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Studies in thermodynamic properties of glycine in aqueous solutions of mono and divalent electrolytes at different temperatures

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ABSTRACT

Ultrasonic velocity, density and viscosity have been measured for glycine in aqueous Nacl and $MgCl_2$ *solution at, 303K, 308K and 313K Thermodynamic parameters such as adiabatic compressibility* (β)*, acoustic impedance (z), intermolecular free length* (L_f) *and relative association* (R_A) *have been obtained from the experimental data for all the mixtures, with a view to investigate the nature of the molecular interactions. Adiabatic compressisibility* (β) *and Intermolecular free length* (L_f) *decreases with increase with glycine concentration and temperature. Acoustic impedance (z) and relative association* (R_A) *are almost constant with increase in temperature and gradually increases with glycine concentration of glycine. These parameters have been further used to interpret the hydrophilic part of the solute and molecular interactions in the mixtures.*

Keywords: Ultrasonic velocity, ion solvent, adiabatic compressibility (β), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A).

INTRODUCTION

Ultrasonic study and transport properties of amino acids in aqueous solutions of electrolytes [1] are very useful to obtain information about various types of interactions in solutions. Consequently, the characterization of these interactions can assist in understanding the thermodynamic stability of proteins and their unfolding behavior. Electrolytes [2] dissolving in water have been classified as structure makers or structure breakers, depending on the charge density. It has been reported that ions with low charge density are net structure breakers; on the other hand ions with a high charge density show a opposite behavior and net structure makers. It is interesting to explore the ionic processes accompanying the aqueous solution of amino acids of electrolytes. Also the interactions of glycine in aqueous solution of electrolytes and temperature dependence of these interactions play a vital role in understanding the nature of action of bioactive molecules or the thermodynamic behavior of biochemical processes in the body system. In fact, there are extensive thermo dynamical property studies of electrolytes in aqueous [3, 4] or non- aqueous [5, 6] solutions but very few in aqueous glycine solutions [7].

We report here in the adiabatic compressibility (β), acoustic impedance (z), intermolecular free length (L_f) and relative association (R_A) of glycine in aqueous solution of electrolytes at various temperatures. Such data are expected to highlight the role of glycine in presence of aqueous electrolytes solutions and its influence with temperature.

MATERIALS AND METHODS

AnalaR grade glycine (99.7%), sodium chloride (99.5%) and magnesium chloride (99.5%) were obtained from Merk Pvt. Ltd., Mumbai. All chemicals were used without further purification. Water used in the present investigation was deionized, distilled and was degassed by boiling, prior to making solutions. All chemicals used were dried over anhydrous CaCl2 in a desiccator before use. All aqueous solutions were prepared in deionized and distilled water, having specific conductivity ~ 10^{-6} S cm^{-1}. The stock solutions [8] of 1M concentration were prepared by weighing the electrolytes on a digital balance with an accuracy of $\pm 1 \times 10^{-5}$ Kg. Solutions of glycine were made on the mole fraction scale. Uncertainties in solution concentrations were estimated at $\pm 1 \times 10^{-5}$ mol kg^{-1} in calculations. The solutions were kept in the special air tight bottles and were used within 12 hrs. Ultrasonic velocity measurements were measured by a single crystal interferometer (F- 81, Mittal Enterprises, New Delhi) operating at a frequency of 2 MHz. The source of ultrasonic waves was a quartz 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 interferometer was calibrated against the ultrasonic velocity of water used at T =303K. The present experimental value is 1508.20 ms^{-1} which is in good agreement with literature value[2] 1509.55 ms^{-1}. Accuracy in the velocity measurement was ± 1.0 ms^{-1}.

The densities of the solutions were determined accurately using 25 ml specific gravity bottle and electronic balance (accuracy ± 0.1 mg). An average of triple measurements was taken into account. Sufficient care was taken to avoid any air bubble entrapment. Viscosity was measured with precalibrated Ostwald type viscometer. The flow 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 %. The experimental temperature was maintained constant by circulating water with the help of thermostatic water bath (accuracy in temperature ± 0.1K).

THEORY AND CALCULATIONS

From the measured values of ultrasonic velocity (U) and density (ρ) various thermodynamic parameters was calculated by using the following standard expressions [9].

