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Excess thermodynamical properties of electrolytes solution with aqueous amino acids at 303.15, 308.15 and 313.15K

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ABSTRACT

The measurements of density, viscosity and velocity have been determined by experimental procedures using specific gravity bottle, Ostwald's viscometer and ultrasonic interferometer technique at frequency of 2 MH_z and at constant temperatures of 303.15,308.15 and 313.15K respectively Ultrasonic velocities (u), densities (ρ) and viscosities (η) have been measured for the binary liquid systems (1M NaCl+1M Serine). Using 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 these liquid systems at frequency of 2 MH_z and at all temperatures shows a similar trend of increasing ultrasonic velocity and decreasing in adiabatic compressibility of the constituent amino acids. Again, this is due to complex formation and coordinate covalent bonds formed between the molecules of the liquid mixtures. 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) have been calculated. The presence of ion – ion, solute – solvent (Amino acid, electrolyte and water) interactions is noticed in the mixed aqueous systems.

Key words: Ultrasonic Velocity; Excess Adiabatic Compressibility; Excess Intermolecular Free Length; Excess Acoustic Impedance; Excess Relative Association.
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INTRODUCTION

Amino acids and peptides are used as probe molecules to understand the complex nature of proteins. There is information on the zwitter-ionic nature of amino acids in water in the literature[1-4]. The properties of proteins such as their structure, solubility, denaturation, activity of enzymes, etc, are greatly influenced by electrolyte[5-6]. An electrolyte, when dissolved in water, perturbs the arrangement of water molecules with the strong electric field of its ions. This property of electrolyte known as structure maker or breaker has been widely used to understand the effect of electrolytes on the structure and function of both proteins and nucleic acids[7]. In the past, thermodynamic properties of amino acids in dilute electrolyte solutions have been studied in order to understand the complex nature of proteins using amino acid-ion interactions[8, 9]. There are instances where high concentrations of electrolytes can affect the function and structures of proteins[10,11]. Ion-ion and ion-amino acid interactions dominate in such situations. The thermodynamics of interaction of concentrated NaCl in dilute amino acids have been reported in the literature[12-14]. How the ion-ion and ion-amino acid interactions together with ion-water and amino acid-water ones are altered in concentrated electrolyte and concentrated amino acid solutions is the object of current investigations. Information is available on activity coefficients, enthalpies and heat capacities of aqueous amino acids in electrolytes[15-18]. To our knowledge no systematic efforts have been made to the ion-ion and ion-amino acid interactions in concentrated electrolyte solutions.

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Excess thermodynamic parameters have been found to be highly useful in elucidating solute-solvent interactions in aqueous solutions and binary mixtures. 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 molecules[19]. 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, interstitial accommodation and orientation ordering, leading to more compact structure making. Derived parameters from ultrasonic velocity measurement and corresponding excess functions provide qualitative information regarding the nature and strength of interactions in liquid mixtures.

EXPERIMENTAL SECTION

All the chemicals used were of AR grade and dried over anhydrous $CaCl_2$ in desiccators before use. All solutions were prepared in deionizer and distilled water (degassed by boiling), having specific conductivity~10^{-6} S cm^{-1}. The stock solutions of 1M concentration were prepared by weighing the serine on a digital balance with an accuracy of $\pm$ 1 x 10^{-4} g. Solutions of NaCl is made by mass on the mole fraction scale. Uncertainties in solution concentrations were estimated at $\pm$ 1 x 10^{-5} mol kg-1 in calculations. The solutions were kept in the special air tight bottles and were used within 12 hrs. After preparation to minimize decomposition due to bacterial contamination. Ultrasonic velocity was measured with a single crystal interferometer (F-81, Mittal Enterprises, New Delhi) at 2MHz The interferometer was calibrated against the ultrasonic velocity of water used at T = 303.15K. The present experimental value is 1508.80 ms^{-1} which is in good agreement with literature value[20,21] 1509.55 ms^{-1}.

