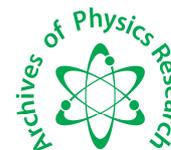




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Archives of Physics Research, 2013, 4 (1):1-14
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ISSN : 0976-0970

CODEN (USA): APRRC7

Excess thermodynamic properties of electrolytes [NaCl, MgCl₂] solutions with aqueous amino acid at different temperatures.

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ABSTRACTS

Ultrasonic velocities, densities and viscosities have been measured for (1M Alanine + 1M NaCl) and (1M Alanine + 1M MgCl₂) at different temperatures. Ultrasonic velocity of mixture has been measured with single crystal interferometer. Using these experimental data, the derived thermo acoustical parameters such as adiabatic compressibility (β_a); acoustic impedance (Z); intermolecular free length (L_f); relative association (R_A) has been calculated. By using experimental as well as derived parameters data, excess thermo acoustical parameters i.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 computed. Results have been analyzed with the variations in thermodynamic parameters as well as excess thermo acoustical parameters with concentrations of solutes and at different temperatures. Both thermodynamic and excess thermodynamic parameters threw some light on the molecular interactions among the liquid mixtures of electrolyte solutions and aqueous amino acid.

Keywords: Ultrasonic velocity; adiabatic compressibility; acoustic impedance; intermolecular free length; relative association and excess thermodynamic parameters.

INTRODUCTION

The ultrasonic velocity and other related thermodynamical parameters were successfully employed to understand the structural changes and the nature of molecular interactions in the mixtures. 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 [1] interstitial accommodation and orientational ordering [2] , leading to more compact structure making. The investigation of ultrasonic and thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solvents has been the area of interest. There has been an increased interest in the state of water in the living cell. The cell is the fundamental structural and functional unit of living organisms. Biomolecules [3] are complex organic molecules. These molecules form the basic structural constituent of a living cell. The important biomolecules are proteins, carbohydrates and fats, enzymes, vitamins, hormones and nucleic acids. Among these, proteins [4] are found in all parts of the body and they have an enormous variety of functions. The organic compounds [5] such as amino acids, nucleotides and monosaccharide serve as building blocks of complex biomolecules and used as a probe molecules [6] to understand the complex nature of proteins. 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. Most of the chemical and biological functions of biomolecules take place in aqueous medium. The choice of water for preparing mixed solvents stems from its important and unique role in determining the structure and stability of proteins. Since its presence is known to give rise to hydrophobic forces, which are of prime importance in stabilizing the native globular structure of proteins. The denaturation of globular protein in aqueous solution is fundamental biological processes which is not yet completely understood and remain a subject of extensive investigations [6-8]. In the

process of denaturation of globular protein in aqueous solutions, the native folded conformation of protein is converted predominantly into an extended unfolded form and during this process various changes will occur in protein solvation. Thus the study of these solute-solvent and solute-solute interactions is essential due to their important contribution to the energetic of protein denaturation. Rohini Badarayani et al [9,10] have measured the density and speed of sound of glycine in aqueous concentrated NaBr, KCl, KBr, and MgCl₂ at 298.15K. They also investigated that the compound MgCl₂ influences the apparent molar and transfer properties of the volumes and compressibilities more strongly than any other 1:1 electrolytes studied. The importance of the parameters involved is also discussed in terms of the ionic interactions.

To the best of our knowledge, ultrasonic velocity, density, and viscosity study of electrolytes with aqueous alanine solution at different temperatures are not reported up to now. Alanine plays a key role in maintaining glucose levels and thus energy supplies in the body. Epstein-Barr virus and chronic fatigue syndrome have been linked to excessive alanine levels and low levels of tyrosine and phenylalanine. It has been found that for people with insulin-dependent diabetes, taking an oral dose of L-alanine effectively prevents nighttime hypoglycemia. Alanine is a hydrophobic molecule. It is ambivalent, meaning that it can be inside or outside of the protein molecule. It plays central roles both as building blocks of proteins and as intermediates in metabolism. It is required for the metabolism of glucose and tryptophan. 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. There is information on the zwitter - ionic nature of amino acids in water in the literature [8-13]. The properties of proteins such as their structure, solubility, denaturation activity of enzymes etc. are greatly influenced by electrolytes [14, 15]. In the present paper, we report that ultrasonic velocity, density and viscosity of 1M NaCl and 1M MgCl₂ in aqueous alanine were measured at 298, 303, and 308 K. From these experimental data, a number of thermodynamic parameters namely, adiabatic compressibility (β), Intermolecular free length (L_f), acoustic impedance (z) and relative association (R_A) have been calculated. Using standard relations; excess thermodynamic parameters such as excess adiabatic compressibility (β^E), excess Intermolecular free length (L_f^E), excess acoustic impedance (z^E) and excess relative association (R_A^E) also have been computed. These thermodynamic parameters were utilized to study various interactions taking place in the solutions of 1M NaCl and 1M MgCl₂ in aqueous alanine. Excess thermodynamic parameters [16] have been found to be highly useful in elucidating solute – solvent interactions in aqueous solutions and binary mixtures.

