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Research Article

EXCESS THERMODYNAMICAL PROPERTITIES OF ELECTROLYTES SOLUTION WITH AQUEOUS BIOMOLECULES AT 298.15K

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ABSTRACT

Ultrasonic velocities (u), densities (ρ) and viscosities (η) have been measured for the binary liquid systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$). The ultrasonic velocity measurements have been carried out by ultrasonic interferometer technique at frequency of 2 MHz and at constant temperature of 298.15 K. Using these experimental data, derived thermodynamic parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), acoustic impedance (z), and relative association (R_A) have been computed using standard formulae. The results have been interpreted on the basis of variations in thermodynamic parameters and excess parameters. The variations in ultrasonic velocity and adiabatic compressibility with concentrations in both the systems show similar trends of increasing ultrasonic velocity and decreasing adiabatic compressibility of constituent electrolytes at 298.15K. This is due to complex formation and coordinate covalent bond form between the molecules of liquid solutions. Excess thermodynamic parameters i.e. excess adiabatic compressibility (β_a^E), excess intermolecular free length (L_f^E), excess acoustic impedance (z^E), and excess relative association (R_A^E) threw more light on the molecular interactions such as hydrogen bonding, ion – ion, ion – solvent, solute – solvent interactions in aqueous solutions and binary mixtures.

Key Words: *Ultrasonic Velocity; Excess Adiabatic Compressibility; Excess Intermolecular Free Length; Excess Acoustic Impedance; Excess Relative Association*

INTRODUCTION

Biomolecules (Mathews *et al.*, 2005) are complex organic molecules. These molecules form the basic structural constituent of a living cell. The organic compounds (Bhal Arun and Bhal B S, 1996) such as amino acids, nucleotides and monosaccharide serve as building blocks of complex biomolecules. The important biomolecules are proteins, carbohydrates and fats, enzymes, vitamins, hormones and nucleic acids. Some of the biomolecules are polymers. For e.g., starch, proteins, nucleic acids are condensation polymers of simple sugars, amino acids and nucleotides respectively. The bimolecules play an important role in the body functions. Proteins (Nelson David *et al.*, 2007) are found in all parts of the body and they have an enormous variety of functions. Amino acids and peptides are used as probe molecules (Thirumaran and Inbam, 2011) to understand the complex nature of protein. It is generally recognized that the investigation of the behavior of model compounds of protein like amino acids and peptides in aqueous and mixed aqueous solvents help in understanding the factors governing the thermodynamic stability of the native structure of proteins. Ultrasonic velocity and its related thermo dynamical properties have been extensively used to study the physic-chemical behavior and molecular interactions in a variety of liquid mixture (Riyazuddeen & Nurul Islam, 1997; Leyendekkers 1986). There is information on the zwitter - ionic nature of amino acids in water in the literature (Kharakoz, 1991; Leyendekkers, 1986; Badaryani Rohini & Kumar Anil, 2003; Banipal T S and Singh Gagandeep 2008). The properties of proteins such as their structure, solubility, denaturation activity of enzymes etc. are greatly influenced by electrolytes (Kumar, 1995; Kanhekar and Bichile 2010). An electrolytes when dissolved in water, changes the arrangement of water molecules with a strong electric field of its ions. This property of electrolytes is known as structure maker or structure breaker has been widely used to understand the effect of electrolytes on the structure and function of both proteins and nucleic acids (Chimankar Omprakash *et al.*, 2011). Thermodynamic properties of electrolytes in aqueous alanine solutions have been studied in order to understand the complex nature of proteins using amino acid-ion interactions (Banipal and Sehgal Gagandeep 1995,; Palani R *et al.*, 2011). There are instances where high concentrations of electrolytes can affect the function and structure of proteins (Baluja Shipra & Oza Swati 2002; Thirumaran and Sabu Job 2011). Ion – ion and ion- amino acids interactions dominate in such situations. The thermodynamics of interactions of NaCl & $MgCl_2$ in aqueous amino acids have been reported in the literature (Bolen D W and Yang M, 2000; Ogawa *et al.*, 1984). How the ion-ion and ion-amino acid interactions together with ion –water and amino acid- water ones are altered in electrolytes and amino acid solutions is the object of current investigations. The investigation of ultrasonic and thermodynamic properties of a amino acids and peptides in aqueous and mixed aqueous solvents have been the area of interest. Therefore, this investigation presents density, viscosity and speed of sound data for systems comprising NaCl, $MgCl_2$ in aqueous alanine.

Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of the liquid mixture. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules (Burghate *et al.*, 1993; Kanhekar, 2012; Naidu Subrahmanyam & Prasad Ravindra 2001; Bahadur Alisha *et al.*, 2001). Excess parameter play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures through charge transfer, dipole – induced dipole and dipole – dipole interactions (Das Debasis and Hazra Dilip, 2003). interstitial accommodation and orientational ordering (Ramanjipa *et al.*, 1993) leading to more compact structure making.