Accuracy in the velocity measurement was 1.0 ms^{-1}. The density measurements were performed with recalibrated specific gravity bottle with an accuracy of 2x10^{-2} kg m^{-3}. An average of triple measurements was taken into account. Sufficient care was taken to avoid any air bubble entrapment. Viscosity was measured with recalibrated Ostwald type viscometer. The flow of time was measured with a digital stop watch capable of registering time accurate to 0.1 s. An average of three or four sets of flow of times for each solution was taken for the purpose of calculation of viscosity. The accuracy of the viscosity measurements was 0.5 %. Accuracy in experimental temperature was maintained at 0.1K by means of thermostatic water bath.

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 (βa); intermolecular free length (L_f); acoustic impedance (z) and relative association (R_A) were investigated for six different vol. fractions of 1M NaCl at frequency 2 MH$_z$ and at constant temperature 303.15,308.15 & 313.15K. From the experimental data of density (ρ), viscosity (η) and ultrasonic velocity (u), the thermodynamic parameters have been calculated by using the following relations[22-25]

Ultrasonic velocity $\quad\quad\quad\quad$ $u = n \times \lambda$ ---------------- (1)
Adiabatic compressibility $\quad\quad$ $\beta_a = 1/u^2 \rho$ -------------- (2)
Intermolecular free length $\quad$ $L_f = K / u.\rho$ --------------(3)
Acoustic impedance $\quad\quad\quad$ $z = u. \rho$ ------------------ (4)
Relative association $\quad\quad\quad$ $R_A = (\rho / \rho_o). (u_o / u)^{1/3}$ --(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_a^E, z^E, L_f^E, and R_A^E have been calculated using the following equations[31]

Excess ultrasonic velocity $\quad\quad\quad$ $u^E = u_{mix} - [(1- x) u_1 + x u_2]$ ------------------- (6)
Excess adiabatic compressibility $\quad$ $\beta_a^E = \beta_{amix} - [(1- x) \beta_{a1} + x \beta_{a2}]$ -------------- (7)
Excess acoustic impedance $\quad\quad\quad$ $z^E = z_{mix} - [(1- x) z_1 + x z_2]$ ------------------ (8)
Excess intermolecular free length $L_f^E = L_{fmix} - [(1- x) L_f 1 + x L_{f 2}$] ----------- (9)
Excess relative association $\quad\quad\quad$ $R_A^E = R_{Amix} - [(1- x) R_{A 1} + x R_{A2}]$ --------- (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 system(1M NaCl+ 1M Serine) ultrasonic velocity (u), density (ρ) and the coefficient of viscosity (η) for various volume fractions have been measured at frequency of 2 MH$_z$ and at constant temperature of 303.15,308.15,313.15K. The experimental values of u, ρ, η, are given in Table–1, thermo dynamical

parameters for the system (1M NaCl+ 1M Serine) & Table-2 thermo dynamical excess parameters for the system (1M NaCl+ 1M Serine). The data obtained are used to evaluate thermodynamic parameters such as β_a , z, L_f, and R_A which is included in the Table1. Using these experimental and computed data, 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 computed. The values of excess parameters have been presented in Table – 2. The graph plotted of excess parameters versus vol. fraction (x) for liquid system as shown in Figure: -1 to 10.

Table-1: Variation of thermodynamic parameters at different   volume fraction (x) and different temperatures for the system (1M NaCl+1M Serine) at 2MHz

Vol.fra (x)	u ms^{-1}	ρ kg m^{-3}	η Nm^{-2}s	βx10^{-1} m^{2}N^{-1}	z x10^6 Nm^{-2}	L_f A^0	R_A
303.15K							
0.0	1554.50	1056	1.0428	3.9188	1.64155	0.41088	1.05025
0.2	1561.70	1058	1.0507	3.8754	1.65228	0.40869	1.05062
0.4	1568.00	1060	1.0578	3.8371	1.66208	0.40657	1.05120
0.6	1570.04	1062	1.0605	3.8199	1.66738	0.40398	1.05272
0.8	1575.10	1061	1.0710	3.7889	1.67590	0.40398	1.05358
1.0	1586.08	1066	1.010	3.7220	1.69076	0.40080	1.05312
308.15K							
0.0	1568.00	1054	0.9478	3.8589	1.65267	0.41141	1.04988
0.2	1571.70	1055	0.9561	3.8371	1.65814	0.41025	1.05005
0.4	1571.00	1058	0.9541	3.8151	1.66529	0.40907	1.05252
0.6	1579.08	1060	0.9691	3.7834	1.67371	0.40737	1.05338
0.8	1581.00	1062	0.9853	3.7671	1.67902	0.40649	1.05494
1.0	1588.07	1064	0.9911	3.7267	1.68970	0.40430	1.05536
313.15K							
0.0	1572.88	1052	0.9227	3.8423	1.67297	0.41360	1.04934
0.2	1587.04	1053	0.9440	3.8136	1.70748	0.41205	1.04919
0.4	1582.07	1055	0.9681	3.7870	1.74472	0.41061	1.05029
0.6	1584.88	1058	0.9802	3.7629	1.77020	0.40930	1.05266
0.8	1586	1060	0.9825	3.7480	1.80087	0.40849	1.05428
1.0	1588.04	1063	0.9909	3.0732	1.84258	0.40752	1.05692

