Adiabatic Compressibility and Intermolecular Free Length of Electrolytes in Aqueous Biomaterial at 298 K

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Abstract: ***Densities, viscosities & speeds of sound of electrolytes (NaCl, $MgCl_2$) in aqueous glycine solutions have been measured at 298 K. Using experimental data, thermodynamic parameters such as adiabatic compressibility and intermolecular free length were calculated. The salt $MgCl_2$ influences the thermodynamic properties more strongly than NaCl. The thermodynamic properties of glycine can be successfully correlated with the concentrations of solutes. These parameters representing the molecular interactions among the amino acids, water and electrolytes. The importance of the thermodynamic parameters involved in these systems is discussed in term of ion-ion and solute-solvent molecular interactions.***

1. 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 electrolytes [5, 8]. An electrolyte when dissolved in water, changes the arrangement of water molecules with a strong electric field of its ions. This property of electrolytes is known as structure maker or structure breaker has been widely used to understand the effect of electrolytes on the structure and function of both proteins and nucleic acids [7, 8] .Thermodynamic properties of electrolytes in aqueous glycine solutions have been studied in order to understand the complex nature of proteins using amino acid-ion interactions. [9, 10]. There are instances where high concentrations of electrolytes can affect the function and structure of proteins [11, 12]. Ion – ion and ion- amino acids interactions dominate in such situations. The thermodynamics of interactions of NaCl & $MgCl_2$ in aqueous amino acids have been reported in the literature [13, 14]. How the ion-ion and ion-amino acid interactions together with ion –water and amino acid- water ones are altered in electrolytes and amino acid solutions is the object of current investigations. Unfortunately, no systematic efforts have been made to study the ion-ion and ion – amino acid interactions in amino acid solutions from thermodynamic properties. Present investigation explains the solute – solute and solute – solvent molecular interactions for systems comprising NaCl, $MgCl_2$ in aqueous glycine and aqueous alanine.

2. Materials & methods:

AR grade glycine, alanine, sodium chloride and magnesium chloride were obtained from Merck (India) and with a high purity (99. 99 %). All chemicals were used without further treatment. Distilled, deionized water (degass by boiling) with specific conductance less than $1.2x10^{-6}\ \Omega^{-1}.cm^{-1}$ was used for preparation of the solutions. All the solutions were made on weight basis using electronic digital balance having an accuracy of ± 0.01 mg. The stock solution of 1M molar concentration of glycine and alanine were prepared. All solutions were kept in special airtight bottles and were used within 12 hrs. after preparation to minimize decomposition due to bacterial contamination. Uncertainties in solution concentration were estimated at ± $1x10^{-5}$ mol kg^{-1} in calculations.

The Density (ρ) of solution was measured with specific gravity bottle by relative measurement method. The weight of the solution was measured using electronic digital balance with an accuracy of ± 0.1mg.The density values from triplicate replication at the required temperature of 298 K are reproducible within ± 2 x 10^{-2} kg m^{-3}.The uncertainties in density is found to be ± $4x10^{-2}$ kg $m-^{3}$.

Pre calibrated Ostwald's viscometer (10 ml capacity) is used for the viscosity measurement. Efflux time was determined using an electronic stop watch with the resolution of 0.01s which was calibrated with distilled, deionised water by measuring the efflux time at 298 K. The average of three reading reproducible within 0.1s was used as final efflux time. An electronically operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature is ± 0.1K.

The sound velocities of the solutions were measured with a single crystal ultrasonic interferometer (Model F-81, Mittal Enterprises) at 2 MHz frequency having maximum uncertainty and precision of 0.5 and 0.1 ms^{-1}, respectively in velocities [16, 17]. The source of ultrasonic waves was a quarts crystal excited by a radio frequency oscillator placed at the 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 to equilibrate for 30 minute prior to making the measurements. The average of ten readings was treated as the final value of sound velocity. The interferometer was calibrated against the speed of sound of water at T=298 K. Our experimental value is 1497.08 ms^{-1} which is in good agreement with the literature value[2] 1496.69. The temperature around the cell was controlled within ± 0.1K by circulating the water from constant temperature bath which is fabricated in the laboratory with a skillful technique.