MATERIALS AND METHODS

All the chemicals used were of AR grade and dried over anhydrous $CaCl_2$ in desiccator's before use. All solutions were prepared in deionized and distilled water (degassed by boiling), having specific conductivity ~ 10^{-6} S cm^{-1}. The stock solutions (Malasane and Anwar, 2005) of 1M concentration were prepared by weighing alanine, NaCl, and $MgCl_2$ on a digital balance with an accuracy of ± 1 x 10^{-5} g. Uncertainties in solution concentrations were estimated at ± 1 x 10^{-5} mol.kg^{-1} in calculations. Mixtures of 1M alanine, 1M NaCl & 1M $MgCl_2$ were prepared by volume fractions. 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 2 MHz and at constant temperature 298.15K. The interferometer was calibrated against the ultrasonic velocity of water used at T = 298.15K. The present experimental value is 1497.08 ms^{-1} which is in good agreement with literature value (Jahagirdar *et al.*, 2000) 1496.69 ms^{-1}. Accuracy in the velocity measurement was ± 1.0 ms^{-1}. The density measurements were performed with precalibrated 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 precalibrated Ostwald type viscometer. The flow 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.

RESULTS AND DISCUSSION

Ultrasonic velocity, density and viscosity of the liquid systems have been measured. Using these data, the thermodynamic parameters such as the adiabatic compressibility (β_a); intermolecular free length (L_f); acoustic impedance (z) and relative association (R_A) were investigated for six different vol. fractions of 1M NaCl & 1M $MgCl_2$ at frequency 2 MHz and at constant temperature 298.18K. From the experimental data of density (ρ), viscosity (η) and ultrasonic velocity (u), the thermodynamic parameters have been calculated by using the following relations (Kanhekar S R *et al.*, 2010; Palani R *et al.*, 2008; Chimankar O P *et al.*, 2011; Mirekar Shilpa A *et al.*, 2011).

Ultrasonic velocity $u = n \times \lambda$ -------------- (1)
Adiabatic compressibility $\beta_a = 1/u^2 \rho$ -------------- (2)
Intermolecular free length $L_f = K / u.\rho$ -------------- (3)
Acoustic impedance $z = u \rho$ -------------- (4)
Relative association $RA = (\rho / \rho_0).(u_o / u)^{1/3}$ -------- (5)

Where, K is the temperature dependant Jacobson constant, T is the absolute temperature, ρ_0, ρ and u_0, u are the density and ultrasonic velocity of solvent and solution respectively.

The excess parameters such as u^E, β^E, z^E, L_f^E, and R_A^E have been calculated using the following equations Excess ultrasonic velocity $u^E = u_{mix} - [(1- x) u_1 + x u_2]$ ------------ (6)
Excess adiabatic compressibility $\beta^E = \beta_{mix} - [(1- x) \beta_1 + x \beta_2]$ ------------ (7)
Excess acoustic impedance $z^E = z_{mix} - [(1- x) z_1 + x z_2]$ ------------ (8)
Excess intermolecular free length $L_f^E = L_{f\,mix} - [(1- x) L_{f\,1} + x L_{f\,2}]$ -------- (9)
Excess relative association $R_A^E = R_{Amix} - [(1- x) R_{A\,1} + x R_{A2}]$ --------- (10)

Where, x- represents vol. fraction of the component and subscript 1 and 2 stands for components 1 & 2.

For the amino acids - electrolytes liquid systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$), ultrasonic velocity (u), density (ρ) and the coefficient of viscosity (η) for various volume fractions have been measured at frequency of 2 MHz and at constant temperature of 298.15K. The experimental values of u, ρ, η, are given in Tables - 1. The data obtained are used to evaluate β, Z, L_f, and R_A which is included in the same Table. Using these experimental and computed data, excess parameters such as excess ultrasonic velocity (u^E), excess adiabatic compressibility (β^E), excess acoustic impedance (z^E), excess intermolecular free length (L_f^E) and excess relative association (R_A^E) have been computed. The values of excess parameters have been presented in Table – 2. The graph plotted of excess parameters versus vol. fraction (x) for two liquid systems as shown in Figure: -1 to 10.

Ultrasonic Velocity (u): The ultrasonic velocity (u) for amino acid electrolytes solutions at 2MHz frequency and at constant temperature have been determined using relation (1) and presented in Tables - 1. From Table – 1, the variations in ultrasonic velocity in liquid mixtures depend on concentrations (x) of solutes. 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 four liquid systems. Consequently, ultrasonic velocity of system increases depending on the structural properties of solutes. The solute that increases the ultrasonic velocity is structure maker. From Tables - 1, ultrasonic velocity increases with increase concentrations of solutes (1M NaCl, 1M $MgCl_2$) in liquid systems investigated such as (1M Alanine +1M NaCl) and (1M Alanine +1M $MgCl_2$). The value of ultrasonic velocity of (1M Alanine + 1M NaCl) is less as compared to the value of ultrasonic velocity in (1M Alanine +1M $MgCl_2$) because of divalent nature of $MgCl_2$. When NaCl or $MgCl_2$ is dissolved in solution, the sodium ion (Na^+) or (Mg^{++}) 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.

