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Research Article

THERMODYANMICAL STUDIES OF ELECTROLYTES SOLUTION WITH AQUEOUS AMINO ACID

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ABSTRACT

Ultrasonic velocities, densities, and viscosities have been measured for binary liquid systems (1M Glycine + 1M NaCl) and (1M Glycine + 1M $MgCl_2$) at 2 MHz frequency and at 298.15, 303.15, 308.15K temperatures. From these experimental data, derived thermodynamic parameters such as the adiabatic compressibility (β_a); intermolecular free length (L_f); acoustic impedance (z) and relative association (R_A) have been computed using the standard relations. The results have been analyzed on the basis of variations in thermodynamic parameters as well as excess parameters. The variations in ultrasonic velocity and adiabatic compressibility with concentrations in both systems show a similar trend of increasing ultrasonic velocity and decreasing in adiabatic compressibility of the constituent electrolytes at different temperatures. This is due to complex formation and coordinate covalent bond form between the molecules of the liquid mixtures. Excess thermodynamic parameters i.e. excess compressibility (β^E) and excess intermolecular free length (L_f^E), excess acoustic impedance (z^E) & excess relative association (R_A^E) throw light on the solute – solvent molecular interactions.

Key Words: *Ultrasonic Velocity, Adiabatic Compressibility, Intermolecular Free Length, Excess Adiabatic Compressibility, Excess Intermolecular Free Length.*

INTRODUCTION

There are many approaches used to determine the structure – function relationship of biomolecules. Among these approaches, Ultrasonic velocity measurements provide an important tool to study the liquid state. Ultrasonic velocity and thermodynamic parameters derived from these measurements are widely used to study of molecular interactions (Riyazuddeen and Islam, 1997; Jahagirdar *et al*., 2000; Basumallic and Mohanty, 1986; Sekar and Dhanalakshmi, 2002) in pure liquid, aqueous solutions and liquid mixtures. The bimolecules play an important role in the body functions. Proteins (Mohanty and Swain, 2010) 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 (Banipal and Sehagal, 1995; Badarayani and Kumar, 2003). 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.

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 (Banipal and Sehagal, 1995; Badarayani and Kumar, 2003; Samatha *et al*., 1998). The properties of proteins such as their structure, solubility, denaturation, activity of enzymes, etc. are greatly influence by electrolytes (Samatha *et al*., 1998; Kundrat and Autschbach, 2006; Malasane and Aswar, 2005). 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. Thermodynamic properties of aqueous amino acids in electrolytes solutions have been studied in order to understand the complex nature of protein using amino acids - ion interactions. How the ion-ion and ion-amino acid interaction together with ion water and amino acid-water ones are altered in electrolytes and amino acid solutions is the subject of current investigation. In few decades, there has been interest in the measurements and modeling thermodynamic properties of pure and mixed aqueous solutions of bio-molecular system. The systematic research programme has been undertaken to understand the interactions of a biomolecules with electrolytes. Thermodynamic excess parameters 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.

In the present investigation, the experimental studies of u, ρ, η and the results of derived thermodynamic parameters i.e. adiabatic compressibility (β), intermolecular free length (L_f), acoustic impedance (z), relative association (R_A), excess compressibility (β^E), and excess intermolecular free length (L_f^E), excess acoustic impedance (z^E) and excess relative association (R_A^E) of aqueous electrolytes in aqueous solution of glycine at different temperatures have been reported. These derived parameters from ultrasonic velocity measurement and the corresponding excess functions provide qualitative information regarding the nature and strength of interactions in liquid mixtures[7]. The excess parameters 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.

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} Scm^{-1}. The stock solutions (Malasane and Aswar, 2005) of 1M concentration of glycine, NaCl and $MgCl_2$ were prepared by weighing the all chemicals on a digital balance with an accuracy of $\pm 1 \times 10^{-4}$ g. required liquid mixture were prepared by volume fractions. The solutions were kept in the special air tight bottles and were used within 12 hrs. 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 298.15, 303.15, and 308.15K temperatures. 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 $\pm 2 \times 10^{-2}$ 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 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.