Where u, ultrasonic velocity; ρ, density of the solution ; η,viscosity of solution; βa, adiabatic compressibility; L$_f$, intermolecular free length; R$_A$, relative association; z, acoustic impedance.

Table-2: Variation of Excess parameters at different volume fraction (x) and different temperatures for the system (1M NaCl+1MSerine) at 2 MHz

u^E ms^{-1}	β^Ex10^{-1} Nm^{-2}	z^E x10^6 A^0	L_f^E	R_A^E
303.15K				
44.4000	-0.51260	0.13784	-0.02467	0.05316
-6.65456	-0.07836	0.02787	-0.00240	0.02372
-3.07928	-0.06213	0.01178	-0.00167	0.01640
-75.7444	0.43432	-0.13766	0.02564	-0.01719
-108.680	0.59783	-0.18526	0.03484	-0.01968
-128.256	0.89628	-0.25161	0.04331	-0.03554
308.15k				
45.9000	-0.48350	0.13970	-0.02501	0.04984
2.91784	-0.10514	0.06438	-0.00560	0.00255
-6.45059	-0.02651	0.01798	-0.00141	-0.00927
-70.3463	0.41574	-0.12859	0.02312	-0.07558
-108.425	0.59106	-0.18907	0.03341	-0.09639
-134.448	0.73295	-0.25713	0.04219	-0.12868
42.8800	-0.46400	0.15521	-0.02426	0.05070
3.55472	-1.11487	0.09395	-0.00658	0.02734
-7.61371	-0.02801	0.09561	-0.00151	0.01922
-70.0156	0.40859	-0.03331	0.02293	-0.01595
-105.118	0.56701	-0.06133	0.03220	-0.01425
-179.305	0.88390	-0.14817	0.05124	-0.02317