Adiabatic compressibility (β_a): When an aqueous electrolytes solution is added to a 1M alanine (solvent), 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 available solvent molecule for the next incoming ion gets decreased. From Table - 1, the compressibility of a solvent is higher than that of a solution and it decreases with increase in concentrations. The adiabatic compressibility is calculated using equation (2). The calculated values of (β_a) have been presented in Tables - 1. The presence of hydrophobic hydration in alanine due to presence of methyl group causes alanine to be under a higher electrostriction effect than other amino acids containing methyl group (Methyl group tightens the water molecules around itself). Hence the values of adiabatic compressibility for alanine are higher than those amino acids containing more methyl group.

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 Tables 1. From Table - 1, it is observed that acoustic impedance (z) increases for different vol. fractions. Acoustic impedance becomes either maximum or minimum depending on the volume concentrations. This is the stage where complex formation is taking place in the liquid system due to increased electrolytes – amino acids interaction. For a given concentration the values of acoustic impendence (z) increases with increase in concentration in liquid systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$). 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 systems.

Intermolecular free length (L_f): The values of intermolecular free length for (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$) systems 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 a predominant factor in determining the variations of ultrasonic velocity in liquid mixtures. From Tables – 1, it has been observed that, in the present investigation, intermolecular free length decreases linearly on increasing vol. fractions. The decrease in L_f with increase of vol. fractions in solution indicates that there are significant interactions between solute and solvent suggesting the structure promoting behavior of solutes. Ultrasonic velocity increases with vol. fractions 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 systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$) 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. From Tables - 1, it is observed that, R_A increases with increase in the vol. fractions (x).

Excess ultrasonic velocity (u^E): The values of excess ultrasonic velocity have been calculated using the standard relation (6) and are presented in Tables- 1 and 2. From Table – 2 and Figure: - 1, and 2, it is clear that the values of u^E are negative at the beginning but becomes positive thereafter by increasing volume fractions of 1M NaCl and 1M $MgCl_2$ in the liquid mixtures. More negative values of u^E indicates that the interactions between 1M alanine and 1M $MgCl_2$ more strong than the 1M alanine and 1M NaCl. Curves shown in Figures – 1 and 2, for (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$) at different temperature and various volume fractions, excess values of u^E are less negative at x – 0.4 then becomes positive with increasing volume fraction. u^E has small negative values (with minimum at x- 0.4) for all systems. Increase in negative values of u^E with x – 0.5 (Figure: -1, 2) is indicative of the decreasing strength of interaction between component molecules of the mixture as suggested by Tiwari et al. This supports our view that the interaction between component molecules in liquid mixtures is weak. Figures 1 and 2, shows that u^E values are small negative for (1M alanine + 1M NaCl) and becomes large negative for (1M alanine + 1M $MgCl_2$). Thus, interactions between the molecules of system (1M Alanine +1M NaCl) are weaker than that in the molecules of system (1M Alanine + 1M $MgCl_2$).

Excess adiabatic compressibility (β_a^E): Excess thermodynamic parameters have been found to be highly useful in elucidating solute – solvent interactions in aqueous solutions and binary mixtures. The variations in excess adiabatic compressibility (β^E) with volume fractions at different temperatures are presented in Tables- 2. From Figures 3 and 4, it is observed that the values of β^E are positive at the lower volume fraction up to x – 0.4 whereas the sign inversion of the β^E values changes by increasing volume fraction beyond x – 0.4 and becomes more negative at the maximum volume fraction x – 1.0. The curves show that the negative values of excess compressibility reaches maximum at 1.0 volume fraction of 1M NaCl. From Tables – 2, the values of excess compressibility changes from positive to negative by increasing vol. fractions of aqueous solutions of NaCl and $MgCl_2$ in 1M alanine. It is clear from Tables that the negative values of β^E more in (1M alanine + 1M NaCl), while less negative values are observed in (1M alanine + 1M $MgCl_2$). These observations support the view point that the mixture has a tendency for a closer packing in the intermediate composition range. The effect of temperature on the compressibility curves is in agreement with the idea that interaction between unlike molecules[1]. Predominantly the rupture of hydrogen bonded structures is the main cause of excess compressibility. The values of β^E decreases with increase in temperatures which indicates that as the temperature of the system is raised, the system tends to attain ideal behavior in which the values of β^E should be zero. This means that the system is temperature sensitive and the interaction between the component molecules decreases with rise of temperature.

The positive values of β^E, for the system suggest the presence of weak interaction between unlike molecules. The size of component molecules almost not equal, it seems that their molecules do not pack well into each other's structures. This results in expansion in volume, and hence positive β^E values.

The negative value of β^E, suggest significant interactions between the component molecules in the mixture, forming donar – acceptor complex between amino acid and electrolytes molecules. As a result there is contraction in volume, resulting in negative values of β^E, with x.