3. Results and Discussion

The measured densities (ρ), Viscosities (η) and speed of sound (u) at different concentration of NaCl, $MgCl_2$ and in aqueous glycine and aqueous alanine solutions are listed in Table-1 and 2. As no data are available for amino acid electrolytes solutions, the experimental density, viscosity and speed of sound values can not be compared with literature values. From Table -1 & 2, it is observed that ultrasonic velocity in aqueous glycine & aqueous alanine solution increases with increase in concentrations of solutes. Also the values of u increases with concentrations of NaCl & $MgCl_2$ in aqueous glycine and aqueous alanine. Ultrasonic velocity in aqueous glycine and alanine solution increases with increase in concentration of solutes. The value of ultrasonic velocity of NaCl in aqueous glycine is less as compared to in aqueous alanine. When NaCl & $MgCl_2$ are dissolved in solution, the sodium ion (Na^+) and magnesium ion (Mg^{++}) has a structure breaking effect, would disrupt the water structure [1, 3]. This could be followed by structural reorganization leaving the molecules in closely fitting helical cavities. This would cause an increase in closed packed structure as the cohesion between water molecules increases. This makes the liquid medium less compressible and hence the ultrasonic velocity increases above that of pure value. The value of speed of sound of electrolytes NaCl & $MgCl_2$ in aqueous glycine is more as compared to in aqueous alanine.

The viscosity of solution increase with concentration of solutes NaCl & $MgCl_2$. Viscosity of the solutions shows a non-linear behavior in both the systems as per Table-1 & 2. Density of the solution in both the systems increases with concentration of solutes. However, density of the solutions is less in aqueous glycine as compared to in aqueous alanine. Also densities & viscosities are less in aqueous glycine as compared to in aqueous alanine of electrolytes. The derived parameters are listed in Table – 1 & 2.

The thermodynamic parameters are derived from the following relations[15, - 22]:

$\beta = 1/u^2 \rho;$

$L_f = K / u. \rho;$

Where, K is temperature constant; ρ and ρ_o are the densities of solution & solvent respectively. u and u_o are ultrasonic velocities of solution & solvent. The thermodynamic parameters are listed in Table-1 & 2. The compressibility of electrolytes in a mixture of aqueous glycine – electrolytes and aqueous alanine – electrolytes can be considered as a sum of long range and short range interaction forces. The amino acid-water and amino acid- ion interactions can be successfully used to calculate adiabatic compressibility (β) and intermolecular free length (L_f). The interactions of glycine and alanine with divalent cation i.e. Mg^{2+} are stronger than with univalent cat ion Na^+. The thermodynamic parameters are varies with the variation of concentrations of electrolytes. But they are large in $MgCl_2$. The electrolytes like NaCl, KCl, $MgCl_2$, etc. interact with charged centre of glycine and alanine resulting into a decreased electrostriction effect. This decreased electrostriction effects give rise to higher volumes of transfer, which is evident from current investigation. As a matter of fact, the effect of $MgCl_2$ on the electrostriction of water molecules is stronger than that of 1:1 electrolytes i.e. NaCl. Thus the addition of $MgCl_2$ to glycine and alanine enhances the transfer volumes more strongly than addition of NaCl. The absence of hydrophobic hydration in glycine due to absence of any methyl group (methyl group tightens the water molecules around itself) causes glycine to be under a higher electrostriction effect than alanine and other amino acids containing methyl group. Hence the values of adiabatic compressibility for glycine are higher than those of such amino acids.

From Table -1 and Table – 2 It is observed that for electrolytic solution, adiabatic compressibility ($\beta^)$) decrease with increase in concentrations of electrolytes as shown in Fig.1, 2, and Fig. 5, 6 for the systems. This is because as the concentrations of electrolytes increases, a larger portion of the water molecules are electrostatic and the amount of bulk water decreases causing the compressibility to decrease. In present study dβ / dc is negative which indicates the electrostriction of water molecules. Hydrophilic solutes often show negative compressibility as well, due to the ordering that is induced by them in water structure. The electrolytes like NaCl, $MgCl_2$, etc. interact with charged centre of glycine. The absence of hydrophobic hydration in glycine due to absence of any methyl group causes glycine to be under a higher electro-striction 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) such amino acids.

Intermolecular free length ($L_{f)}$ is a predominant factor in determining the variation of ultrasonic velocity in fluids and in their solutions. In the present investigation, it has been observed from Table –1 and Table –2 that intermolecular free length decreases on increasing concentrations of solute in all systems. The decrease in L_f with increase of solutes concentrations in solution indicates that there is significant interaction between solute and co-solvent suggesting the structure promoting behavior on addition of electrolytes (Fig. 3, 4 and Fig. 7, 8). In water - glycine – NaCl & water – alanine - NaCl systems, ultrasonic velocity increases with concentrations 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.