RESULTS AND DISCUSSION

Ultrasonic velocity, density and viscosity of the liquid systems have been measured. Using these data, various thermodynamic parameters such as the adiabatic compressibility (β_a); acoustic impedance (z); intermolecular free length (L_f); relative association (R_A); were investigated for different vol. concentrations (x) of 1M NaCl & 1M $MgCl_2$ at temperatures 298.18K, 303.15K and 308.15K and at 2 MHz frequency. From the experimental data of ultrasonic velocity (u), density (ρ), and viscosity (η) by using the following relations (Mehra, 2005; Thirumaran and Inbam, 2011; Pal and Kumar, 2005; Pandey *et al*., 2008; Pallani *et al*., 2007; Ikhe *et al*., 2005; Muraliji *et al*., 2002; Rathnam *et al*., 2011; Mahendran and Palaniappan, 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 $R_A = (\rho / \rho_o).(u_o / u)^{1/3}$ ------------- (5)

The excess parameters such as u^E, β^E, L_f^E, z^E and R_A^E have been calculated using the equation

$Y^E = Y_{mix} - [(1- x) Y_1 + x Y_2]$ ---------------------------- (6)

Where, Y^E is u^E, β^E or L_f^E or z^E, R_A^E, x- represents vol. fraction of the component and subscript 1 and 2 stand for components 1 & 2 and K is the temperature dependant Jacobson constant.

For the amino acids - electrolytes liquid systems (1M Glycine + 1M NaCl) and (1M Glycine + 1M $MgCl_2$), ultrasonic velocity (u), density (ρ) and the coefficient of viscosity (η) for various vol. fractions have been measured at constant frequency of 2 MHz and at temperatures 298.18K, 303.15K and 308.15K. The data obtained are used to evaluate u, ρ, η, β, z, L_f, and R_A. The experimental values of u, ρ, η, and calculated values of β, z, L_f, R_A are also given in Table - 1 and 2. Using these experimental and calculated

Table 1: Variation of thermodynamic parameters at different concentrations (x) and different temperatures for the system (1M Glycine + 1M NaCl) at 2 MHz.

Vol.fract. (x)	u m / s	ρ Kg / m³	η N s m⁻²	$\beta x10^{-10}$ $m^2 N^{-1}$	$zx10^6$ $N m^{-2}$	L_f ^0A	R_A
				298.15K			
0.0	1551.92	1053.2	10.2780	3.94231	1.63448	0.408385	1.00000
0.2	1558.90	1054.4	10.3069	3.90116	1.64432	0.406248	1.00002
0.4	1564.32	1055.2	10.4348	3.87270	1.65067	0.404763	1.00013
0.6	1566.80	1057.0	10.4369	3.85315	1.65642	0.403740	1.00061
0.8	1571.00	1059.6	10.6854	3.82536	1.66400	0.402281	1.00160
1.0	1581.92	1060.4	10.9637	3.76844	1.67746	0.399277	1.00043
				303.15K			
0.0	1569.50	1051.6	9.5544	3.86035	1.65048	0.40780	1.00000
0.2	1570.70	1051.6	9.5828	3.85445	1.65174	0.40749	0.99974
0.4	1571.60	1054.0	9.5983	3.84127	1.65646	0.40679	1.00183
0.6	1576.30	1056.8	9.6309	3.80829	1.66583	0.40504	1.00349
0.8	1578.10	1058.0	9.9113	3.79529	1.66963	0.40435	1.00425
1.0	1583.60	1060.0	9.9156	3.76186	1.67861	0.40256	1.00498
				308.15K			
0.0	1572.72	1049.6	8.7872	3.85189	1.65072	0.41103	1.00000
0.2	1576.26	1050.8	8.8375	3.83022	1.65633	0.40987	1.00039
0.4	1581.00	1052.0	8.8395	3.80295	1.66321	0.40841	1.00053
0.6	1582.80	1055.2	8.9650	3.78280	1.67017	0.40733	1.00319
0.8	1583.50	1056.8	9.0692	3.77373	1.67344	0.40684	1.00456
1.0	1583.90	1058.0	9.1575	3.76755	1.67576	0.40650	1.00562

u = Ultrasonic velocity; ρ = Density; η = Viscosity; β = Ad. Compressibility; z = Acoustic impedance; L_f = Intermolecular free length; R_A = Relative association 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 using the equation (6). The values of excess parameters have been presented in Table –3 and 4. The graph plotted of excess parameters versus vol. fraction (x) for two liquid systems as shown in Fig. -1 to 10.

1) Ultrasonic Velocity (u)

The ultrasonic velocity (u) for amino acid electrolytes solutions at 2MHz frequency and at different temperatures have been determined using relation (1) and presented in Tables -1, 2.