Excess acoustic impedance (Z^E): Excess acoustic impedance (z^E) has been calculated using relation (6) and calculated values of z^E are presented in Tables- 2. From Table - 2, it is clear that the values of z^E are negative at the beginning but becomes positive thereafter by increasing volume fractions of 1M NaCl and 1M $MgCl_2$ in the liquid mixtures. More negative values of z^E indicates that the interactions between 1M alanine and 1M $MgCl_2$ more strong than the 1M alanine and 1M NaCl. Curves shown in Figures – 5, 6 for (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$) at different temperature and various volume fractions, excess values of z^E are less negative at x – 0.4 then becomes positive with increasing volume fraction. z^E has small negative values (with minimum at x- 0.4) for all systems. Increase in negative values of z^E with x – 0.5 (Figure: - 5, 6) is indicative of the decreasing strength of interaction between component molecules of the mixture as suggested by Tiwari et al. This supports our view that the interaction between component molecules in liquid mixtures is weak. Figures 5 and 6, shows that z^E values are small negative for (1M alanine + 1M NaCl) and becomes large negative for (1M alanine + 1M $MgCl_2$). Thus, interactions between the molecules of system (1M Alanine +1M NaCl) are weaker than that in the molecules of system (1M Alanine + 1M $MgCl_2$).

Excess intermolecular free length (L_f^E): Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of the liquid mixture. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules. The changes in excess intermolecular free length (L_f^E) have been calculated with the help of equation - (4).The values of L_f^E are mention in the Tables-1 and 2. The plot of (L_f^E) versus vol. fraction (x) at 298.15K is shown in Figures - 7 and 8 for both systems. L_f^E values are positive at the beginning then become negative with increasing volume fraction (x) for all the systems at all temperatures suggesting weak specific interactions between amino acids and electrolytes molecules. L_f^E becomes more negative for 1M $MgCl_2$ as compared to 1M NaCl suggesting more of specific interaction of amino acids with divalent molecules. It is further assumed that complex formation between amino acids and electrolytes is due to polarization effect and not due to charge transfer interactions.

Figures – 7 and 8 shows variation in L_f^E at constant temperature 298.15K. It is seen that L_f^E values are positive at lower volume fraction of 1M NaCl and 1M $MgCl_2$ then becomes negative at higher volume fractions. The sign of L_f^E play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures through charge transfer, dipole – induced dipole and dipole – dipole interactions, interstitial accommodation and orientational ordering, leading to more compact structure making. Negative L_f^E in the present investigation is an indication of strong interactions in the liquid mixtures, as well as interstitial accommodation of sodium and magnesium chloride into the alanine. In the present investigation, it is seen that negative L_f^E values follow the order glycine > alanine. This trend suggests that hetero association and homo association of molecules decrease with electrolytes.

The values of L_f^E becomes more positive which may be due to thermal dissociation of the homo and hetero aggregates in the liquid mixtures and more interstitial accommodation of electrolytes molecules into amino acids at higher temperatures. The excess value of L_f^E being negative indicates a strong interaction in the amino acids – electrolytes solutions. However, the excess value in free length shows positive values and the changes are very small. The positive value indicates that interactions between electrolytes (salt) and amino acid is not very strong. The excess value for free length worked out for amino acid – electrolytes mixture shows negative value beyond x- 0.4 and the negative value keeps increasing beyond that point. This shows that there must have been a strong interaction in the amino acid – electrolytes.

For the mixtures of amino acid with electrolytes, L_f^E values are positive at lower vol. fraction of electrolytes solution. An inversion in sign from positive to negative is found with increase in volume fraction for all the systems. The positive L_f^E arises due to breaking of H – bonds in the self associated amino acids. Again the values of L_f^E are more negative for the system comprising $MgCl_2$ as compared to the system comprising NaCl, suggests that the strong interactions occur between amino acids and $MgCl_2$, while weak interactions between the amino acids and NaCl.

Table 1: Ultrasonic velocity, density, viscosity and its related thermodynamic parameters for both the system (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$) at various vol. concentrations (x) and constant temperature of 298.15 K and frequency of 2 MHz

Vol.fract. (x)	u m / s	ρ Kg / m^3	η N s m^{-2}	β x 10^{-10} $m^2 N^{-1}$	z x 10^6 N m^{-2}	L_f ^0A	R_A
(1M Alanine + 1M NaCl)							
0.0	1541.28	1050.8	0. 99238	4.01000	1.61957	0.41200	1.0000
0.2	1542.88	1053.6	1.10089	3.99000	1.62557	0.41100	1.00231
0.4	1544.96	1056.0	1.11728	3.97000	1.63147	0.41000	1.00415
0.6	1550.00	1058.8	1.14083	3.93000	1.64114	0.40800	1.00462
0.8	1569.20	1062.0	1.16882	3.82000	1.66649	0.40400	1.00572
1.0	1570.60	1048.4	1.28548	3.87000	1.64661	0.40200	1.00691
(1M Alanine + 1M $MgCl_2$)							
0.0	1544.96	1050.8	1.20359	3.99000	1.62344	0.41100	1.0000
0.2	1564.56	1065.8	1.22236	3.86000	1.65655	0.40400	1.00338
0.4	1565.44	1061.2	1.23636	3.85000	1.66124	0.40300	1.00547
0.6	1576.40	1074.4	1.28555	3.75000	1.69368	0.39800	1.01561
0.8	1589.70	1082.0	1.32381	3.66000	1.72005	0.39300	1.01993
1.0	1598.80	1092.4	1.33242	3.58000	1.74652	0.38900	1.02778

u = Ultrasonic velocity; ρ = Density; η = Viscosity; β = Adiabatic Compressibility;
z = Acoustic impedance; L_f = Intermolecular free length; R_A = Relative association;