Where, u^E = Excess ultrasonic velocity; βa ^{E}= Excess   ad. compressibility; z^E=Excess acoustic impedance; L$_f^E$=Excess intermolecular free length; R$_A^E$ = Excess relative association.
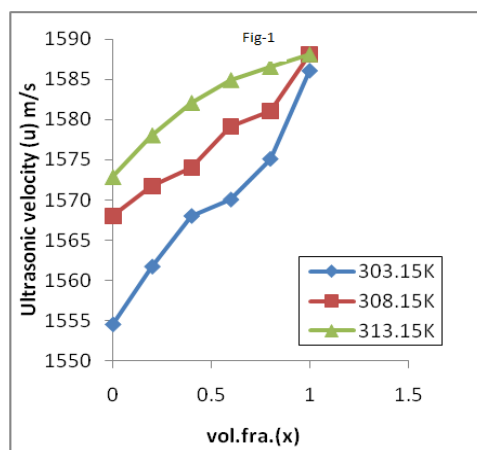
Fig. 1- Plot of ultrasonic velocity (u) against volume fraction (x) of the system (1M NaCl + 1M serine) at2 MHz and 303.15, 308.15 and 3013.15K temperatures
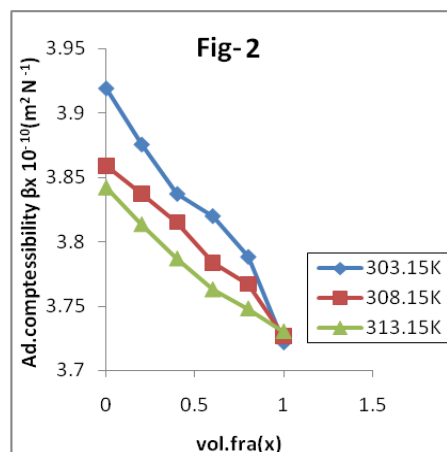
Fig. 2- Plot of adiabatic compressibility (β_a) against volume fraction (x) of system (1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures
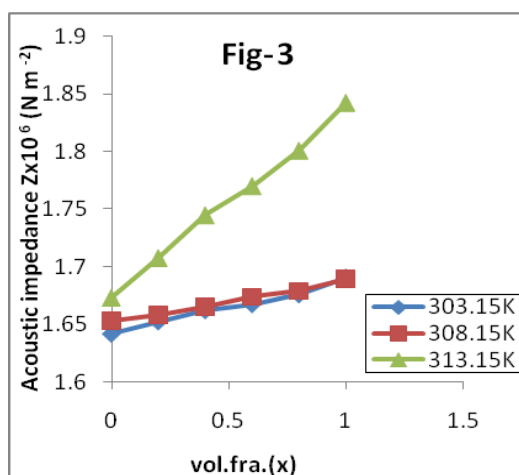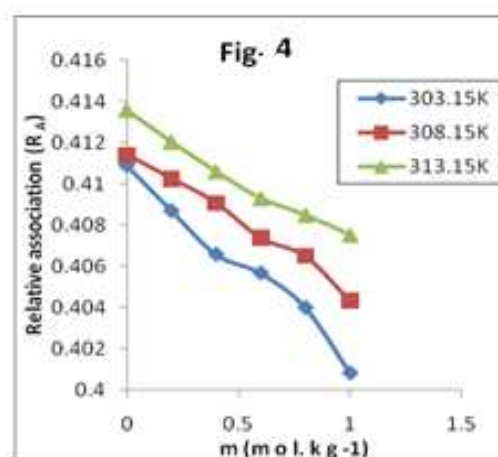

Fig. 3-Plot of acoustic impedance (z) against volume fraction (x) of system(1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures

Fig. 4- Plot of intermolecular free length (L$_f$) against volume fraction (x) of the system (1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures

Ultrasonic Velocity (u):
The ultrasonic velocity (u) for amino acid electrolytes solutions at 2MH$_z$ frequency and at different temperatures have been determined using relation (1) and presented in Tables 1thermo dynamical parameters for the system (1M NaCl + 1M Serine) &Table-2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine), the variations in ultrasonic velocity in liquid mixtures depend on concentration (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.

The variations in ultrasonic velocity and adiabatic compressibility with concentrations in these liquid systems at frequency of 2 MH$_z$ and at all temperatures shows a similar trend of increasing ultrasonic velocity and decreasing in adiabatic compressibility of the constituent amino acids. Again, this is due to complex formation and coordinate covalent bonds formed between the molecules of the liquid mixtures.

From Tables-1 & 2 ultrasonic velocity increases with increase with increase in concentrations of solute (1M serine) in liquid system investigated such as (1M NaCl + 1M serine). When NaCl is dissolved in solution, the sodium ion (Na^+) has a structures breaking effect, would disrupt the water structure[26]. 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 amino acids solution is added to a 1M electrolytes (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[27]. The calculated values of (β_a) have been presented in Tables1 and 2.

Acoustic Impendence (z)
Acoustic impedance (z) is found to be almost inversely proportional to the adiabatic compressibility (β_a). Specific acoustic impendence is calculated by using earlier standard relation (4). The calculated values of (z) are mention is Tables 11thermo dynamical parameters for the system (1M NaCl + 1M Serine) &Table-2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine),From Fig- 3&8, it is observed that acoustic impendence(z) increases for different volume fractions. Acoustic impedance becomes either maximum or minimum depending on the concentrations and different temperatures[28]. 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 system (1M NaCl + 1M serine) and. 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 increase in concentrations of solutes can be explained in terms of inter and intra molecular interactions between the molecules of liquid systems. This indicates significant interaction in liquid system. From Tables1 thermo dynamical parameters for the system (1M NaCl + 1M Serine) &Table-2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine),it is seen that values of acoustic impendence (z) are minimum in 1M NaCl.