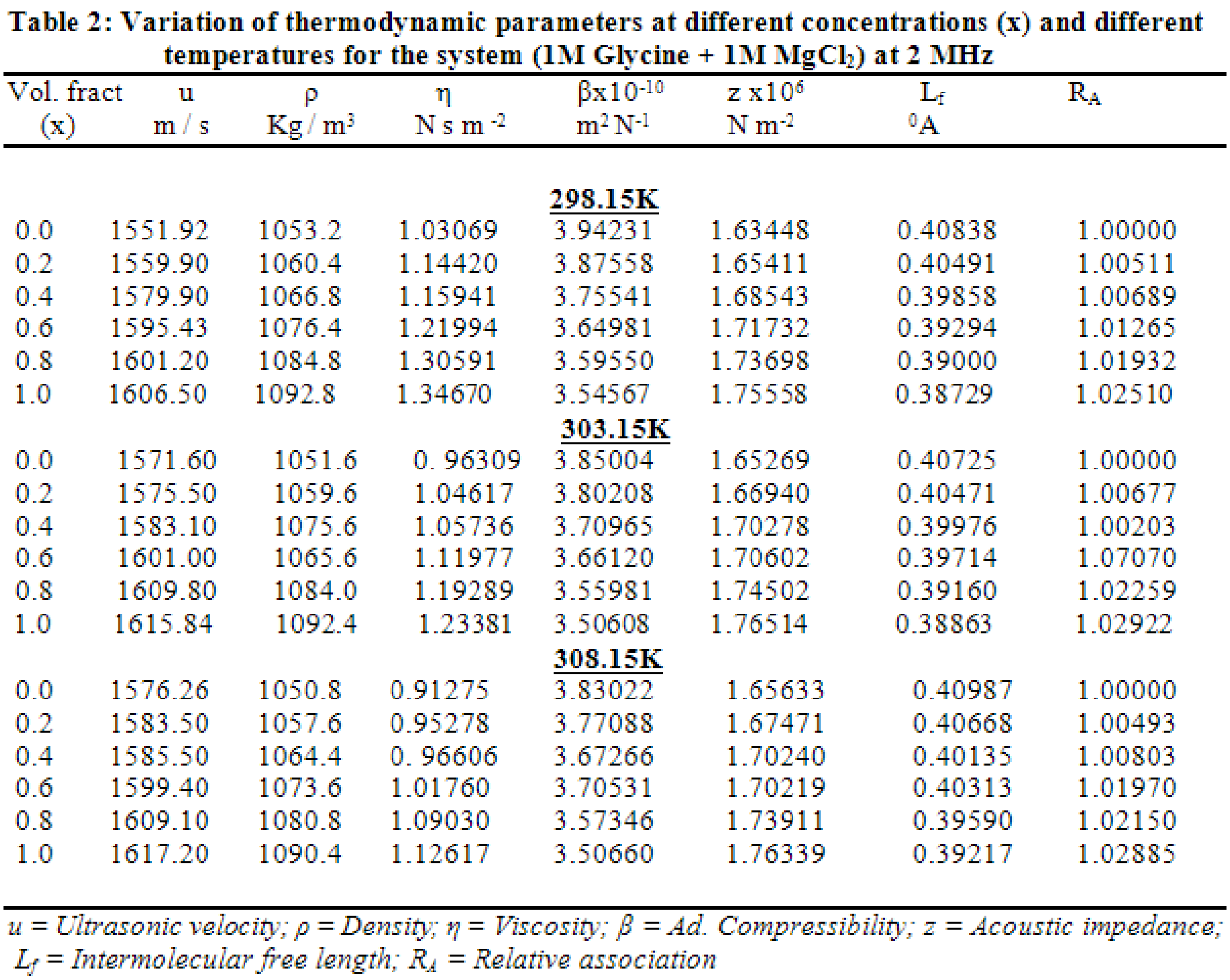

Table 2: Variation of thermodynamic parameters at different concentrations (x) and different temperatures for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz

Vol. fract (x)	u m / s	ρ Kg / m³	η N s m⁻²	βx10⁻¹⁰ m² N⁻¹	z x10⁶ N m⁻²	L_f ⁰A	R_A
				298.15K			
0.0	1551.92	1053.2	1.03069	3.94231	1.63448	0.40838	1.00000
0.2	1559.90	1060.4	1.14420	3.87558	1.65411	0.40491	1.00511
0.4	1579.90	1066.8	1.15941	3.75541	1.68543	0.39858	1.00689
0.6	1595.43	1076.4	1.21994	3.64981	1.71732	0.39294	1.01265
0.8	1601.20	1084.8	1.30591	3.59550	1.73698	0.39000	1.01932
1.0	1606.50	1092.8	1.34670	3.54567	1.75558	0.38729	1.02510
				303.15K			
0.0	1571.60	1051.6	0. 96309	3.85004	1.65269	0.40725	1.00000
0.2	1575.50	1059.6	1.04617	3.80208	1.66940	0.40471	1.00677
0.4	1583.10	1075.6	1.05736	3.70965	1.70278	0.39976	1.00203
0.6	1601.00	1065.6	1.11977	3.66120	1.70602	0.39714	1.07070
0.8	1609.80	1084.0	1.19289	3.55981	1.74502	0.39160	1.02259
1.0	1615.84	1092.4	1.23381	3.50608	1.76514	0.38863	1.02922
				308.15K			
0.0	1576.26	1050.8	0.91275	3.83022	1.65633	0.40987	1.00000
0.2	1583.50	1057.6	0.95278	3.77088	1.67471	0.40668	1.00493
0.4	1585.50	1064.4	0. 96606	3.67266	1.70240	0.40135	1.00803
0.6	1599.40	1073.6	1.01760	3.70531	1.70219	0.40313	1.01970
0.8	1609.10	1080.8	1.09030	3.57346	1.73911	0.39590	1.02150
1.0	1617.20	1090.4	1.12617	3.50660	1.76339	0.39217	1.02885

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

From Tables the variations in ultrasonic velocity in liquid mixtures depend on concentrations (x) of solutes and temperatures. 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. Ultrasonic velocity increases with increase in concentrations of solutes (1M NaCl, 1M $MgCl_2$) in liquid systems investigated such as (1M Glycine + 1M NaCl) and (1M Glycine +1M $MgCl_2$). The value of ultrasonic velocity of (1M Glycine + 1M NaCl) in is less as compared to the value of (1M Glycine +1M $MgCl_2$). 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.

2) Adiabatic compressibility (β)

When an aqueous electrolytes solution is added to a 1M Glycine (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 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 Tables - 1, 2. From tables- 1& 2 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 glycine due to absence of any methyl group causes glycine 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 glycine are higher than those of other amino acids.

3) 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, 2. From these tables, it is observed that acoustic impedance (z) increases for different vol. fractions. Acoustic impedance becomes either maximum or minimum depending on the concentrations and different temperatures. 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 glycine + 1M NaCl) and (1M glycine + 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.

4) Intermolecular free length (L_f)

The values of intermolecular free length for (1M glycine + 1M NaCl) and (1M Glycine + 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, & 2, 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 behaviour 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.

5) Relative association (R_A)

The values of relative association (R_A) for liquid systems (1M Glycine + 1M NaCl) and (1M Glycine + 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 Figures – 9, 10 and Tables -1, & 2, it is observed that, R_A increases with increase in the vol. fractions (x).

6) Excess ultrasonic velocity (u^E)

The values of excess ultrasonic velocity have been calculated using the standard relation (6) and are presented in Tables- 3 and 4. From tables and from Fig. - 1, 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. The values of excess ultrasonic velocity are less negative in (1M glycine +1M NaCl) as compared to (1M glycine + 1M $MgCl_2$). More negative values of u^E indicates that the interactions between 1M glycine and 1M $MgCl_2$ more strong than the 1M glycine and 1M NaCl.

Curves shown in Figures – 1 and 2 for (1M Glycine + 1M NaCl) and (1M Glycine + 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. Similar behaviour is also observed in case of (1M glycine + 1M $MgCl_2$). 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 (Fig.-13, 14) is indicative of the decreasing strength of interaction between component molecules of the mixture. This supports our view that the interaction between component molecules in liquid mixtures is weak.