Excess relative association (R_A^E): The variation of excess relative association function with volume fraction (x) is mention in Tables - 2 and graphically depicted in Figures –9 and 10. Figures show that R_A^E is small but negative for the system (1M Alanine + 1M NaCl). But the values of R_A^E are high and more negative for the system (1M Alanine + 1M $MgCl_2$). R_A^E is positive for liquid mixtures as the volume fraction increases as per Tables. The negative value of R_A^E suggests significant interactions between the component molecules in the mixture, forming donar – acceptor complex between amino acid and electrolytes molecules. As a result there is contraction in volume, resulting in negative values of R_A^E with x. The positive values of R_A^E for the system suggest the presence of weak interaction between unlike molecules.

In case of alanine based system, the values of R_A^E are positive over the entire range of volume fraction except at x – 1.0, suggest that there are weak interactions between alanine and NaCl. But the values of R_A^E are more negative for the alanine – $MgCl_2$ system at lower volume fractions indicating remarkable strong interaction between component molecules. As volume fractions increases, there is no strong interaction between them as shown in Figure: -10.

Table-2: Variation of excess parameters at different concentrations (x) and constant Temperature of 298.15 K for the system (1M Alanine + 1M NaCl) and (1M Alanine + 1M $MgCl_2$) at 2MHz

Vol. fract. (x)	u^E m / s	$\beta^E x10^{-10}$ $m^2 N^{-1}$	$z^E x10^6$ $N m^{-2}$	L_f^E ^0A	R_A^E
(1M Alanine + 1M NaCl)					
0.0	-29. 320	0.14000	-0.02104	0.00800	-0.00854
0.2	-21.856	0.09200	-0.01563	0.00540	-0.00914
0.4	-13.912	0.04400	-0.00432	0.00280	-0.00927
0.6	-03.008	-0.02400	0.01075	-0.00080	0.00913
0.8	-22.056	-0.16200	0.04151	-0.00840	0.00632
1.0	-29.320	-0.14000	0.02704	-0.00800	0.00854
(1M Alanine + 1M $MgCl_2$)					
0.0	-53.840	0.41000	-0.12308	0.02200	-0.02778
0.2	-23.472	0.19800	-0.06535	0.01060	-0.01884
0.4	-11.824	0.10600	-0.03604	0.00520	-0.01119
0.6	09.904	-0.07600	0.02100	-0.00420	0.00449
0.8	33.972	-0.24800	0.07199	-0.01360	0.01437
1.0	53.840	-0.41000	0.12308	-0.02200	0.02778

u^E = Excess ultrasonic velocity; β_a^E = Excess ad. Compressibility; z^E = Excess acoustic impedance; L_f^E = Excess intermolecular free length; R_A^E = Excess relative association.

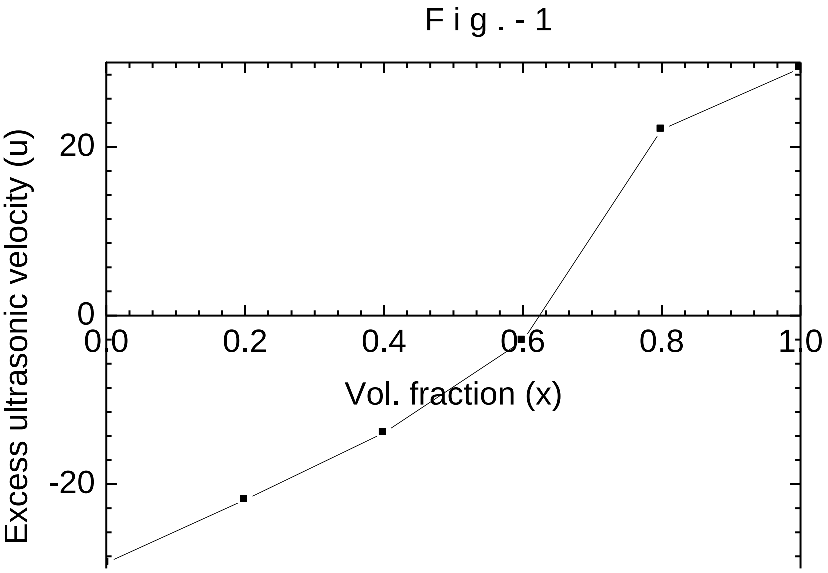

Figure 1: Plot of excess ultrasonic velocity (u^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