4. Conclusion

The variation in ultrasonic velocity, density and viscosity and other related thermodynamic parameters such as adiabatic compressibility, intermolecular free length of NaCl & $MgCl_2$ in aqueous solutions of glycine and alanine at various concentrations shows the non-linear increase or decrease behaviour. The non linearity confirms the presence of solute-solvent, ion-ion, dipole-dipole, ion-solvent interactions. Consequently 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. It has been observed that intermolecular free length decreases linearly on increasing concentration of solute in all systems. It is concluded that the variation in ultrasonic velocity, density and viscosity as well as the related thermodynamic parameters such as adiabatic compressibility (β), intermolecular free length, are more in Water+Glycine+$MgCl_2$ system as compared to Water+Glycine+NaCl systems due to the divalent cation Mg^{2++}. As a matter of fact, the effect of $MgCl_2$ on the electrostriction of water molecules is stronger than that of 1:1 electrolytes i.e. NaCl. Thus the addition of $MgCl_2$ to glycine and alanine enhances the transfer volumes more strongly than monovalant cat ion Na+.

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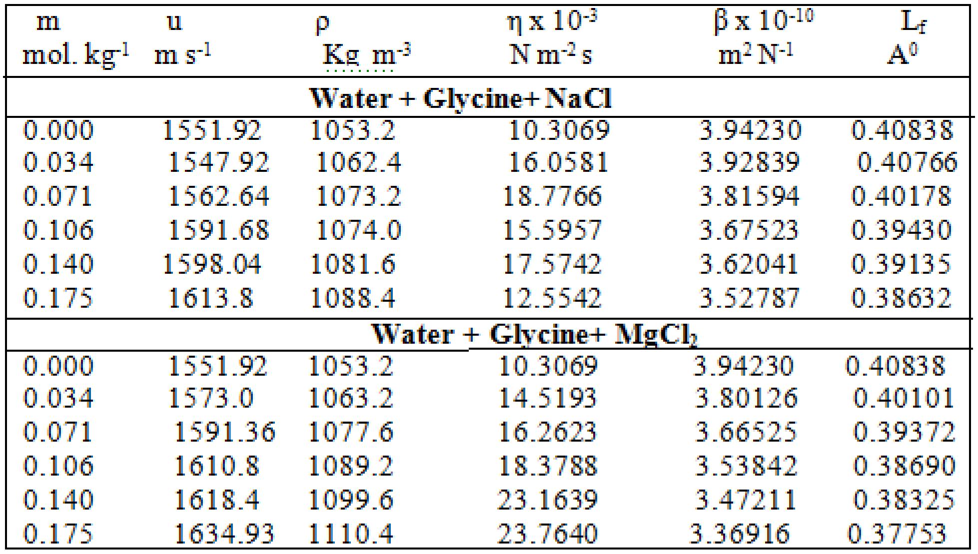
Figures Captions

Table-1: Ultrasonic velocity (u), Density (ρ), viscosity (η), adiabatic compressibility (β) And Inter-Molecular free length (L_f) of Water + Glycine + NaCl; and Water + Glycine + $MgCl_2$ Systems at 298 K



m mol. kg^{-1}	u m s^{-1}	ρ Kg m^{-3}	$\eta \times 10^{-3}$ N m^{-2} s	$\beta \times 10^{-10}$ m^2 N^{-1}	L_f A^0
Water + Glycine+ NaCl					
0.000	1551.92	1053.2	10.3069	3.94230	0.40838
0.034	1547.92	1062.4	16.0581	3.92839	0.40766
0.071	1562.64	1073.2	18.7766	3.81594	0.40178
0.106	1591.68	1074.0	15.5957	3.67523	0.39430
0.140	1598.04	1081.6	17.5742	3.62041	0.39135
0.175	1613.8	1088.4	12.5542	3.52787	0.38632
Water + Glycine+ $MgCl_2$					
0.000	1551.92	1053.2	10.3069	3.94230	0.40838
0.034	1573.0	1063.2	14.5193	3.80126	0.40101
0.071	1591.36	1077.6	16.2623	3.66525	0.39372
0.106	1610.8	1089.2	18.3788	3.53842	0.38690
0.140	1618.4	1099.6	23.1639	3.47211	0.38325
0.175	1634.93	1110.4	23.7640	3.36916	0.37753