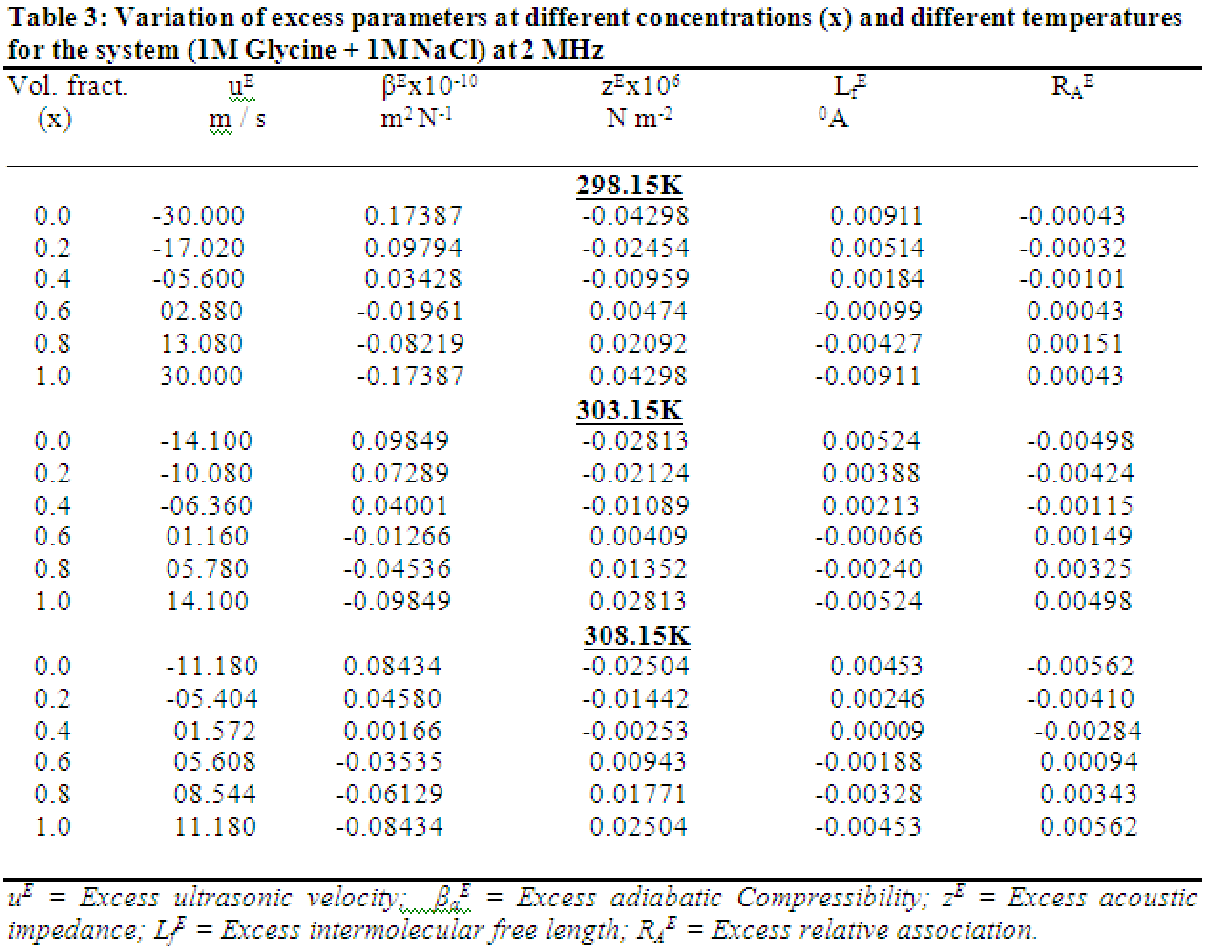

Table 3: Variation of excess parameters at different concentrations (x) and different temperatures for the system (1M Glycine + 1M NaCl) at 2 MHz

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
			298.15K		
0.0	-30.000	0.17387	-0.04298	0.00911	-0.00043
0.2	-17.020	0.09794	-0.02454	0.00514	-0.00032
0.4	-05.600	0.03428	-0.00959	0.00184	-0.00101
0.6	02.880	-0.01961	0.00474	-0.00099	0.00043
0.8	13.080	-0.08219	0.02092	-0.00427	0.00151
1.0	30.000	-0.17387	0.04298	-0.00911	0.00043
			303.15K		
0.0	-14.100	0.09849	-0.02813	0.00524	-0.00498
0.2	-10.080	0.07289	-0.02124	0.00388	-0.00424
0.4	-06.360	0.04001	-0.01089	0.00213	-0.00115
0.6	01.160	-0.01266	0.00409	-0.00066	0.00149
0.8	05.780	-0.04536	0.01352	-0.00240	0.00325
1.0	14.100	-0.09849	0.02813	-0.00524	0.00498
			308.15K		
0.0	-11.180	0.08434	-0.02504	0.00453	-0.00562
0.2	-05.404	0.04580	-0.01442	0.00246	-0.00410
0.4	01.572	0.00166	-0.00253	0.00009	-0.00284
0.6	05.608	-0.03535	0.00943	-0.00188	0.00094
0.8	08.544	-0.06129	0.01771	-0.00328	0.00343
1.0	11.180	-0.08434	0.02504	-0.00453	0.00562

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

Table 4: Variation of excess parameters at different concentrations (x) and different temperatures for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz

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
			298.15K		
0.0	-54.580	0.39664	-0.12110	0.02109	-0.02571
0.2	-35.684	0.25058	-0.07725	0.01340	-0.01545
0.4	-04.768	0.05108	-0.02171	0.00285	-0.00853
0.6	21.678	-0.13384	0.03440	-0.00700	0.00236
0.8	38.364	-0.26478	0.07828	-0.01416	0.01417
1.0	54.580	-0.39664	0.12110	-0.02109	0.02571
			303.15K		
0.0	-44.240	0.34396	-0.11245	0.01862	-0.02922
0.2	-31.492	0.22720	-0.07325	0.01235	-0.01660
0.4	-15.044	0.06598	-0.01738	0.00368	-0.01550
0.6	11.704	-0.05125	0.00835	-0.00266	0.05901
0.8	29.352	-0.22143	0.06984	-0.01192	0.01674
1.0	44.240	-0.34396	0.11245	-0.01862	0.02922
			308.15K		
0.0	-40.940	0.32362	-0.10706	0.01770	-0.02885
0.2	-25.512	0.19955	-0.06726	0.01097	-0.01815
0.4	-01.424	0.03661	-0.01816	0.00210	-0.00928
0.6	-07.136	0.55453	0.00303	0.00034	0.00816
0.8	24.652	-0.19203	0.06136	-0.01043	0.01573
1.0	40.940	-0.32362	0.10706	-0.01770	0.02885

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

7) Excess adiabatic compressibility (β^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 calculated by using equation (6) presented in Tables - 3, 4. From Figures 3, 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. The values of excess compressibility becomes more negative in (1M glycine + 1M $MgCl_2$) as compared to in (1M glycine + NaCl) system at the same temperature and same vol. fraction, due to divalent nature of $MgCl_2$.

From Tables - 3, & 4, the values of excess compressibility changes from positive to negative by increasing vol. fractions of aqueous solutions of NaCl and $MgCl_2$ in 1M glycine. It is clear from Tables that the negative values of β^E more in (1M glycine + 1M NaCl), while less negative values are observed in (1M glycine + 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. 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 behaviour 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.

8) 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 - 3, 4. From tables, 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. The values of excess acoustic impedance are less negative in (1M glycine +1M NaCl) as compared to (1M glycine + 1M $MgCl_2$). More negative values of Z^E indicates that the interactions between 1M glycine and 1M $MgCl_2$ more strong than the 1M glycine and 1M NaCl. Curves shown in Figures –5 and 6 for (1M Glycine + 1M NaCl) and (1M Glycine + 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. Similar behaviour is also observed in case of (1M glycine + 1M $MgCl_2$). 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 (Fig.-13, 14) is indicative of the decreasing strength of interaction between component molecules of the mixture. This supports our view that the interaction between component molecules in liquid mixtures is weak.

9) 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 - (6).The values of L_f^E are mention in the Tables –3 and 4. The plot of (L_f^E) versus vol. fraction (x) at 298.15, 303.15, 308.15K, are shown in Figures –7, 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 298.15, 303.15 and 308.15K. 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 glycine. This trend suggests that hetero association and homo association of molecules decrease with electrolytes.

The values of L_f^E becomes more positive and those of L_f^E values becomes more negative with increase of temperature, 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 –

Fig.-1

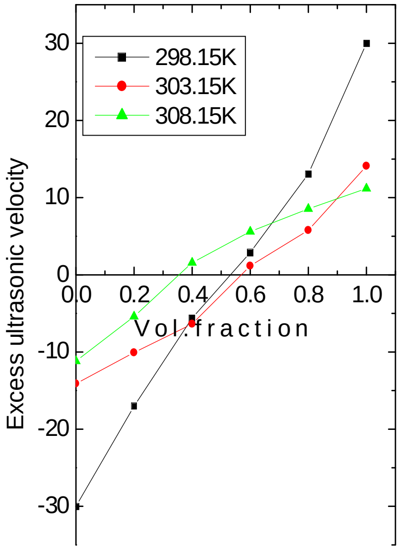

Figure 1: Plot of Excess Ultrasonic Velocity (u^E) against vol. fraction (x) for the system (1M Glycine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 3 08.15K temperatures.

