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Original Article

"Ultrasonic Velocity, Density and Viscosity Measurement of Amino Acid in Aqueous Electrolytic Solutions at 308.15K"

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ABSTRACT

Objective: The objective of the study was molecular interactions in the liquid mixtures is very much important to study the structural properties of molecules and great deal of interest in investigating the solute-solute, solute-solvent and solvent-solvent interaction.

Methods: With a view to understand the molecular interaction in electrolyte with amino acid based liquid system There are many approaches and spectroscopic techniques used to determine the structure-function relationship of bio-molecules. The methods are often interconnected and therefore providing a complementary information about the studied biomolecular structure. Among the techniques used, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular systems and physico–chemical behavior in liquid mixtures.

The ultrasonic velocity (U) in liquid and liquids mixtures have been measured using an ultrasonic interferometer (Mittal type, Model F-81) working at 2 MH_z frequency with an accuracy of ± 0.1 ms^{-1}.

The density of pure liquids and liquid mixtures was determined using specific gravity bottle by relative measurement method with accuracy of ±0.1Kgm^{-3} .An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of ±0.0001NSm^{-2}. The temperature around the viscometer and specific gravity bottle was maintained within ±0.1K in an electronically operated constant temperature water bath.

Results: Density and ultrasonic velocity provide interesting information regarding the ion-ion ion-solvent and solvent-solvent interactions and also on structural effects of solute and solvent in solutions. A systematic study using ultrasonic velocity (u), density (ρ) and viscosity (η) measurements as a function of mole fraction has been carried out. The temperature dependence of these quantities has also been investigated at 308.15K using this experimental data, thermodynamic parameters such as the adiabatic compressibility (β_a), intermolecular free length

(L_f), acoustic impedance (z) and relative association (R_A) of amino acids in aqueous solution of electrolyte at 308.15K temperature and at different concentrations of solutes have been studied and have been estimated using the standard relations. The results have been analyzed on the basis of variations of thermodynamic parameters. The presence of strong interactions is noticed in the ternary system.

Conclusion: At various concentrations and temperature in valine-based system, shows the non-linear increase or decrease behavior. The non linearity confirms the presence of solute-solvent, ion-ion, dipole-dipole, ion-solvent interactions. The observed molecular interaction, complex formation, hydrogen bond formation are responsible for the heteromolecular interaction in the liquid mixture. This provides useful information about inter and intra molecular interactions of liquid systems.

Keywords: Ultrasonic velocity, Acoustical properties, Molecular interactions, Valine (amino acid), NaCl (electrolyte), Binary liquid mixture.

INTRODUCTION

Ultrasonic velocity and thermodynamic parameters derived from these measurements are widely used to study of molecular interactions[1-3] in pure liquid, aqueous solutions and liquid mixtures. The bimolecules play an important role in the body functions. Proteins[4] are found in all parts of the body and they have an enormous variety of functions. The denaturation of globular protein in aqueous solution is fundamental biological processes which is not yet completely understood and remain a subject of extensive investigation[5]. In the process of denaturation of globular proteins in aqueous solutions, the native folded conformation of protein is converted predominantly into an extended unfolded form and during this process various changes will occurs in protein salvation. Thus the study of these solute-solvent and solute-solute interactions is essential due to their important contribution to the energetic of protein denaturation.

Amino acids and peptides are used as probe molecules to understand the complex nature of protein. The most remarkable thing is the amino acids serve not only as precursors of hormones, alkaloids, purphysis pruines, nerves, transition of all growth and many other biomolecules Amino acids in aqueous solution are ionized and can act as acid or bases. Knowledge of acid-base properties of amino acids is extremely important in understanding many properties of proteins. The addition of salts/solvents to protein solution is known to affect their structure and configuration. Most of the chemical and biological functions of bimolecules take place in aqueous medium. Electrolytes are expected to influence water structure, and the importance of contribution from structural changes of the solvent to the thermodynamic properties of aqueous solutions of biological molecules has often stressed. The information on the zwitter-ionic nature of amino acids in water is given in the literature[5,6]. The properties of proteins such as their structure, solubility, denaturation, activity of enzymes, etc. are greatly influence by electrolytes[7,8]. An electrolytes, when dissolve in water, perturbs the arrangement of water molecules with the strong electric field of its ions. This property of electrolytes known as structure makers or breaker has been widely used to understand the effect of electrolytes on the

structure and function of proteins.

