2 | 1020.7 | 0.8832 | 1541.7 | 4.180 | 0.131001 | 0.6671 | 0.99688 |
| 0.3 | 1023.9 | 0.8931 | 1549.2 | 4.133 | 0.130762 | 0.6673 | 0.99716 |
| 0.4 | 1027.1 | 0.9193 | 1556.7 | 4.083 | 0.130333 | 0.6674 | 0.99755 |
| 0.5 | 1030.3 | 0.9229 | 1564.2 | 4.034 | 0.129487 | 0.6675 | 0.99850 |

Table-1 shows that, ultrasonic velocity, density, viscosity, acoustic impedance and relative

association increases while adiabatic compressibility and intermolecular free length decreases with concentration of amino acid in electrolyte at temperature 303.15K

From the Table.1 The ultrasonic velocity increases with the concentration. The trend in ultrasonic velocity values in this system indicates stronger interactions between electrolyte and L-Valine. Thus complication is concentration dependent.

Ultrasonic velocity (u) is related to intermolecular free length. As the free length decreases due to the increase in concentrations, the ultrasonic velocity has to increase. Consequently, ultrasonic velocity of the systems increases depending on the structural properties of solutes. The solute increases the ultrasonic velocity is structure maker¹⁰. In (water+ $MgNO_3$ + valine) system, ultrasonic velocity increases with concentrations of solutes indicates stronger the intermolecular forces in the solution. This gives increase in closed packed structure of aqueous amino acids i.e. enhancement of the closed structure. This provides the cohesion between amino acids and water molecules increases. Thus the inter molecular distance decreases with concentrations of solutes. The decrease in intermolecular free length may due to the gain of dipolar association, making up of hydrogen bonds in the molecules of the liquid mixtures.

The variation of ultrasonic velocity of valine at various concentrations, co- solvent of water and $MgNO_3$ shows the variation to be non-linear. The nature of variation of ultrasonic velocity (u) with concentration (m) is evident from Table, 1 this non linear variation indicates the presence of strong interactions in the system.

The increase in ultrasonic velocity (u) in these solutions may be attributed to the cohesion brought about by the ionic hydration. When the amino acid are dissolved in aqueous $MgNO_3$, water molecules are attracted to the ions strongly by the electrostatic forces¹¹. This introduces a greater cohesion in the solution. Thus cohesion increases with L-Valine concentration in the solution. The increased associations obtained in these solutions may also be due to water enhancement brought by the increase in electrostriction in the presence of sodium chloride and magnesium chloride. The electrostriction effect brings about the shrinkage in the volume of solvent caused by the zwitterionic portion of the valine.

The increase in density with molar concentration suggest a solute-solvent interaction exist between the electrolyte and water. In other words the increase in density may be interpreted to the structure maker of the solvent due to H-bonding.

The viscosity is an important parameter in understanding the structure as well as molecular interaction occurring in the solutions. From above Table-1, it is observed that viscosity of the solutions shows a non-linear behavior in the system¹². The increase in viscosity with concentration

in the system suggests that the extent of complexation increase with increase in concentration and more association between solute and solvent molecules¹³⁻¹⁴.

Adiabatic compressibility is calculated using Eq. (4).

The calculated experimental values of (β) are presented in Table 1, for system (water + MgNO_3 + valine). In the present case, adiabatic compressibility (β) decreases with increase in concentrations of valine.

This is because as the concentrations of solute increases, a larger portion of water molecules are electrostatic and the amount of bulk water decreases causing the compressibility to decrease. It is well known that solutes causing electrostriction lead to decreases in the compressibility of the solution. Hydrophilic solutes often show negative compressibility as well, due to ordering that is induced by them in water structure¹⁵.

Acoustic impedance is calculated by using Eq. (4). From Table.1, it is observed that the adiabatic compressibility (β_a) decreases with increase in concentrations, whereas, acoustic impedance (z) increases for the same concentrations. For a given concentration, adiabatic compressibility (β_a) decreases and acoustic impedance (z) increases. So the composition is the specific composition, where the acoustic parameter becomes either maximum or minimum. This is the stage where complex formation is taking place in the system due to increased ion – solvent interaction. For a given concentration the values of acoustic impedance (z) increases with increase in concentration in liquid system (water+ MgNO_3 +valine). It is in good agreement with the theoretical requirements because ultrasonic velocity increases with increase in concentrations of solutes in liquid mixtures. The increase in (z) with the increase in concentration of solution can be explained on the basis of hydrophobic interaction between solute and solvent molecules¹⁶⁻¹⁷. It increases the intermolecular distance, making relatively wider gap between the molecules.

The variation in ultrasonic velocity depends on the Intermolecular free length (L_f) on mixing. It is a predominant factor in determining the variation of ultrasonic velocity in fluids and in their solutions. It has been observed that, in the present investigation, intermolecular free length decreases with increase in valine concentration at all temperatures. The decrease¹⁸ in L_f indicates that there is significant interaction between solute and co-solvent suggesting the structure promoting behavior on addition of electrolyte.

The values of relative association (R_A) for (water+ MgNO_3 +valine) system are calculated by using Eq. (7). The variations of relative association (R_A) with concentration conclude that R_A increases with concentration of valine. The property which can be studied to understand the molecular interaction is the relative association (R_A).

It is influenced by two factors: (i) Breaking up of the associated solvent molecules on addition of solute in it and (ii) The salvation of solute molecule. The thermodynamic parameters are given in Table 1

CONCLUSION:

Ultrasonic technique is a powerful tool for characterising the physical properties and existence of molecular interaction in the mixture. The results of the present investigation reveal that solute-solvent and solvent-solvent interactions play a vital role for explaining the different thermo-acoustical parameters of electrolytes in aqueous Magnesium nitrate systems at 303.15K. Strong dispersive type intermolecular interactions are confirmed in the system investigated. All the experimental determinations of acoustic parameters are strongly correlated with each other.

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