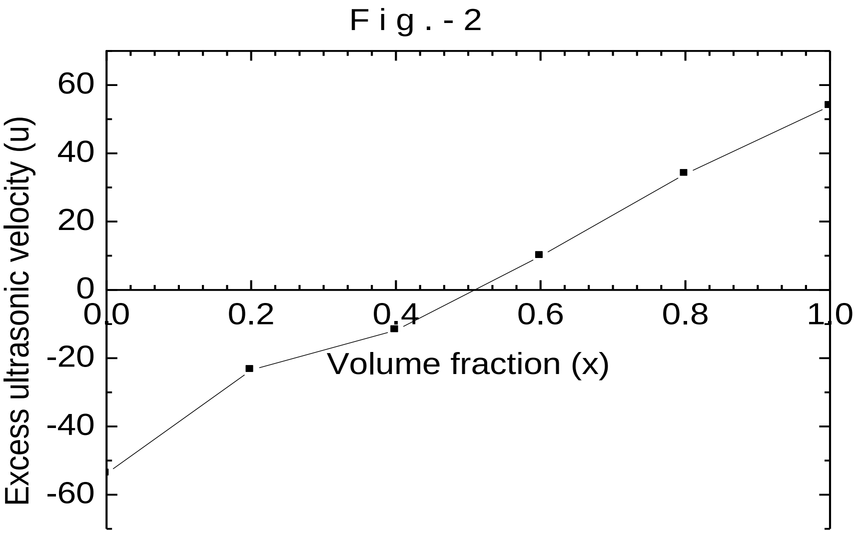

Figure 2: Plot of excess ultrasonic velocity (u^E) against vol. fraction (x) for the system (1M Alanine + 1M $MgCl_2$) at 2 MHz and at constant temperature 298.15 K.

Fig.-3

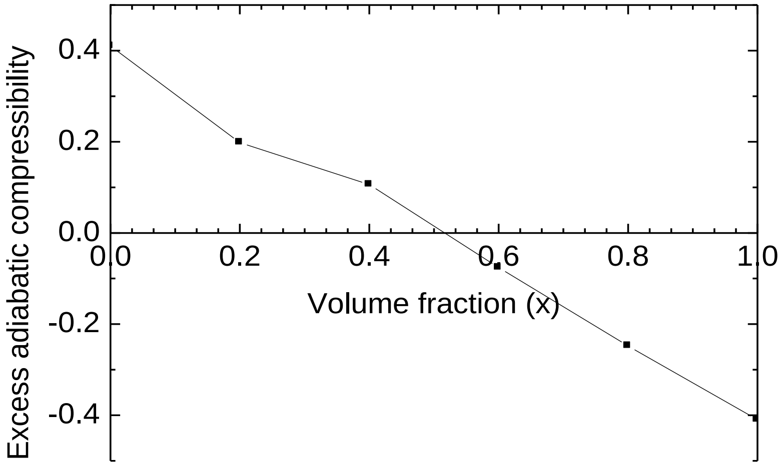

Figure 3: Plot of excess adiabatic compressibility (β_a^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

Fig.-4

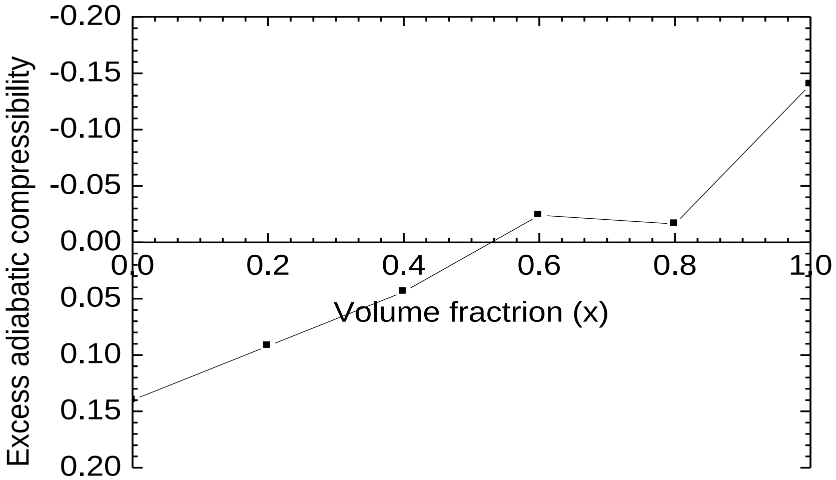

Figure 4: Plot of excess ad. compressibility (βa^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

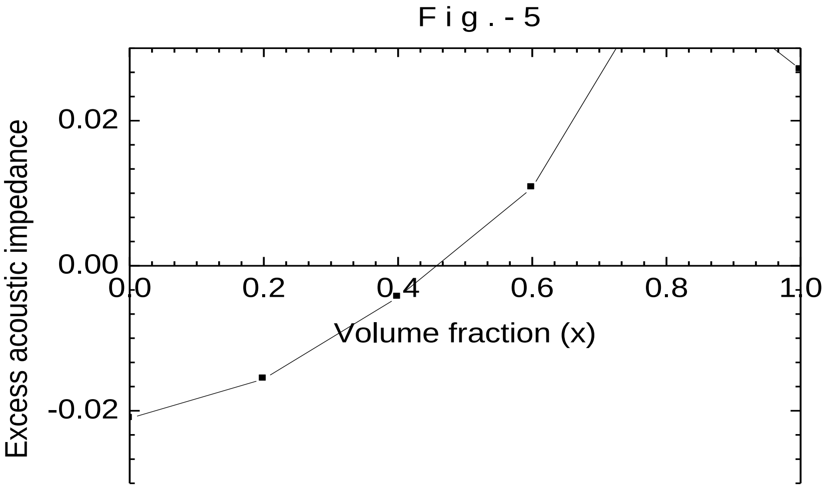

Figure: 5 – Plot of excess acoustic impedance (z^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