MATERIAL AND METHOD

All the chemicals used were of AR grade and dried over anhydrous CaCl₂ in desiccator's before use. All solutions were prepared in deionized and distilled water (degassed by boiling), having specific conductivity $\sim 10^{-6}$ Scm⁻¹. The stock solutions of 1M concentration of Alanine, NaCl and MgCl₂ were prepared by weighing the all chemicals on a digital balance with an accuracy of $\pm 1 \times 10^{-5}$ Kg. Solutions of 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) operating at a frequency of 2MHz and at different temperatures of 298, 303, and 308K. The source of ultrasonic waves was a quartz crystal excited by a radio frequency oscillator placed at bottom of a double jacketed metallic cylindrical container. The cell was filled with the desired solution and in the outer jacket constant temperature water was circulated. The cell was allowed equilibrate for 30 minutes prior to making the measurements. The interferometer was calibrated against the ultrasonic velocity of water used at T = 298 K. The present experimental value is 1497.08 ms⁻¹ which is in good agreement with literature value [20] 1496.69 ms⁻¹. Accuracy in the velocity measurement was ± 1.0 ms⁻¹. Accuracy in the velocity measurement was ± 1.0 ms⁻¹.

The densities of the mixtures were determined accurately using 25 ml specific gravity bottle and electronic balance. The accuracy of electronic balance is ± 0.1 mg and the accuracy in the density measurement is $\pm 2 \times 10^{-2}$ 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 precalibrated Oswald 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 ± 0.1 K by means of thermostatic water bath.

THEORY AND FORMULATION

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 MgCl₂ at frequency 2 MHz and temperatures 298, 303, 308 K. From the experimental data of ultrasonic velocity (u), density (ρ) and viscosity (η), the thermodynamic parameters have been calculated by using the following relations [17-20]

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

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

$$\text{Intermolecular free length} \quad L_f = K / u \cdot \rho \quad \text{----- (3)}$$

$$\text{Acoustic impedance} \quad Z = u \rho \quad \text{----- (4)}$$

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

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 [16]

$$\text{Excess ultrasonic velocity} \quad u^E = u_{\text{mix}} - [(1-x) u_1 + x u_2] \quad \text{----- (6)}$$

$$\text{Excess adiabatic compressibility} \quad \beta^E = \beta_{\text{mix}} - [(1-x) \beta_1 + x \beta_2] \quad \text{----- (7)}$$

$$\text{Excess acoustic impedance} \quad Z^E = Z_{\text{mix}} - [(1-x) Z_1 + x Z_2] \quad \text{----- (8)}$$

$$\text{Excess intermolecular free length} \quad L_f^E = L_{f \text{ mix}} - [(1-x) L_{f1} + x L_{f2}] \quad \text{----- (9)}$$

$$\text{Excess relative association} \quad R_A^E = R_{A \text{ mix}} - [(1-x) R_{A1} + x R_{A2}] \quad \text{----- (10)}$$

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

RESULTS AND DISCUSSION

For the amino acids - electrolytes liquid systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M MgCl₂), ultrasonic velocity (u), density (ρ) and the coefficient of viscosity (η) for various volume fractions have been measured at constant frequency of 2 MHz and at different temperatures. The experimental values of u , ρ , η , are given in Tables - 1 and 2. The data obtained are used to evaluate β , Z , L_f , and R_A which is included in the same Tables. Using these experimental and calculated 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 – 3 and 4. The graph plotted of excess parameters versus vol. fraction (x) for two liquid systems as shown in Fig. - 1 - 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, and 2. From Tables – 1 and 2, 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.

From Tables – 1 and 2, ultrasonic velocity increases with increase in concentrations of solutes (1M NaCl, 1M MgCl₂) in liquid systems investigated such as (1M Alanine +1M NaCl) and (1M Alanine +1M MgCl₂). The value of ultrasonic velocity of (1M Alanine + 1M NaCl) is less as compared to the value of ultrasonic velocity in (1M Alanine +1M MgCl₂). When NaCl or MgCl₂ is dissolved in solution, the sodium ion (Na⁺) or (Mg⁺⁺) has a structure breaking effect, would disrupt the water structure^{1, 3}. 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 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 Tables – 1 and 2, 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 and 2. 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 alanine.

3. Acoustic impedance (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 Tables – 1 and 2; 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 impedance (Z) increases with increase in concentration in liquid systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M MgCl₂). 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 [2, 3] of liquid mixtures. This indicates significant interactions in the liquid systems. Similar behavior is also observed in alanine based liquid systems

4. Intermolecular free length (L_f):

The values of intermolecular free length for (1M Alanine + 1M NaCl) and (1M Alanine + 1M MgCl₂) 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 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.