Adiabatic compressibility (β) = $1/u^2\rho$ (m^2 N^{-1})
Intermolecular free length (L_f) = $k\ \square^{1\square}$ (A^0)

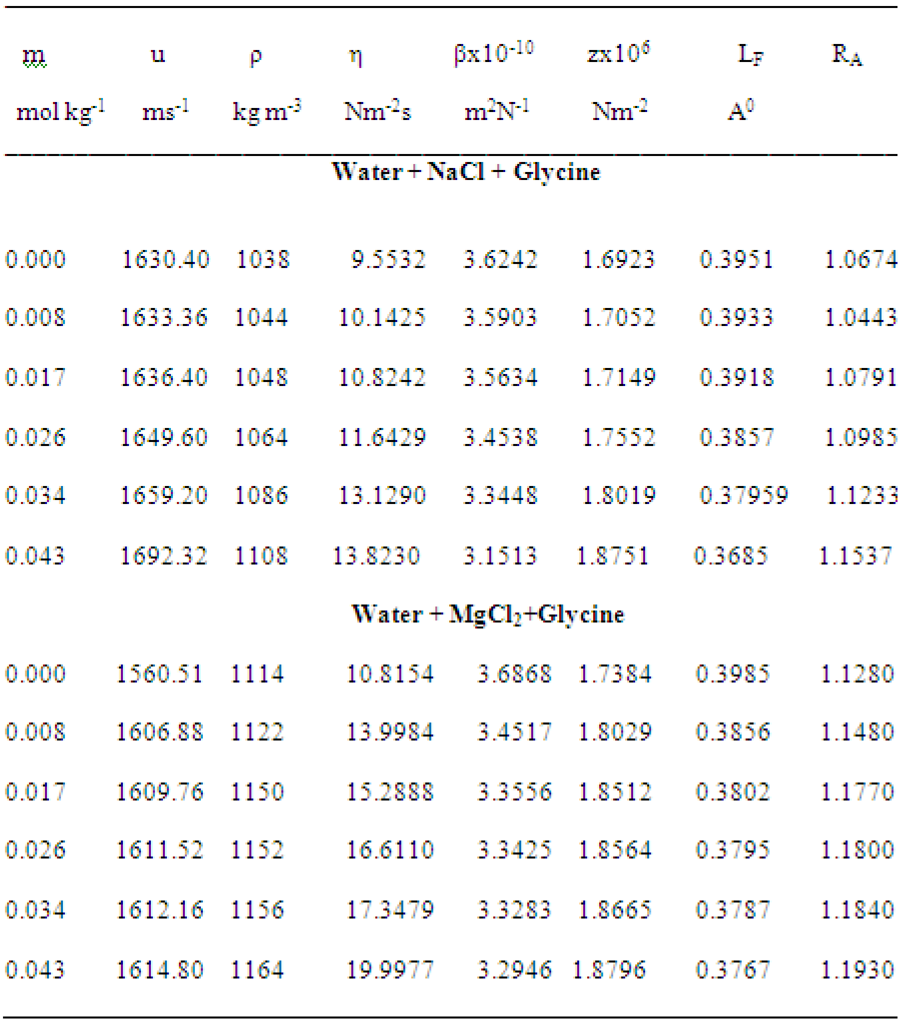
Where k is temperature dependent constant called as Jacobson constant it is 631×10^{-6}, 642×10^{-6} and 651×10^{-6} for 303, 308 and 313 K respectively [10]

Specific acoustic impedance (Z) = ρ u (Nm^{-2})

$$R_A = (\rho_0/\rho)x(u_0/u)^{1/2}$$

ρ= density of solute
$\rho_{0=}$ density of solvent
u= velocity of solute
$u_{0=}$ velocity of solvent