EXPERIMENTAL DETAILS

All the chemicals used were of AR grade and dried over anhydrous $CaCl_2$ in desiccators before use. All solutions were prepared in deionizer and distilled water (degassed by boiling), having specific conductivity ~ 10^{-6} S cm^{-1}. The stock solutions of 1M concentration were prepared by weighing the valine on a digital balance with an accuracy of ± 1 x 10^{-4} g. Solution of NaCl were made by mass on the mole fraction scale. Uncertainties in solution concentrations were estimated at ± 1 x 10^{-5} mol kg^{-1} in calculations. The solutions were kept in the special air tight bottles and were used within 12 hrs. After preparation to minimize decomposition due to bacterial contamination. Ultrasonic velocity was measured with a single crystal interferometer (F- 81, Mittal Enterprises, New Delhi) at $2MH_z$. Accuracy in the velocity measurement was ± 1.0 ms^{-1}. The density measurements were performed with recalibrated specific gravity bottle with an accuracy of ± 2x10^{-2} kg m^{-3}. An average of triple measurements was taken into account. Sufficient care was taken to avoid any air bubble entrapment. Viscosity was measured with recalibrated Ostwald type viscometer. The flow of time was measured with a digital stop watch capable of registering time accurate to ± 0.1 s. An average of three or four sets of flow of times for each solution was taken for the purpose of calculation of viscosity. The accuracy of the viscosity measurements was ± 0.5 %. Accuracy in experimental temperature was maintained at ± 0.1K by means of thermostatic water bath. The various acoustical parameters such as adiabatic compressibility (β_a), free length (L_f), Acoustic impedance (Z) and Relative association (R_A), have been calculated from the measured data using the following standard expressions[9-18].

Ultrasonic velocity $u = n \times \lambda$ ($m\ s^{-1}$).....(1)

Adiabatic compressibility $\beta_a = 1/u^2 \rho$ (m^2N^{-1})……..(2)

Intermolecular free length $L_f = k\ \beta^{1/2}$ (A^0)…… (3)

Where k is temperature dependent constant called as Jacobson constant it is 631×10^{-6}, 642×10^{-6} and 651×10^{-6} for 303.15, 308.15 and 313.15 K respectively[10].

Specific acoustic impedance $Z = \rho . u$ (Nm^{-2})……..…… (4)

Relative association $R_A = (\rho_0/\rho)x\ (u_0/u)^{1/2}$ ……...…….(5)

ρ= density of solute, $\rho_{0=}$ density of solvent, u= velocity of solute, $u_{0=}$ velocity of solvent.

RESULTS AND DISCUSSION

The experimentally measured values of Density (ρ), Ultrasonic velocity (U) and Viscosity (η) and thermodynamic parameters Adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A) of binary liquid (amino acid in electrolyte) system at temperature 308.15 K at frequency $2MH_z$ are presented in Table-1.

Table-1 shows that, ultrasonic velocity, density, viscosity, acoustic impedance and relative association increases while adiabatic compressibility and inter-molecular free length decreases with concentration of amino acid in electrolyte at temperature 308.15K.

Ultrasonic velocity (u)

The ultrasonic velocity (u) for amino acid electrolyte solutions at 2MHz frequency and at 308.15k temperature have been determined using relation (1) and presented in Table-1. From Table-1 the variations in ultrasonic velocity in liquid mixtures depend on concentrations (x) of solutes and

temperature. Ultrasonic velocity (u) is related to, intermolecular free length. As the free length decreases due to the increase in concentrations of solutes, the ultrasonic velocity has to increase. The experimental results support the above statement in liquid system. Consequently, ultrasonic velocity of system increases depending on the structural properties of solutes. The solute that increases the ultrasonic velocity is structure maker. Ultrasonic velocity increases with increase in concentrations of solutes. When NaCl is dissolved in solution, the sodium ion Na^+ has a structure breaking effect, would disrupt the water structure. This makes the liquid medium less compressible and hence the ultrasonic velocity increases above that of pure value.

The increase in density with molal 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. Similarly, the decrease in density with concentration indicator structure-breaker of the solvent. It may be also true that solvent-solvent interactions bring about a bonding, probably H-bonding between them. So, size of the resultant molecule increases and hence there will be decrease in density.

The viscosity is an important parameter in understanding the structure as well as molecular interaction occurring in the solutions. From above table, it is observed that viscosity of the solutions shows a non-linear behavior in the system. The increase in viscosity with concentration in all the system suggests that the extent of complexation increase with increase in concentration.