Intermolecular Free Length (L_f)
The values of intermolecular free length for (1M NaCl + 1M serine) system have been calculated using equations (3). Increase in concentrations leads to decrease in gap between two species which is referred by intermolecular free length (L_f) has to decrease. Intermolecular free length (L_f) is a predominate factor in determining the variations of ultrasonic velocity in liquid mixtures. From Fig- 4, and Tables-1thermo dynamical parameters for the system (1M NaCl + 1M Serine) , it has been observed that, in the present investigation, intermolecular free length decreases linearly on increasing volume fractions of serine &. The decrease in L_f with increase of volume fractions in 1M NaCl solution indicates that there are significant interactions between solute and solvent suggesting the structure promoting behavior of solutes[29]. Ultrasonic velocity increases with volume fractions of solutes indicated 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, ions and water molecules increases. Thus the intermolecular distance decreases with concentration[30]. 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 NaCl+ serine) a have been estimated using earlier 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[34]. The former leads to the decrease and later to the increase of relative association. In Fig- 5 , Tables 1 , it is observed that the variation is very small and (R_A) increases with increase in the volume fractions (x) but decreases with temperature.

Excess Ultrasonic Velocity (u^E)
The values of excess ultrasonic velocity have been calculated using the standard relation (2) and are presented in Tables 2 . From Table 2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine), and Fig-6 it is clear that the values of (u^E) are positive at the beginning but becomes negative thereafter by increasing volume fractions of 1M serine in the liquid mixture. The values of excess velocity decreasing. More negative values of u^E in case of (1M NaCl+1M serine) indicates that the interaction between 1M NaCl and 1M serine is more stronger. Graphs shown in Fig-6 for (1M NaCl+1M serine) at different temperature and various volume fractions, excess values of (u^E) are less positive at x-0.0 then become negative with increasing volume fraction.

Increase in negative values of (u^E) with x-0.3 (Fig-6) is indicative of the increasing strength of interaction between component molecules of the mixtures. This supports our view that the interaction between component molecules in

liquid mixtures is strong[31]. Fig-6 , shows that (u^E) values are large negative for (1M NaCl + 1M serine). Thus interactions between the molecules of system (1M NaCl + 1M serine) are weaker.
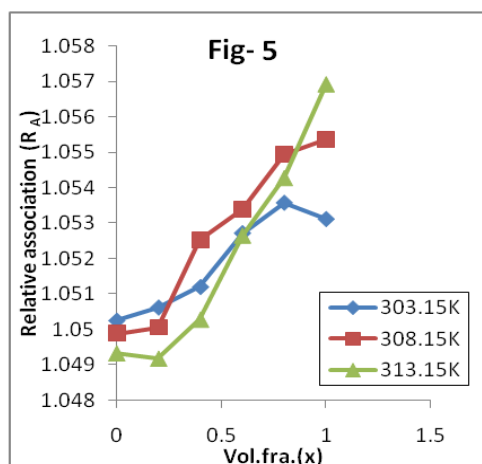

Fig. 5- Plot of relative association (R $_A$) against volume fraction (x) of the system (1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures
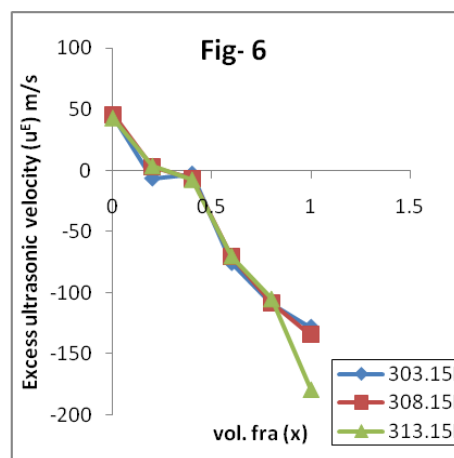
Fig. 6 –Plot of excess ultrasonic velocity (u^E) against volume fraction (x) of system(1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures
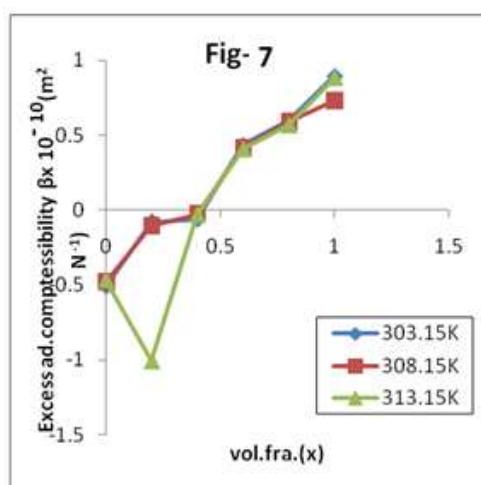