Table-1: Ultrasonic velocities, densities and viscosities of glycine in aqueous solution of NaCl and $MgCl_2$ at 2 MHz and at 303K



m mol kg^{-1}	u ms^{-1}	ρ kg m^{-3}	η Nm^{-2}s	$\beta x 10^{-10}$ m^{2}N^{-1}	$z x 10^6$ Nm^{-2}	L_F A^0	R_A
			Water + NaCl + Glycine				
0.000	1630.40	1038	9.5532	3.6242	1.6923	0.3951	1.0674
0.008	1633.36	1044	10.1425	3.5903	1.7052	0.3933	1.0443
0.017	1636.40	1048	10.8242	3.5634	1.7149	0.3918	1.0791
0.026	1649.60	1064	11.6429	3.4538	1.7552	0.3857	1.0985
0.034	1659.20	1086	13.1290	3.3448	1.8019	0.37959	1.1233
0.043	1692.32	1108	13.8230	3.1513	1.8751	0.3685	1.1537
			Water + $MgCl_2$+Glycine				
0.000	1560.51	1114	10.8154	3.6868	1.7384	0.3985	1.1280
0.008	1606.88	1122	13.9984	3.4517	1.8029	0.3856	1.1480
0.017	1609.76	1150	15.2888	3.3556	1.8512	0.3802	1.1770
0.026	1611.52	1152	16.6110	3.3425	1.8564	0.3795	1.1800
0.034	1612.16	1156	17.3479	3.3283	1.8665	0.3787	1.1840
0.043	1614.80	1164	19.9977	3.2946	1.8796	0.3767	1.1930

Where m, mole fraction; ρ, density of the solution ; η,viscosity of solution; u, ultrasonic velocity;β, adiabatic compressibility; L_f, intermolecular free length; R_A, relative association ; z,aucostic impedance.

RESULTS AND DISCUSSION

Experimentally measured values of ultrasonic velocities (u) and densities (ρ) and calculated values of thermodynamic parameters such as adiabatic compressibility (β), specific acoustic impedance(Z),intermolecular free length(Lf) and relative association (R_A) of glycine in aqueous solution of Nacl and $MgCl_2$ at, 303K, 308K and 313K are given in Table – 1, 2, and 3.

Table-2: Ultrasonic velocities, densities and viscosities of glycine in aqueous solution of NaCl and $MgCl_2$ at 2 MHz and at 308K

m mol kg^{-1}	u ms^{-1}	ρ kg m^{-3}	η Nm^{-2}s	βx10^{-10} m^{2}N^{-1}	zx10^6 Nm^{-2}	L$_F$ A^0	R$_A$
			Water + NaCl+Glycine				
0.000	1652.50	1058	9.8735	3.4612	1.7483	0.3896	1.1075
0.008	1645.60	1062	10.6196	3.4772	1.7476	0.3905	1.1093
0.017	1640.80	1068	11.6276	3.4779	1.7524	0.3906	1.1131
0.026	1639.20	1094	12.6407	3.4019	1.7933	0.3862	1.1406
0.034	1634.48	1106	13.7625	3.3844	1.8077	0.3853	1.1514
0.043	1631.80	1114	14.4294	3.3712	1.8178	0.3845	1.1588
			Water + $MgCl_2$+Glycine				
0.000	1583.60	1109	12.5680	3.5956	1.7562	0.3971	1.1290
0.008	1620.80	1118	14.2838	3.4048	1.8120	0.3864	1.1470
0.017	1621.76	1120	15.8042	3.3947	1.8164	0.385	1.1490
0.026	1622.64	1138	16.9419	3.3374	1.8466	0.3826	1.1680
0.034	1623.76	1144	17.6670	3.3153	1.8576	0.3813	1.1740
0.043	1624.48	1150	18.3989	3.2951	1.8682	0.3801	1.1810

Where m, mole fraction; ρ, density of the solution ; η,viscosity of solution; u, ultrasonic velocity;β, adiabatic compressibility; L_f, intermolecular free length; R_A, relative association;z,aucostic impedance.