Fig.-2

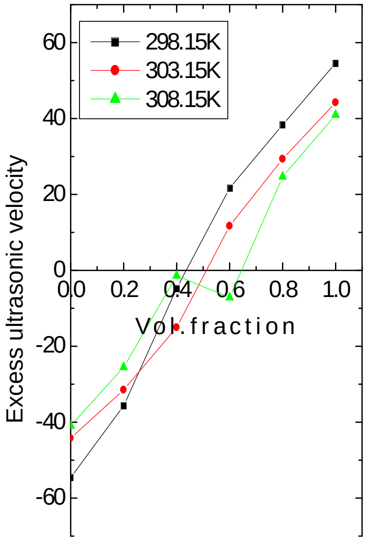

Figure 2: Plot of Excess Ultrasonic Velocity (u^E) against vol. fraction (x) for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz and at 298.15, 303.15, 3 08.15K temperatures.

Fig.-3

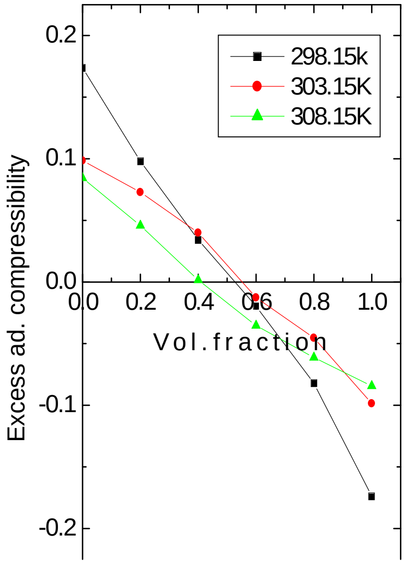

Figure 3: Plot of Excess Ad. Compressibility (βa^E) against vol. fraction (x) for the system (1M Glycine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 3 08.15K temperatures.

Fig.-4

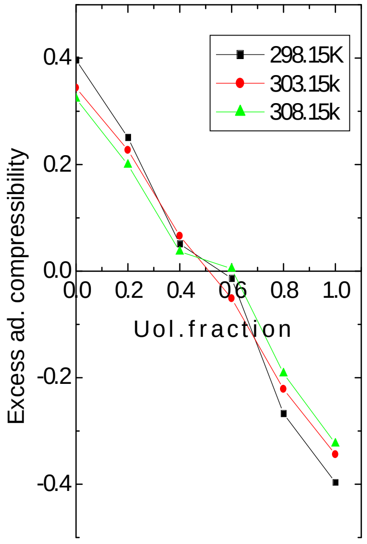

Figure 4: Plot of Excess ad. compressibility (β_a^E) against vol. fraction (x) for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz and at 298.15, 303.15, 3 08.15K temperatures.

Fig.-5

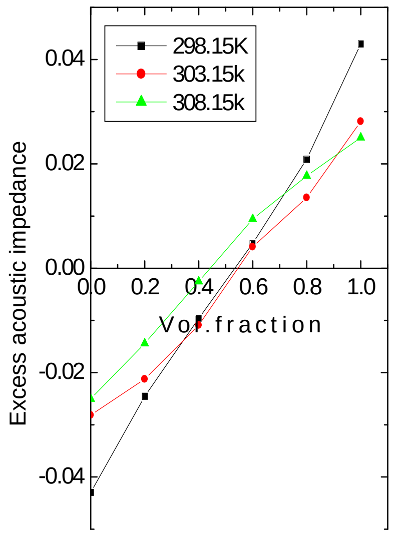

Figure 5: Plot of Excess Acoustic impedance (z^E) against vol. fraction (x) for the system (1M Glycine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 3 08.15K temperature.

Fig.-6

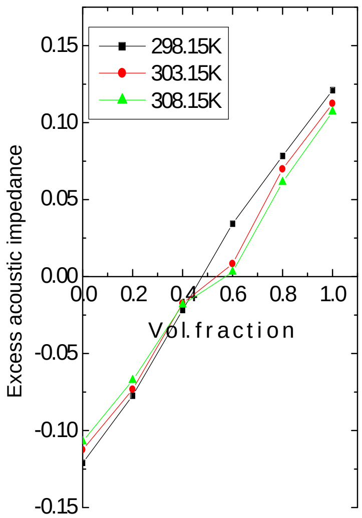

Figure 6: Plot of Excess acoustic impedance (z^E) against vol. fraction (x) for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz and at 298.15, 303.15, 3 08.15K temperatures.