Fig. 7- Plot of excess adiabatic compressibility (β_a^E) against volume fraction (x) of system (1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures
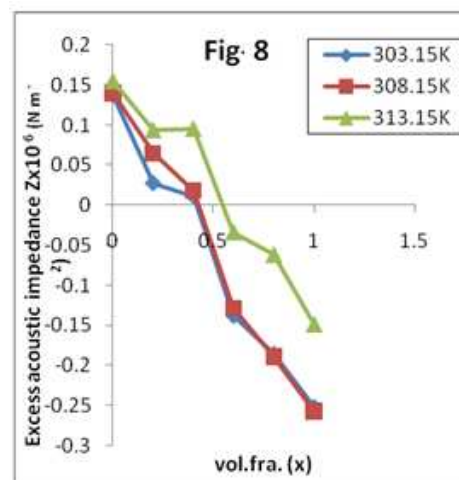
Fig. 8–Plot of excess acoustic impedance (z^E) against volume fraction (x) of system(1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures

Excess Adiabatic Compressibility (β_a^E)

Excess thermodynamic parameters have been found to be highly useful in solute-solvent interactions in aqueous solutions and binary mixtures. The variations in excess adiabatic compressibility (β_a^E) with volume fractions at different temperatures are presented in Tables-2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine), and From Fig- 7 it is observed that the values of β_a^E are negative at the lower volume fraction up to x-0.4 whereas the sign inversion of the β_a^E values changes by increasing volume fraction x-1.0. The curves show that the positive values of excess compressibility reaches maximum at x=1.0 volume fraction of 1M serine. From Table 2thermo dynamical excess parameters for the system (1M NaCl + 1M Serine), , the values of excess compressibility changes from negative to positive by increasing volume fractions of aqueous solutions of serine in 1M NaCl .

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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 graph 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_a^E decreases[32] 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_a 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 negative value of β_a^E, suggest significant interactions between the component molecules in the mixture, forming donor-acceptor complex between electrolytes and amino acid molecules. As a result there is contraction in volume, resulting in negative values of β_a^E, with. The positive values of β_a^E, for the system suggest the presence of weak interaction between unlike molecules. The size of component molecules almost no equal, it seems that their molecules do not pack well into each other structures. This results in expansion in volume, and hence positive β_a^E values.

The negative value of β_a^E suggests significant interaction between component molecules in the mixture forming donor-acceptor complex between amino acids and electrolytes. As a result there is contraction in volume resulting negative values of β_a^E with volume fraction (x).

Excess Acoustic Impedance (z^E):
Excess acoustic impedance (z^E) has been calculated using relation (4) and calculated values of z^E are presented in Tables 2 From Table, it is clear that the values of z^E are positive at the beginning but becomes negative thereafter by increasing volume fractions of 1M serine in the liquid mixtures.

Graphs shown in Fig – 8 for (1M NaCl + 1M serine) at different temperature and various volume fractions, excess values of z^E are less positive at x – 0.4 then becomes negative with increasing volume fraction. z^E has more positive values (with minimum at x-0-8) over entire range of volume fraction except x=1.0. Increase in positive values of z^E with x-0.4 Fig- 8 is indicative of the decreasing strength of interactions between component molecules of the mixture as suggested by Tiwari et al. This supports our view that the interaction of the component molecules in liquid mixtures is weak[33]. Fig- 8 show that z^E values are small positive for (1M NaCl + 1M serine)

Excess Intermolecular Free Length (L_f^E):
The changes in excess intermolecular free length (L_f^E) have been calculated with the help of equation - (5).The values of L_f^E are given in the Tables – 2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine), . The plot of (L_f^E) versus vol. fraction (x) and 303.15, 308.15 & 313.15K are shown in Fig-9 . L_f^E values are negative at the beginning then become positive with increasing volume fraction (x) for all the systems at all temperatures suggesting strong specific interactions between amino acids and electrolytes molecules. Fig 9 , shows variation in L_f^E at 303.15, 308.15, and 313.15K. It is seen that L_f^E values are negative at lower volume fraction of 1M NaCl . 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[34], interstitial accommodation and orientation 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 chloride into the serine . This trend suggests that hetero association and homo association of molecules decreases with electrolytes.