Adiabatic compressibility (β)

When an aqueous electrolyte solution is added to a valine, it attracts certain solvent molecules towards itself by wrenching the molecules from bulk of the solvent due to the forces of electrostriction. Due to this the volume available in solvent molecule for the next incoming ion gets decreased. The adiabatic compressibility is calculated using equation (2). The calculated values of (β_a) have been presented in Table-1, From table- 1 it is clear that the compressibility of a solvent is higher than that of a solution and it decreases with increase in concentrations. The absence of hydrophobic hydration in valine due to absence of any methyl group causes valine under a higher electrostriction effect than other amino acids containing methyl group (Methyl group tightens the water molecules around itself).

Acoustic impendence (z)

Acoustic impedance (z) is found to be almost inversely to the adiabatic compressibility (β_a). Specific acoustic impedance is calculated by using standard relation (3). The calculated values of z are mention in Table -1. From this table, it is observed that acoustic impedance (z) increases with increase in concentrations. Acoustic impedance becomes either maximum or minimum depending on the concentrations and at temperature 308.15K. This is the stage where complex formation is taking place in the liquid system due to increased electrolyte-amino acid interaction. For a given concentration the values of acoustic impendence (z) increases with increase in concentration in liquid system (Water + NaCl + 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 concentrations of solutes can be explained in terms of inter and intra molecular interactions between the molecules of liquid mixtures. This indicates significant interactions in the liquid system.

Intermolecular free length (L_f)

The values of intermolecular free length for (Water + NaCl + Valine) system have been calculated using equation (4). Increase in concentrations leads to decrease in gap between two species which is referred by intermolecular free length (L_f). With the increase in concentrations of solutes, intermolecular free length (L_f) has to decrease. Intermolecular free length (L_f) is predominant factor in determining the variations of ultrasonic velocity in liquid mixtures. From Table -1, it has been observed that, in the present investigation, intermolecular free length decreases linearly on increasing concentration. The decrease in L_f with increase of concentration in solution indicates that there are significant interactions between solute and solvent suggesting the structure promoting behavior of solutes. Ultrasonic velocity increases with concentration 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. The reduction in degree of dissociation among the liquid molecules of the mixture. Thus the inter molecular distance decreases with concentration. The decrease in free length may due to the gain of dipolar association, making up of hydrogen bonds in the molecules of the liquid mixtures.

Relative association (R_A)

The values of relative association (R_A) for liquid system (Water + NaCl + Valine) have been estimated using relation (5). The property which can be studied to understand the 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 former leads to the decrease and later to the increase of relative association.

Table-1, it is observed that, R_A increases with increase in the concentrations.

CONCLUSION

The observed trends and variations of thermo dynamical parameters with molar concentrations of amino acid provide useful information about the nature of intermolecular forces existing in the mixture. The existence of ion-solvent (or) solvent-solvent interaction resulting in attractive forces promote the structure-making tendency, while ion-ion are solute-solute interaction resulting dipole-dipole, dipole induced dipole and electrostrictive forces enhance the structure-breaking properties of amino acid. An appreciable existence of solute-solvent and solute-solute interactions present in the system with varying degrees hence it is evident that the ultrasonic velocity measurement in the given medium serves as a parerful probe in characterizing the physico-chemical properties of the medium.

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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 Relative association (R_A) with respect to mole fractions of amino acid in electrolyte at temperature 308.15K and at 2MHz frequency.

m mol kg^{-1}	u ms^{-1}	ρ $kg\ m^{-3}$	η $Nm^{-2}s$	$\beta_a x10^{-10}$ m^2N^{-1}	$zx10^6$ Nm^{-2}	L_f A^0	R_A
Water + NaCl + valine							
0.000	1594.20	1064	1.2376	3.6980	1.69622	0.39914	1.05401
0.008	1574.20	1063	1.0761	3.7962	1.67337	0.40805	1.06053
0.017	1618.70	1086	1.2394	3.5143	1.75791	0.38909	1.07035
0.026	1627.20	1092	1.2708	3.4543	1.77710	0.38510	1.07417
0.034	1628.20	1096	1.3049	3.4459	1.78341	0.38505	1.07832
0.043	1638.24	1104	1.3189	3.3750	1.80861	0.38130	1.08375

Where m, mole fraction; ρ, density of the solution ; η,viscosity of solution; u, ultrasonic velocity;β_a, adiabatic compressibility; L_f, intermolecular free length; R_A, relative association; z, acoustic impedance.