5. Relative association (R_A):

The values of relative association (R_A) for liquid systems (1M Alanine + 1M NaCl) and (1M Alanine + 1M MgCl₂) 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, 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 – 3 and 4 and Fig. – 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 MgCl₂ in the liquid mixtures. More negative values of u^E indicates that the interactions between 1M alanine and 1M MgCl₂ 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 MgCl₂) 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 $x = 0.5$ (Fig.-1, 2) is indicative of the decreasing strength of interaction between component molecules of the mixture as suggested by Tiwari et al [12]. 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 MgCl₂). Thus, interactions between the molecules of system (1M Alanine +1M NaCl) are weaker than that in the molecules of system (1M Alanine + 1M MgCl₂).

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 presented in Tables- 3 and 4. From Figures 3 and 4, it is observed that the values of β^E are positive at the lower volume fraction upto $x = 0.4$ 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 - 3 and 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 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 .

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 and 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. 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 and 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 $x = 0.5$ (Fig.- 5, 6) is indicative of the decreasing strength of interaction between component molecules of the mixture as suggested by Tiwari et al [12]. 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 $MgCl_2$).

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^{10, 11}. 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- 3 and 4. The plot of (L_f^E) versus vol. fraction (x) at 298, 303 and 308 K are shown in Figures - 7, 8, for all 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 [31].

Figures – 7 and 8 shows variation in L_f^E at 298, 303 and 308 K. 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 [15], interstitial accommodation and orientational ordering [16], leading to more compact structure making. Negative L_f^E in the present investigation is an indication of strong interactions in the liquid mixtures [17], as well as interstitial accommodation of sodium and magnesium chloride into the glycine and 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 and those of L_r^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 – 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 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 Fig.-10.

Table-1: Variations in thermodynamic parameters with various concentrations (x) for the system (1M Alanine + 1M NaCl) at different temperatures and at frequency of 2 MHz.

Vol. fract. (x)	u	ρ	η	$\beta \times 10^{-10}$	$Z \times 10^6$	L_f	R_A
	(x)	m / s	Kg / m ³	N s m ⁻²	m ² N ⁻¹	N m ⁻²	⁰ A
298.15K							
0.0	1541.28	1050.8	0.99238	4.01000	1.61957	0.41200	1.00000
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
303.15K							
0.0	1560.48	1047.6	0.93045	3.92000	1.63475	0.41100	1.00000
0.2	1566.32	1048.0	1.04089	3.89000	1.64150	0.40900	0.99913
0.4	1568.48	1052.8	1.05430	3.86000	1.65129	0.40800	1.00325
0.6	1570.32	1054.0	1.05182	3.85000	1.65517	0.40700	1.00393
0.8	1576.00	1055.2	1.08799	3.82000	1.66299	0.40500	1.00400
1.0	1578.00	1061.2	1.18719	3.78000	1.67457	0.40400	1.00671
308.15K							
0.0	1577.40	1044.4	0.87445	3.85000	1.64743	0.41100	1.00000
0.2	1578.2	1046.4	0.95408	3.84000	1.65142	0.41000	1.00174
0.4	1581.92	1050.8	0.96734	3.80000	1.66228	0.40800	1.00516
0.6	1583.30	1050.8	0.97496	3.80000	1.66373	0.40800	1.00587
0.8	1584.00	1051.6	1.02355	3.79000	1.66573	0.40800	1.00549
1.0	1587.40	1058.8	1.09829	3.75000	1.68073	0.40500	1.00654

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

Table-2: Variations in thermodynamic parameters with various concentrations (x) for the system (1M Alanine + 1M MgCl₂) at different temperatures and at frequency of 2 MHz.

Vol. fract.	u (x)	ρ m / s	η Kg / m ³	$\beta \times 10^{-10}$ N s m ⁻²	$Z \times 10^6$ m ² N ⁻¹	L_f N m ⁻²	R_A °A
298.15K							
0.0	1544.96	1050.8	1.20359	3.99000	1.62344	0.41100	1.00000
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
303.15K							
0.0	1570.32	1048.0	1.09713	3.87000	1.64569	0.40800	1.00000
0.2	1582.24	1057.2	1.13821	3.78000	1.67274	0.40300	1.00623
0.4	1582.80	1059.6	1.16068	3.77000	1.67713	0.40300	1.00840
0.6	1588.80	1071.2	1.18726	3.70000	1.70192	0.39900	1.01815
0.8	1597.20	1080.0	1.20347	3.63000	1.72497	0.39500	1.02472
1.0	1616.20	1090.4	1.23128	3.51000	1.76230	0.38900	1.03051
308.15K							
0.0	1585.92	1046.4	1.01825	3.80000	1.65950	0.40865	1.00000
0.2	1587.40	1056.4	1.06153	3.76000	1.67692	0.40166	1.00924
0.4	1587.90	1058.0	1.07982	3.75000	1.67999	0.39978	1.01066
0.6	1598.50	1069.2	1.09832	3.66000	1.70911	0.39178	1.01191
0.8	1607.60	1078.0	1.11706	3.59000	1.73299	0.38765	1.02554
1.0	1616.40	1087.6	1.12314	3.52000	1.75799	0.38272	1.03279

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

Table-3: Variations in excess thermodynamic parameters with various concentrations (x) for the System (1M Alanine + 1M NaCl) at different temperatures and at frequency of 2 MHz.

