

Ultrasonic Investigation of Molecular Interactions in Binary Mixtures at 303.15K

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Abstract: *The ultrasonic velocity, density and viscosity at 303K have been measured in binary systems of amino acids with electrolytes. From experimental data acoustical parameters such as adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f), relative association (R_A) have been estimated using the standard relations. The results have been analyzed in terms of molecular interaction between the components of the mixtures.*

Keywords: *ultrasonic velocity (u), density (ρ), viscosity (η), acoustical parameters.*

1. INTRODUCTION

Ultrasonic investigation in aqueous solutions of electrolytes and non –electrolytes with amino acids provides useful information in understanding the behavior of liquid systems because intermolecular and intermolecular association, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variation in the ultrasonic velocity. During the last two decades, the ultrasonic study has been carried out to investigate hydration of proteins through volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration¹⁻⁷. Due to complex molecular structure of proteins, direct study is somewhat difficult there for the useful approach is to study simple's model compounds such as amino acids which are building blocks of proteins. Most of studies on amino acids and bio-molecules have been carried out in pure and mixed aqueous solutions⁸⁻¹⁰. Amino acids and peptides are the fundamental structural units of protein. The investigations on volumetric and thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solvents have been the area of interest of a number of researchers the thermodynamics of interaction of concentrated NaCl in dilute amino acids have been reported in the literature¹¹⁻¹³. How the ion-ion and ion-amino acid interactions together with ion-water and amino acid-water ones are altered in concentrated electrolyte and concentrated amino acid solutions is the object of current investigations. Information is available on activity coefficients, enthalpies and heat capacities of aqueous amino acids in electrolytes¹⁴⁻¹⁷. To our knowledge no systematic efforts have been made to the ion-ion and ion amino acid interactions in concentrated electrolyte solutions.

2. EXPERIMENTAL

All the chemicals used were of AR grade and dried over anhydrous CaCl₂ in desiccators before use. All solutions were prepared in deionized and distilled water (degassed by boiling), having specific conductivity $\sim 10^{-6}$ S cm⁻¹. The stock solutions of 1M concentration were prepared by weighing the serine on a digital balance with an accuracy of $\pm 1 \times 10^{-4}$ g. Solutions of NaCl & MgCl₂ were made by mass on the mole fraction scale. Uncertainties in solution concentrations

were estimated at $\pm 1 \times 10^{-5} \text{ mol kg}^{-1}$ 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 2MHz. The interferometer was calibrated against the ultrasonic velocity of water used at $T = 303.15\text{K}$. The present experimental value is 1508.80 ms^{-1} which is in good agreement with literature value 1509.55 ms^{-1} . Accuracy in the velocity measurement was $\pm 1.0 \text{ ms}^{-1}$. The density measurements were performed with recalibrated specific gravity bottle with an accuracy of $\pm 2 \times 10^{-2} \text{ kg m}^{-3}$. 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 $\pm 0.1 \text{ s}$. 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 $\pm 0.5 \%$. Accuracy in experimental temperature was maintained at $\pm 0.1\text{K}$ by means of thermostatic water bath.

3. RESULTS AND DISCUSSION

From the measured values ultrasonic velocity (u), density (ρ) and viscosity (η) various acoustical parameters such as the adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A) were calculated by using the following relations¹⁸⁻²¹

$$\text{Ultrasonic velocity} \quad (u) = n \times \lambda \quad (1)$$

$$\text{Adiabatic compressibility} \quad (\beta_a) = 1/u^2 \rho \quad (2)$$

$$\text{Acoustic impedance} \quad (z) = u \cdot \rho \quad (3)$$

$$\text{Intermolecular free length} \quad (L_f) = K / u \cdot \rho^{1/2} \quad (4)$$

$$\text{Relative association} \quad (R_A) = (\rho / \rho_0) \cdot (u_0 / u)^{1/3} \quad (5)$$

Where, K is the temperature dependant Jacobson constant¹⁰.