Fig.-7

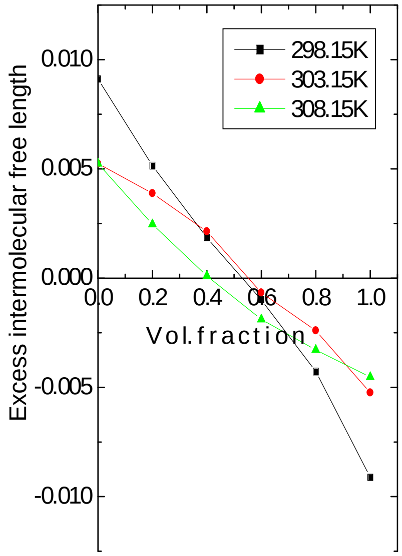

Figure 7: Plot of Excess Intermolecular free length (L_f^E) against vol. fraction (x) for the system (1M Glycine + 1M NaCl) at 2 MHz and at 298.15, 303.15,3 08.15K temperature.

Fig.-8

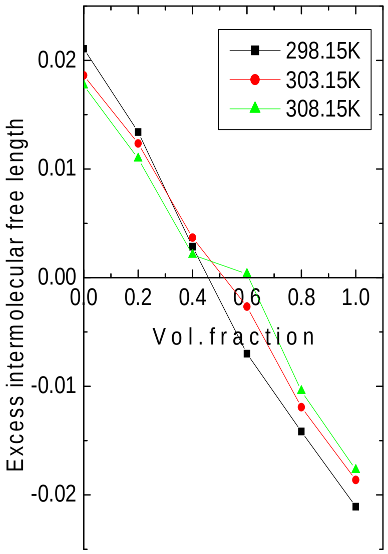

Figure 8: Plot of Excess Inter. free length (L_f^E) against vol. fraction (x) for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz and at 298.15,303.15,3 08.15K temperatures.

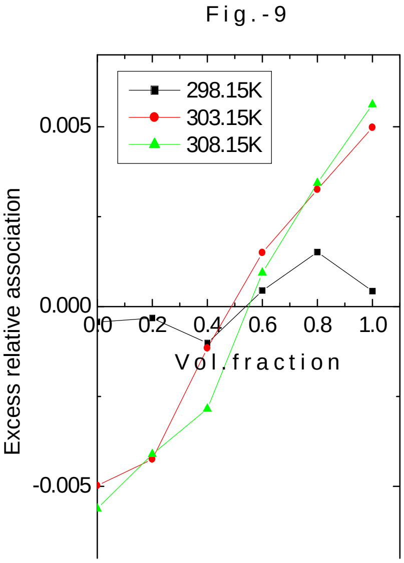

Figure 9: Plot of Excess Relative Association (R_A^E) against vol. fraction (x) for the system (1M Glycine + 1M NaCl) at 2 MHz and at 298.15, 303.15,3 08.15K temperatures.

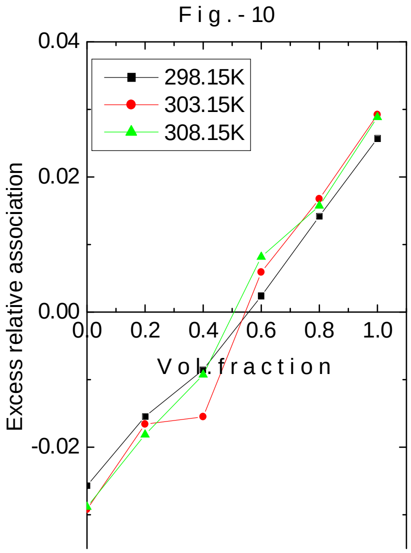

Figure 10: Plot of Excess Relative Association (R_A^E) against vol. fraction (x) for the system (1M Glycine + 1M $MgCl_2$) at 2 MHz and at 298.15,303.15,3 08.15K temp.

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.

10) Excess relative association (R_A^E)

The variation of excess relative association function with volume fraction (x) is mention in Tables – 3, 4 and graphically depicted in Figures –9 and 10. Figures show that R_A^E is small but negative for the system (1M glycine + 1M NaCl). But the values of R_A^E are high and more negative for the system (1M glycine + 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. Interactions between $MgCl_2$ and glycine again stronger than NaCl. The positive values of R_A^E for the system suggest the presence of weak interaction between unlike molecules.

Conclusion

Ultrasonic velocity, density and viscosity have been measured for 1M NaCl and 1M $MgCl_2$ in aqueous glycine solution at 298.15, 303.15, and 308.15K. The variation in ultrasonic velocity, density and viscosity and other related thermodynamic parameters such as adiabatic compressibility(β), acoustic impedance (z), intermolecular free length (L_f), relative association (R_A), of NaCl & $MgCl_2$ at various concentrations and temperatures in the glycine – based systems, shows the non-linear increase or

decrease behaviour. 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.
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. It is further assumed that complex formation between amino acids and electrolytes is due to polarization effect and not due to charge transfer interactions.
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. 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.

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