Vol. fract.	u^E (x)	$\beta_a^E \times 10^{-10}$ m / s	$z^E \times 10^6$ m ² N ⁻¹	L_f^E N m ⁻²	R_A^E °A
298.15K					
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
303.15K					
0.0	-17.520	0.14000	-0.03982	0.00700	-0.00921
0.2	-08.176	0.08200	-0.02510	0.00360	-0.00823
0.4	-02.512	0.02400	-0.00735	0.00120	-0.00227
0.6	-02.832	-0.01400	0.00443	-0.00120	0.00031
0.8	12.016	-0.07200	0.02027	-0.00460	0.00208
1.0	17.520	-0.14000	0.03982	-0.00700	0.00921
308.15K					
0.0	-10.000	0.10000	-0.03330	0.00600	-0.01165
0.2	-07.200	0.07000	-0.02265	0.00380	-0.00578
0.4	-01.480	0.01000	-0.00513	0.00060	-0.00183
0.6	01.900	-0.01000	0.00298	-0.00060	0.00021
0.8	04.600	-0.04000	0.01164	-0.00180	0.00316
1.0	10.000	-0.10000	0.03330	-0.00600	0.00654

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: Variations in excess thermodynamic parameters with various concentrations (x) for the System (1M Alanine + 1M MgCl₂) at different temperatures and at frequency of 2 MHz.

Vol. fract.	u^E (x)	$\beta_a^E \times 10^{-10}$ m / s	$Z^E \times 10^6$ $m^2 N^{-1}$	L_f^E $N m^{-2}$	R_A^E 0A
298.15K					
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
303.15K					
0.0	-45.880	0.36000	-0.11661	0.01900	-0.03051
0.2	-24.784	0.19800	-0.06623	0.01020	-0.01817
0.4	-15.048	0.11600	-0.03852	0.00640	-0.00990
0.6	00.128	-0.02600	0.22958	-0.00140	0.00594
0.8	17.704	-0.16800	0.05595	-0.00920	-0.98138
1.0	45.880	-0.36000	0.11661	-0.01900	0.03051
308.15K					
0.0	-30.480	0.28000	0.09849	0.01400	-0.03279
0.2	-22.904	0.18400	-0.06137	0.01020	-0.01699
0.4	-16.308	0.11800	-0.03860	0.00640	-0.00901
0.6	00.388	-0.02800	0.01021	-0.00040	-0.00120
0.8	15.584	-0.15400	0.05379	-0.00720	0.01898
1.0	30.480	-0.28000	0.09849	-0.01400	0.03279

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.

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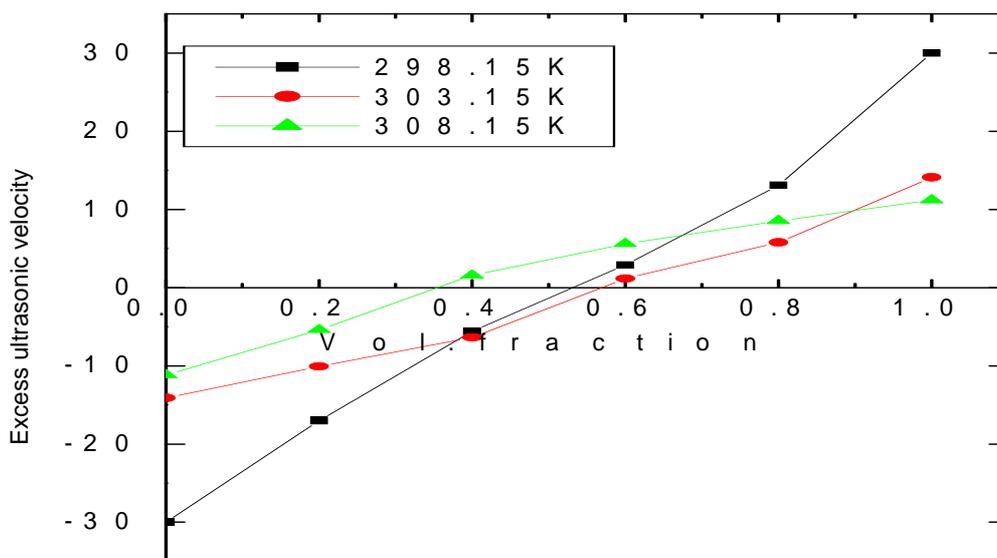


Fig. 1 – Plot of Excess Ultrasonic Velocity (u^E) against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