Table 2: Ultrasonic velocity (u), Density (ρ), viscosity (η), adiabatic compressibility (β) And Inter- Molecular free length (L_f) of Water + Alanine + NaCl; and Water + Alanine + $MgCl_2$ Systems at 298K

m mol. kg^{-1}	u m s^{-1}	ρ Kg m^{-3}	$\eta \times 10^{-3}$ N m^{-2} s	$\beta \times 10^{-10}$ $m^2 N^{-1}$	L_f A^0
Water + Alanine+ NaCl					
0.000	1543.60	1050.0	12.3235	3.99706	0.41121
0.034	1585.80	1056.4	12.4818	3.76421	0.39905
0.071	1578.64	1063.2	12.4963	3.77414	0.39957
0.106	1604.90	1072.0	12.6167	3.62167	0.39142
0.140	1607.46	1080.8	12.9934	3.58075	0.38920
0.175	1618.12	1085.2	12.9230	3.51940	0.38585
Water + Alanine+ $MgCl_2$					
0.000	1543.60	1050.0	12.3235	3.99706	0.41121
0.034	1566.24	1065.0	12.4241	3.82550	0.40228
0.071	1612.3	1070.0	13.4280	3.59521	0.38999
0.106	1608.84	1086.32	14.2701	3.05270	0.38788
0.140	1618.64	1100.0	15.5268	3.46981	0.38313
0.175	1636.22	1109.2	16.7291	3.36749	3.77439