Ultrasonic velocity of glycine in binary solvent mixture of sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) and water (H_2O) have been measured with the help of ultrasonic interferometer at 2MHz. The variation of ultrasonic velocity of glycine at various concentrations and temperatures in co- solvent of water and NaCl and $MgCl_2$ shows the variation to be non-linear. The nature of variation of ultrasonic velocity (u) with concentration (m) is evident from Table 1, 2 and 3. This non linear variation indicates the presence of strong interactions in both the systems. The variation of adiabatic compressibility (β) as a function of concentration of electrolytes NaCl and $MgCl_2$ at different temperatures (303,308 and 313 K) are displayed in Fig 1 and 2 respectively. The variation of ultrasonic velocity of system with concentration of NaCl in H_2O and glycine can be expressed in terms of density & adiabatic compressibility by equation [10]

$$\frac{du}{dc} = -\frac{u}{2} \times \frac{1}{d} \times \frac{d\rho}{dc} + -\frac{1}{\beta} \times \frac{d\beta}{dc} \qquad ----- (5)$$

The sign and magnitude of quantity d ρ / dc and dβ /dc indicate that the H-bonded structure of H_2O is disrupted by the addition of glycine. Consequently ultrasonic velocity of system increases depending on the structural properties of solutes [11]. The solute that increases the ultrasonic velocity is of structure maker [12, 13] types. Ultrasonic velocity of NaCl+H_2O and

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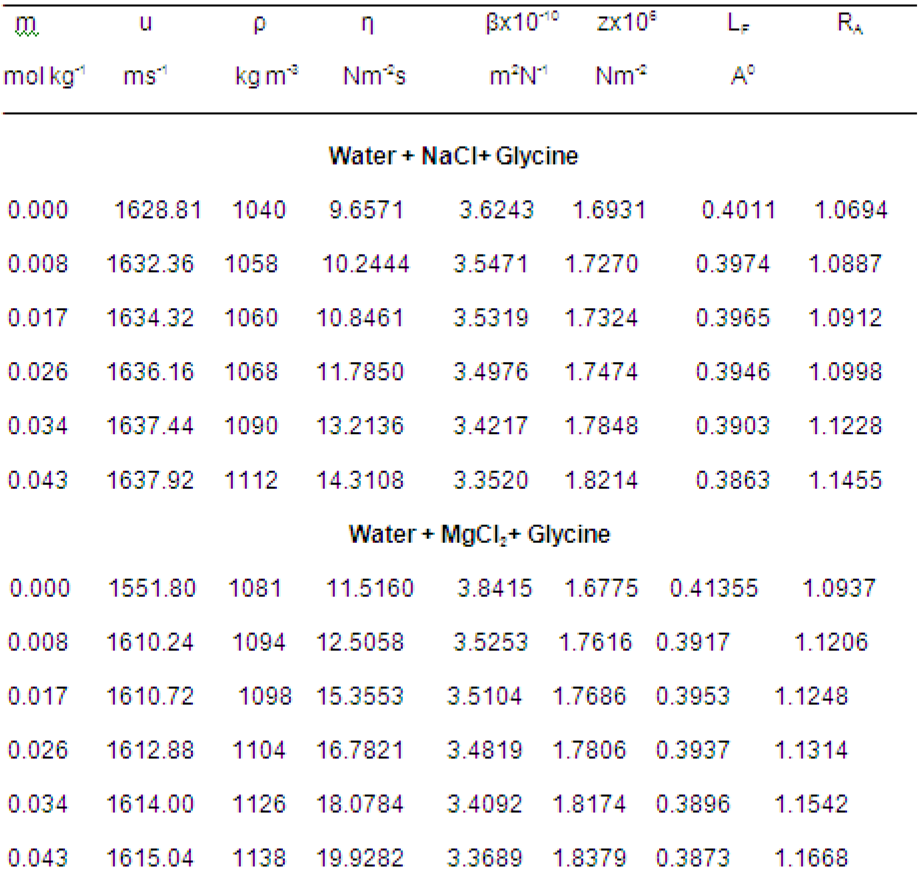
$MgCl_2$+H_2O increases in the presence of glycine with increase in temperature. The electrolytes occupy the interstitial space of water and tend to break the original ordered state of water due to its self association. But with increase in temperature, there occurs a structural rearrangement as a result of hydration [14] leading to a comparatively more ordered state. Therefore ultrasound speed increases with increases in temperature.