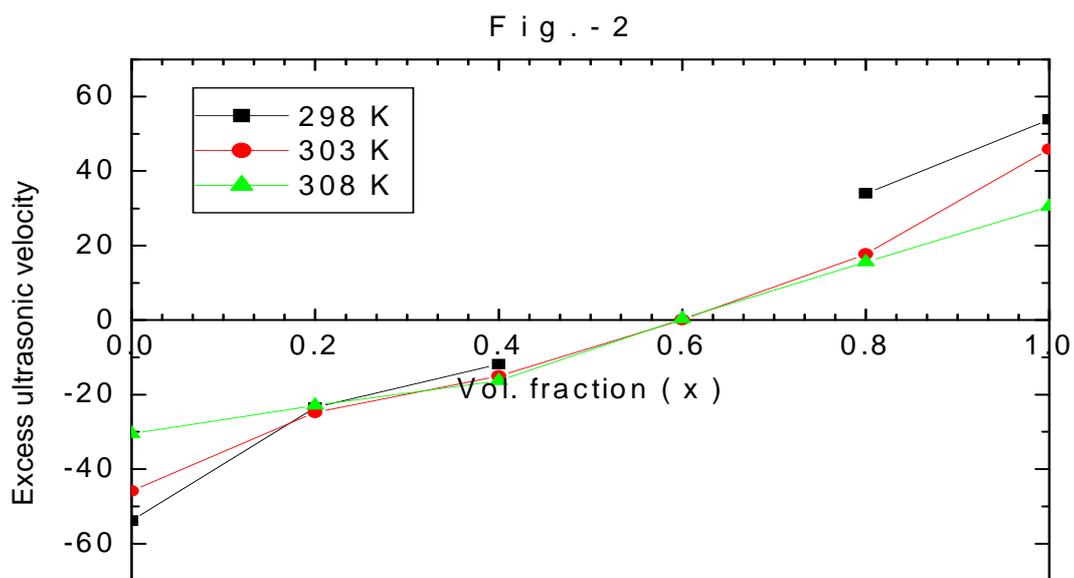


Fig. 2 – Plot of Excess Ultrasonic Velocity (u^E) against vol. fraction (x) for the system (1M Alanine + 1M MgCl₂) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

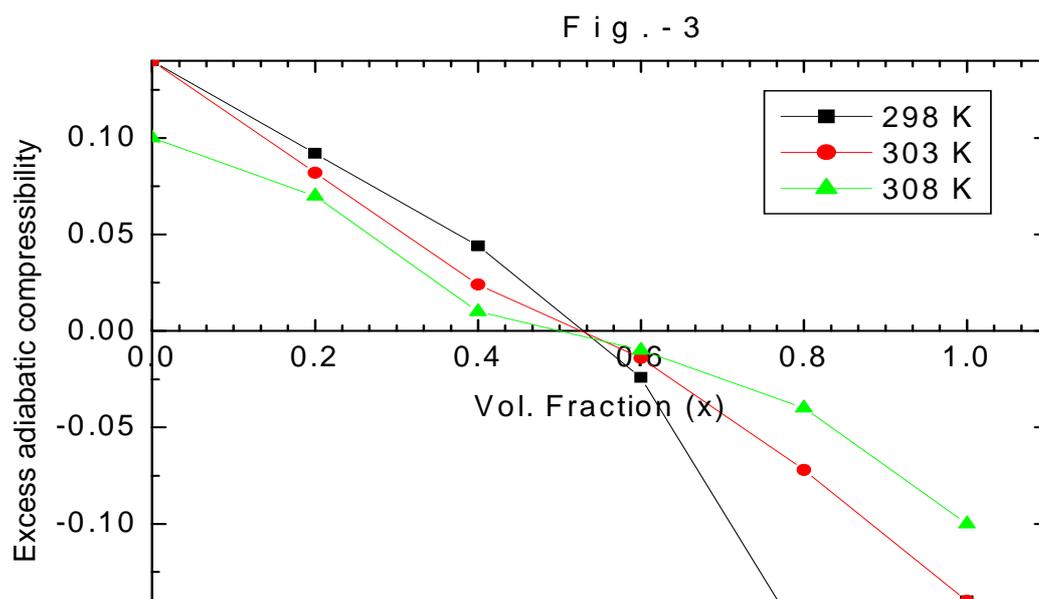


Fig. 3 – Plot of excess adiabatic compressibility against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