Fig.-1

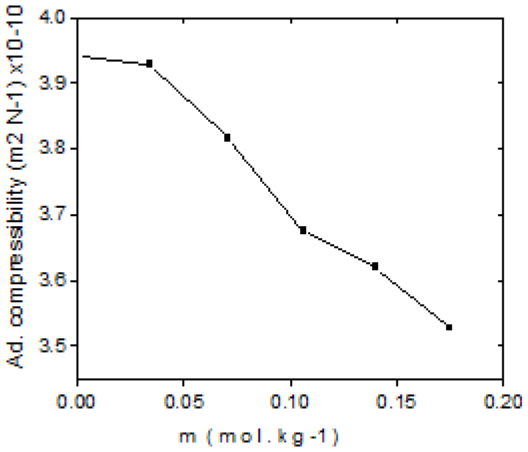


Fig.-2

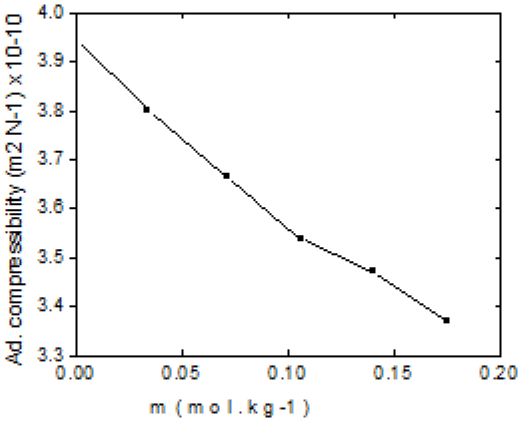


Fig.-3

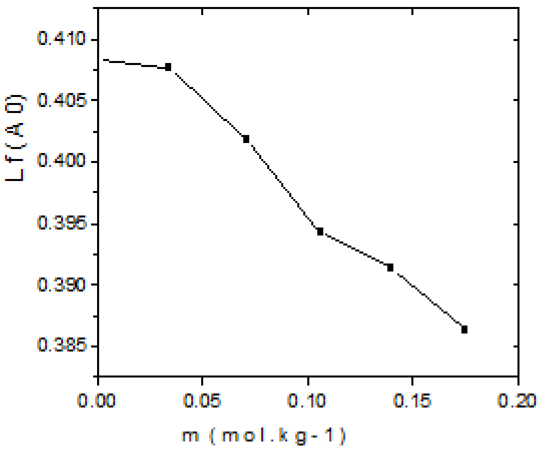


Fig.-4

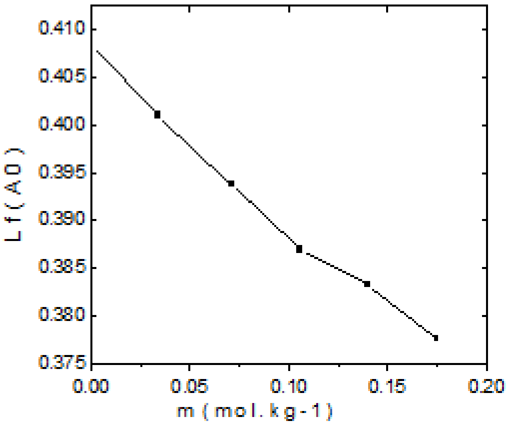


Fig.-5

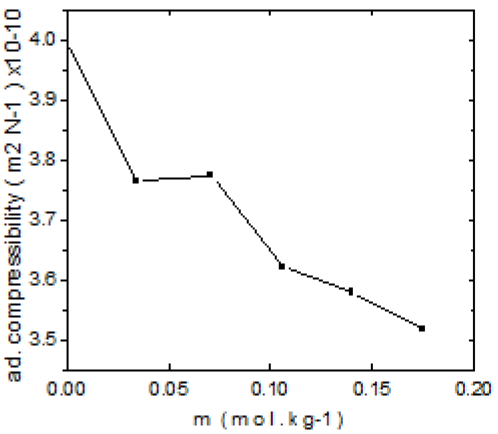


Fig.-6

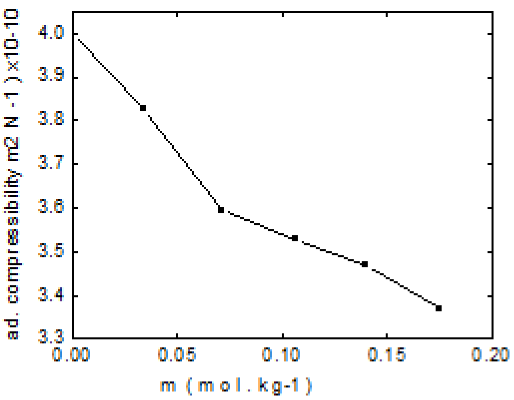


Fig.-7

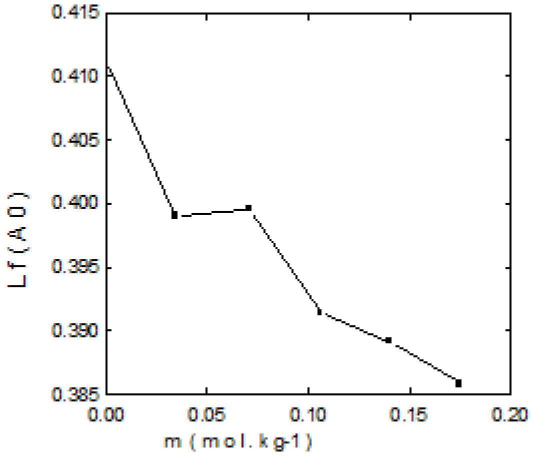


Fig.-8

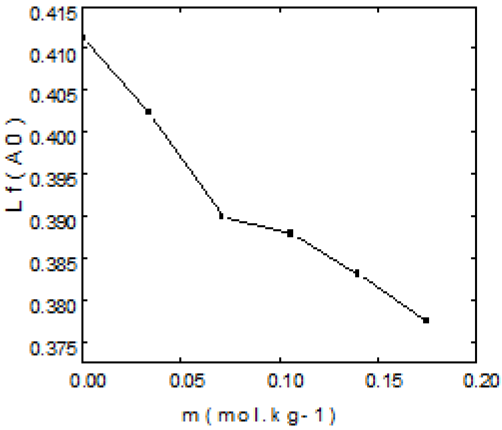


Figure 1- Plots of adiabatic compressibility Vs concentration of NaCl in aq. glycine solution at 298 K.
Figure 2- Plots of adiabatic compressibility Vs concentration of $MgCl_2$ in aq. glycine solution at 298 K.
Figure 3- Plots of intermolecular free length (L_f) Vs conc. of NaCl in aq. glycine solution at 298 K
Figure 4- Plots of intermolecular free length (L_f) Vs conc. of $MgCl_2$ in aq. glycine solution at 298 K.
Figure 5- Plots of adiabatic compressibility Vs concentration of NaCl in aq. alanine solution at 298 K.
Figure 6- Plots of adiabatic compressibility Vs concentration of $MgCl_2$ in aq. alanine solution at 298 K.
Figure 7- Plots of intermolecular free length (L_f) Vs conc. of NaCl in aq. alanine solution at 298 K.
Figure 8- Plots of intermolecular free length (L_f) Vs conc. of $MgCl_2$ in aq. alanine solution at 298 K.