The values of $K \times 10^4$ are taken as 207.556×10^{-8} , 209.431×10^{-8} and 211.306×10^{-8} at 303.15 , 308.15 and 313.15K . T is the absolute temperature, ρ_0 , ρ and u_0 , u are the density and ultrasonic velocity of solvent and solution respectively.

The experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) of the solutions and calculated values of acoustical parameters such as adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A) are reported in Table -1 for the systems (water + NaCl + serine) and for the system (water + MgCl_2 + serine) respectively.

Table 1. Variation of thermodynamic parameters at different mole fractions (x) and different temperatures for the system (NaCl + Serine) & (MgCl_2 + Serine) at 303.15K

m mol kg^{-1}	u ms^{-1}	ρ Kg m^{-3}	η Nm^{-2}s	$\beta \times 10^{-10}$ m^2N^{-1}	$z \times 10^{-6}$ Nm^{-2}	L_f \AA^0	R_A
NaCl + Serine							
0.000	1551.80	1058.11	1.06195	3.92502	1.64180	0.41120	1.05285
0.008	1564.88	1064.54	1.16268	3.83071	1.66816	0.40623	1.05785
0.017	1593.18	1078.71	1.37615	3.65472	1.71745	0.39679	1.06339
0.026	1601.16	1081.52	1.55944	3.60831	1.73085	0.39426	1.06458
0.034	1618.12	1087.01	1.61528	3.51368	1.75890	0.38905	1.06674
0.043	1651.64	1094.01	1.87772	3.35085	1.80689	0.37994	1.06630

m mol kg^{-1}	u ms^{-1}	ρ Kg m^{-3}	η Nm^{-2}s	$\beta \times 10^{-10}$ m^2N^{-1}	$z \times 10^{-6}$ Nm^{-2}	L_f \AA^0	R_A
MgCl_2 + Serine							

0.000	1560.51	1058.38	1.06103	3.88131	1.65101	0.40891	1.05089
0.008	1581.00	1064.78	1.17284	3.74601	1.68851	0.40172	1.05622
0.017	1599.76	1081.34	1.38746	3.61468	1.72934	0.39817	1.06489
0.026	1618.88	1096.66	1.56448	3.48142	1.74234	0.39461	1.07540
0.034	1627.20	1100.24	1.38931	3.43346	1.78992	0.38459	1.07749
0.043	1642.80	1116.85	1.89523	3.32024	1.83336	0.38384	1.08969

On comparing NaCl and MgCl₂ the zigzag values are obtained for β_a , but for MgCl₂ the increasing trend is observed, its shows that the interaction is higher in the second systems.. The variation of ultrasonic velocity in a solution depends on the intermolecular free length (L_f). Intermolecular free length is a predominant factor, as it determines the sound velocity in fluid state. Presence of an ion alters the intermolecular free length. Therefore, ultrasonic velocity of a solution will be different from that of the solvent.

According to model proposed by Eyring and Kincaid^{22, 23} the increase in ultrasonic velocity with the decrease in intermolecular free length (L_f) and vice versa in a result of mixing components. The decrease or increase in the values of L_f can be explained on the basis of interactions between the solute and solvent molecules.for a given concentration.

The values of acoustic impedance (z) increases with increase in concentrations. It is in good agreement with the theoretical requirements because ultrasonic velocity increases with increase in concentrations of serine. The increase in acoustic impedance (z) with the increase in concentration of solution can be explained on the basis of hyophobic interaction between solute and solvent molecules^{24,25} which increases the intermolecular distance, making relatively wider gap between the molecules. This also indicates significant interactions in the systems of serine in aqueous NaCl as a co-solvent. The values of acoustic impedance are maximum in aqueous MgCl₂ solution, moderate in water and minimum in NaCl.

The values of relative association (R_A) for (NaCl + serine) and (MgCl₂ + serine) systems were calculated using Eq. (5).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 solvation of solute molecule²⁶. The former leads to the decrease and later to the increase of relative association. From Tables 4.14.1 and 4.14.3, it is observed that, R_A increases with increase in the solute concentrations (serine &valine) in the NaCl solution.

The values of relative association (R_A) are minimum in water, moderate in aqueous MgCl₂ and maximum in aqueous NaCl.

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