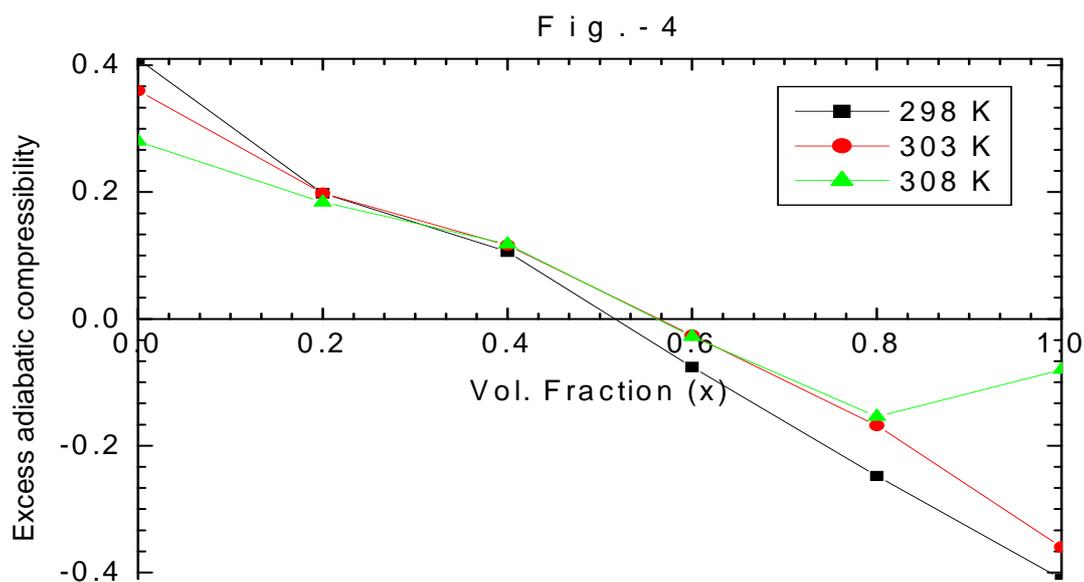


Fig. 4 – Plot of excess adiabatic compressibility against vol. fraction (x) for the system (1M Alanine + 1M MgCl₂) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

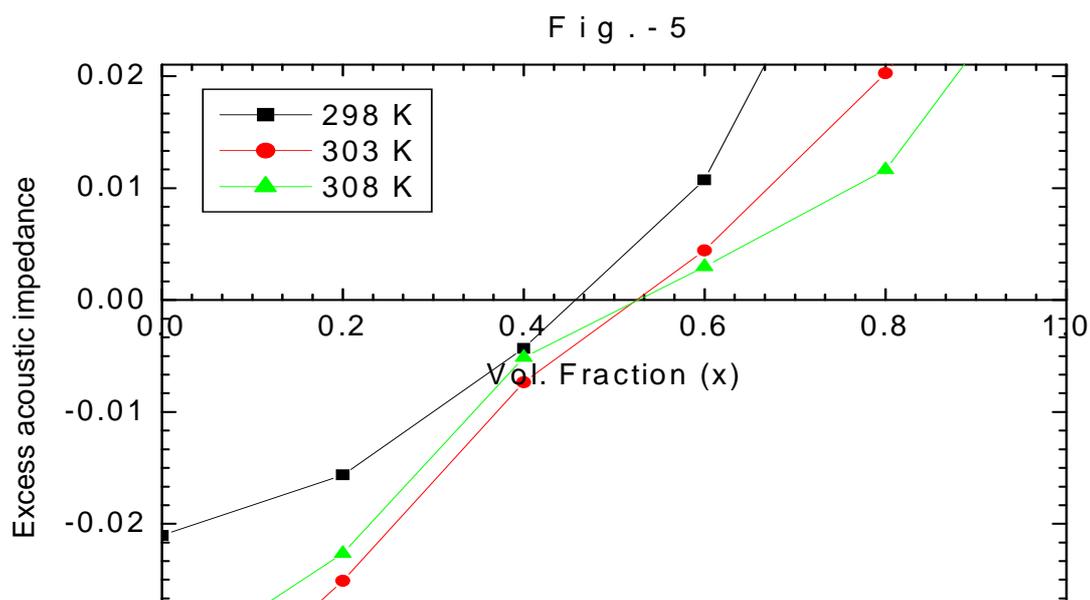


Fig. 5 – Plot of excess acoustic impedance against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

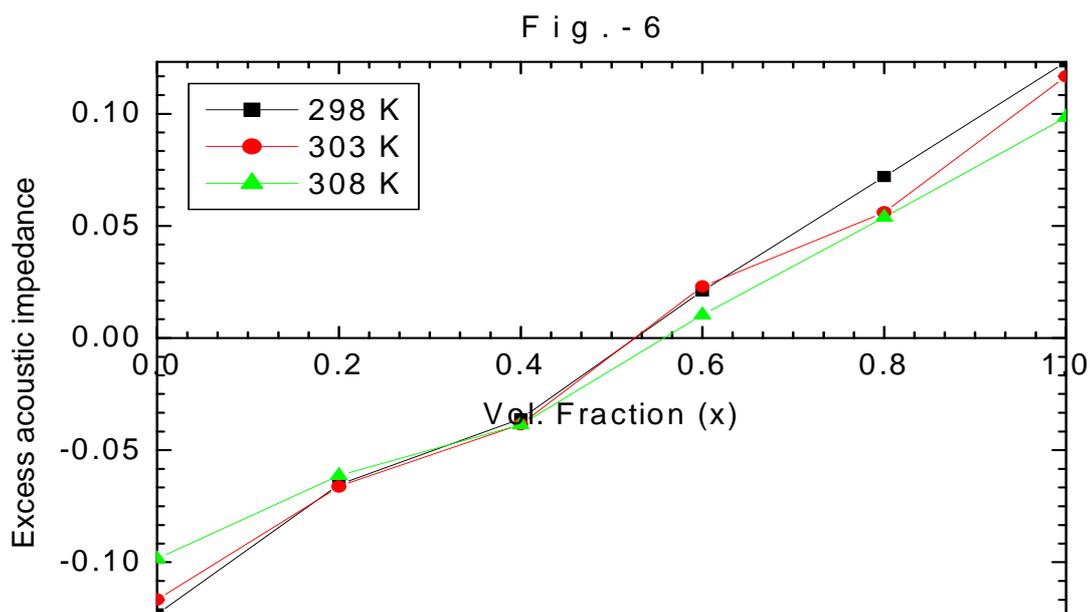


Fig. 6 – Plot of excess acoustic impedance against vol. fraction (x) for the system (1M Alanine + 1M MgCl₂) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