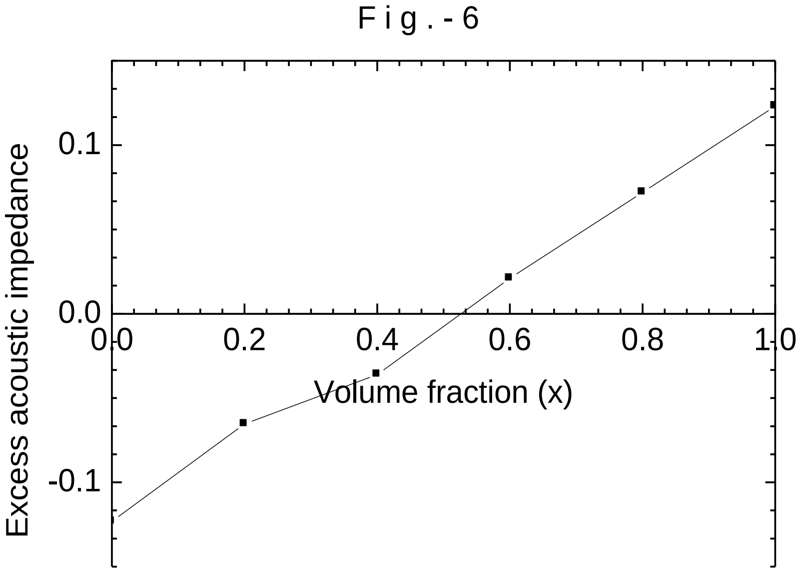

Figure 6: Plot of excess acoustic impedance (z^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

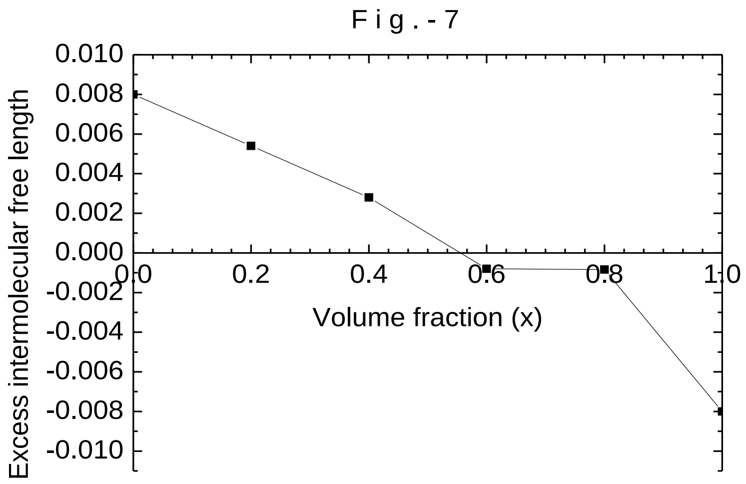

Figure 7: Plot of excess inter. free length (L_f^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

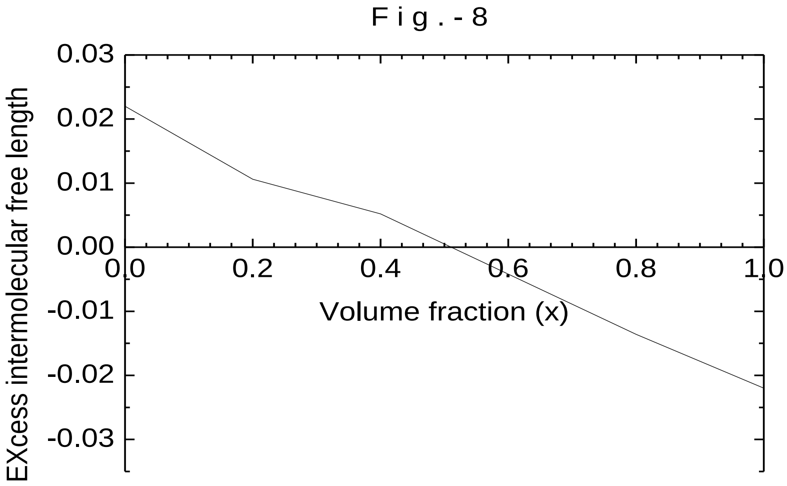

Figure 8: Plot of excess inter.free length (L_f^E) against vol. fraction (x) for the system (1M Alanine + 1M $MgCl_2$) at 2 MHz and at constant temperature 298.15 K.