The excess value of L_f^E being negative indicates strong interaction in the electrolytes – amino acids solutions. However, the excess value in free length shows positive values and the changes are very small. The negative value indicates that interactions between electrolytes (salt) and amino acid are not very strong. The excess value for free length worked out for electrolytes-amino acids positive value at x-0.4 and negative value not keeps increasing beyond that point. This shows that there must have been strong interactions in the electrolytes – amino acids.

For the mixtures of electrolytes with amino acids, L_f^E values are negative at lower vol. fraction of amino acids solution. And inversion in sign from negative to positive 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 negative for the system NaCl suggests that the strong interactions occur between electrolytes and serine.

Excess relative association (R_A^E):
The variation of excess relative association function with volume fraction (x) is mention in Tables- 2 thermo dynamical excess parameters for the system (1M NaCl + 1M Serine), and graphically depicted in Fig - 10 . Figure show that R_A^E is more positive for the system (1M NaCl +1Mserine). At beginning values R_A^E is positive for

liquid mixtures as the volume fraction increases up to x= 0.4 as per Tables. The negative value of R_A^E suggests significant interactions between the component molecules in the mixture, forming donor – 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.
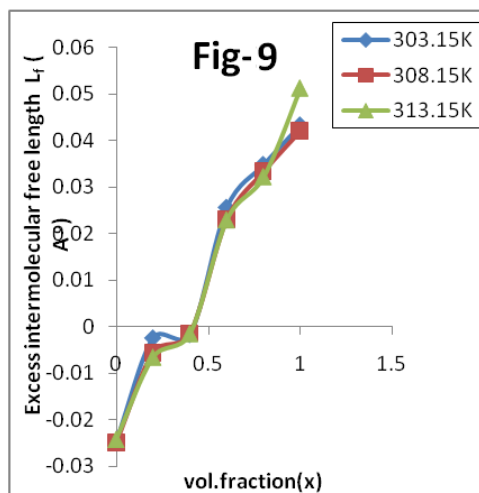

Fig.C9- Plot of excess intermolecular free length (L_f^E) against volume fraction (x) of system (1M NaCl + 1M serine) at 2MH$_z$ and 303.15, 308.15, 3013.15K temperatures
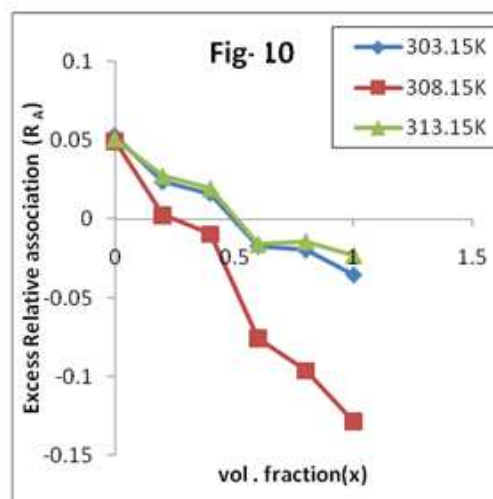
Fig.C10–Plot of excess relative association (R_A^E) against volume fraction (x) of system(1M NaCl+1M serine) at 2MH$_z$ and 303.15, 308.15 and 3013.15K temperatures

CONCLUSION

Ultrasonic velocity, density and viscosity have been measured for serine and valine in aqueous NaCl solution at 303.15,308.15 and313.15K. The variation in ultrasonic velocity, density and viscosity as well as the related thermodynamic parameters such as adiabatic compressibility (β_a), acoustic impedance (z), intermolecular free length (L_f), relative association (R_A) of serine at various concentrations and temperatures. 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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