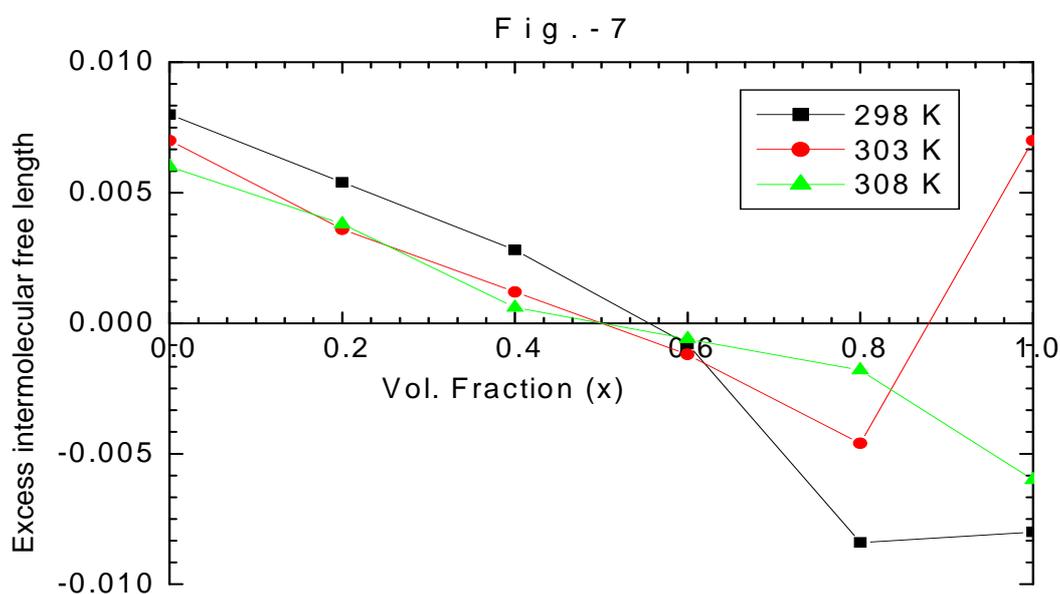


Fig. 7 – Plot of excess intermolecular free length against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

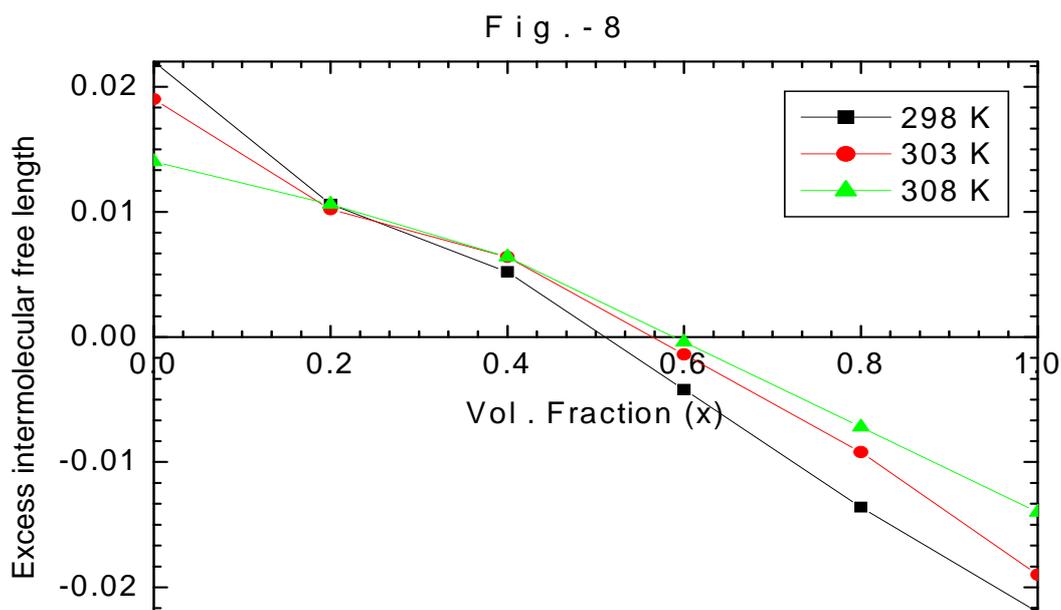


Fig. 8 – Plot of excess intermolecular free length against vol. fraction (x) for the system (1M Alanine + 1M MgCl₂) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