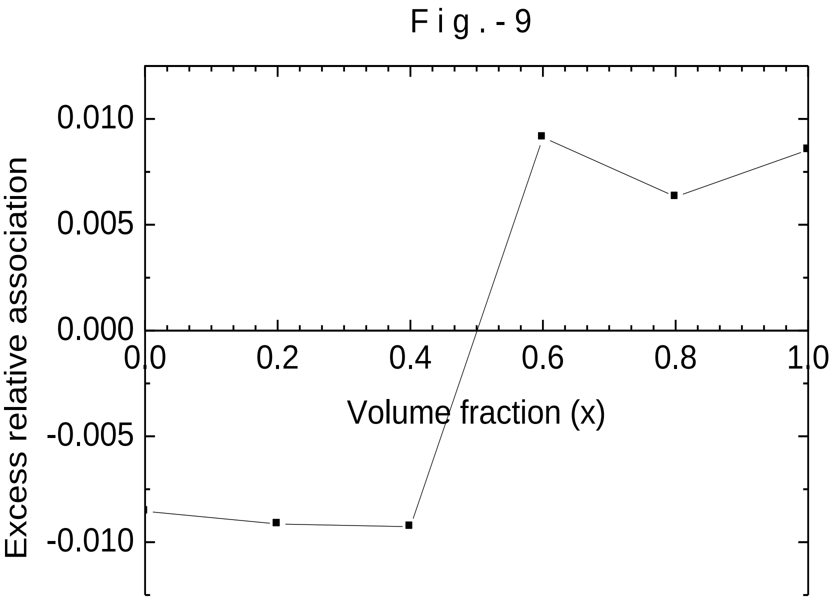

Figure 9: Plot of Excess Relative Association (R_A^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

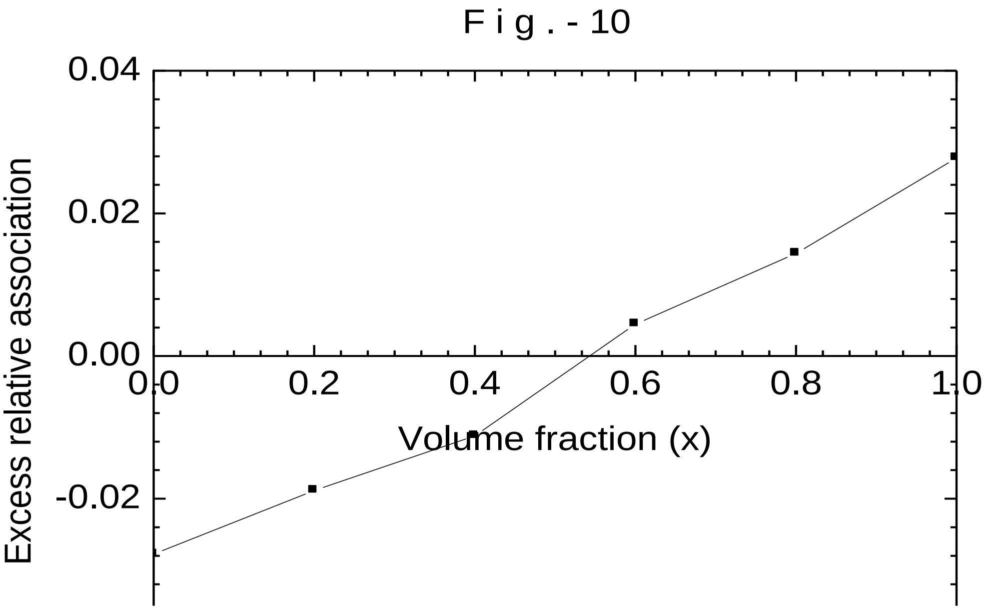

Figure 10: Plot of Excess Relative Association (R_A^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at constant temperature 298.15 K.

CONCLUSION

Ultrasonic velocity, density and viscosity have been measured for NaCl and $MgCl_2$ in aqueous alanine solution at 298.15. The variation in ultrasonic velocity, density and viscosity as well as the related thermodynamic parameters such as adiabatic compressibility (β), acoustic impedance (z), intermolecular free length (L_f), relative association (R_A), are more in the system containing $MgCl_2$ as compared to the system having NaCl due to the divalent cation (Mg^{2++}) of $MgCl_2$. As a matter of fact, the effect of $MgCl_2$ on the electrostriction of water molecules is stronger than that of 1:1 electrolytes i.e. NaCl. Thus the addition of $MgCl_2$ to alanine enhances the transfer volumes more strongly than monovalant cat ion Na^+. The variation in ultrasonic velocity, density and viscosity and other related thermodynamic parameters 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 hetero molecular interaction in the liquid mixture. This provides useful information about inter and intra molecular interactions of liquid systems.

It is also concluded that ultrasonic velocity of system increases depending on the structural properties of solutes. It is well known that solutes causing electrostriction lead to decrease in the compressibility of the solution. Hydrophilic solutes often show negative compressibility, due to ordering that is induced by them in water structure. The solute that increases the ultrasonic velocity is of structure maker (SM). It has been observed that intermolecular free length decreases linearly on increasing concentrations of solutes in the systems. The excess parameters such as excess ultrasonic velocity (u^E); excess adiabatic compressibility (β_a^E); excess acoustic impedance (z^E); excess intermolecular free length (L_f^E) and excess relative association (R_A^E) have been studied in this investigation.these excess thermodynamic parameters threw more light on the molecular interactions such as hydrogen bonding, ion – ion, ion – solvent, solute – solvent interactions in aqueous solutions and binary mixtures.

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