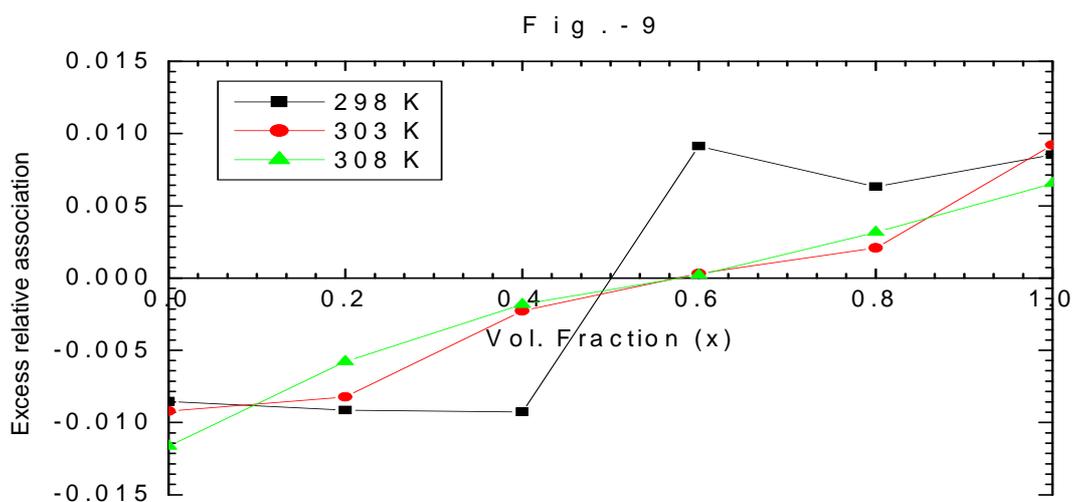


Fig. 9– Plot of excess relative association against vol. fraction (x) for the system (1M Alanine + 1M NaCl) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

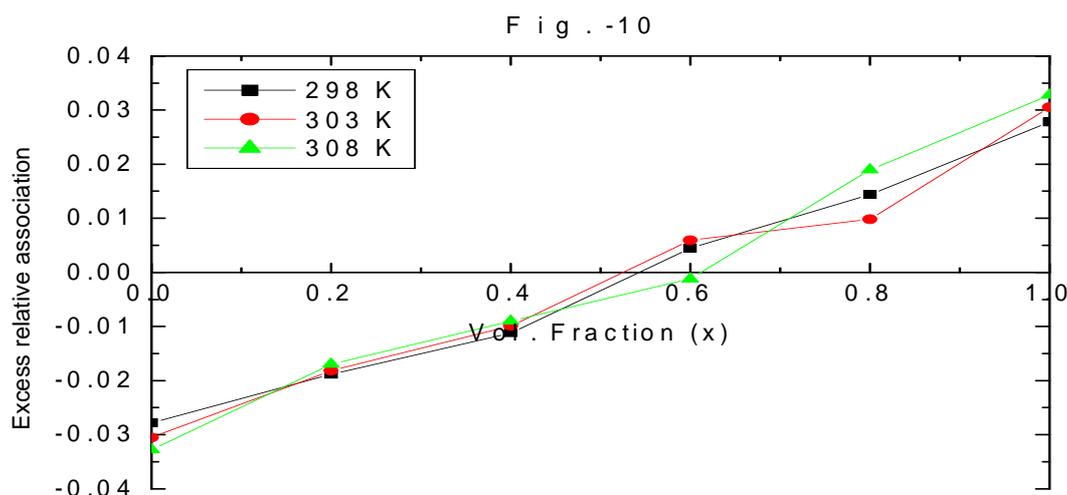


Fig. 10 – Plot of excess relative association against vol. fraction (x) for the system (1M Alanine + 1M MgCl₂) at 2 MHz and at 298.15, 303.15, 308.15K temperatures.

CONCLUSION

Ultrasonic velocity, density and viscosity have been measured for NaCl and MgCl₂ in aqueous alanine solution at 308 K. The variation in ultrasonic velocity, density and viscosity and other related thermodynamic parameters such as adiabatic compressibility (β_a), acoustic impedance (Z), intermolecular free length (L_f), relative association (R_A) of NaCl & MgCl₂ at various concentrations in both the alanine – based systems, 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. 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 variation in ultrasonic velocity, density and viscosity as well as the related thermodynamic parameters are more in the system containing MgCl₂ as compared to the system having NaCl due to the divalent cation (Mg²⁺⁺) of MgCl₂. As a matter of fact, the effect of MgCl₂ on the electrostriction of water molecules is stronger than that of 1:1 electrolytes i.e. NaCl. 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.

Acknowledgement

I am thankful to Dr. K. M. Jadhav, Professor and Former Head, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, and Aurangabad to avail the library facility. I also thanks to Dr. Sonawane, Reader in Physics, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for useful discussion about electrolytes and amino acids.

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