Table-3: Ultrasonic velocities, densities and viscosities of glycine in aqueous solution of NaCl & $MgCl_2$ at 2 MHz and at 313K



m mol kg^{-1}	u ms^{-1}	ρ kg m^{-3}	η Nm^{-2}s	βx10^{-10} m^{2}N^{-1}	zx10^6 Nm^{-2}	L$_F$ A°	R$_A$
			Water + NaCl+ Glycine				
0.000	1628.81	1040	9.6571	3.6243	1.6931	0.4011	1.0694
0.008	1632.36	1058	10.2444	3.5471	1.7270	0.3974	1.0887
0.017	1634.32	1060	10.8461	3.5319	1.7324	0.3965	1.0912
0.026	1636.16	1068	11.7850	3.4976	1.7474	0.3946	1.0998
0.034	1637.44	1090	13.2136	3.4217	1.7848	0.3903	1.1228
0.043	1637.92	1112	14.3108	3.3520	1.8214	0.3863	1.1455
			Water + MgCl$_2$+ Glycine				
0.000	1551.80	1081	11.5160	3.8415	1.6775	0.41355	1.0937
0.008	1610.24	1094	12.5058	3.5253	1.7616	0.3917	1.1206
0.017	1610.72	1098	15.3553	3.5104	1.7686	0.3953	1.1248
0.026	1612.88	1104	16.7821	3.4819	1.7806	0.3937	1.1314
0.034	1614.00	1126	18.0784	3.4092	1.8174	0.3896	1.1542
0.043	1615.04	1138	19.9282	3.3689	1.8379	0.3873	1.1668

Where m, mole fraction; ρ, density of the solution ; η,viscosity of solution; u, ultrasonic velocity;β, adiabatic compressibility; L_f, intermolecular free length; R_A, relative association; z,aucostic impedance.

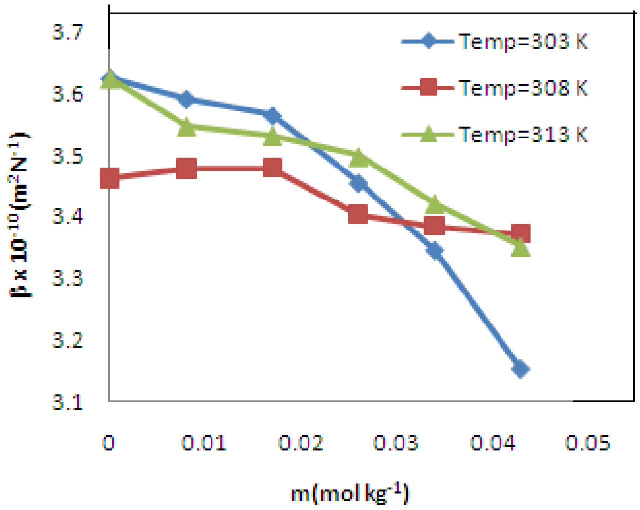


Fig1: Adiabatic compressibility (β) against mole fraction of glycine in aqueous solution of NaCl

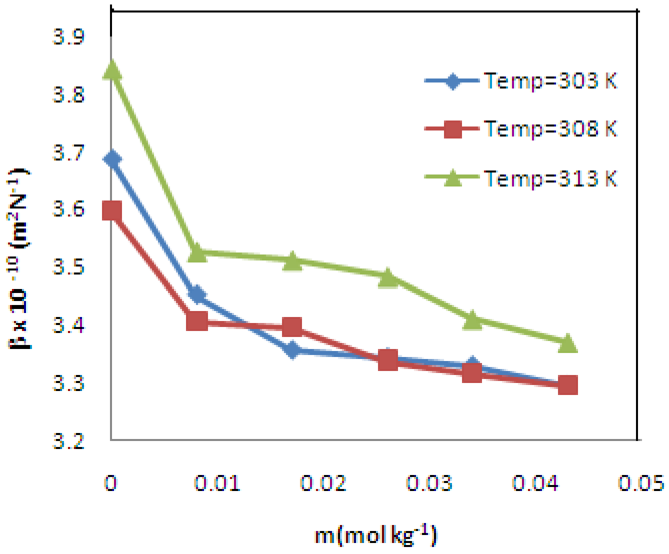


Fig 2 : Adiabatic compressibility (β) against mole fraction of glycine in aqueous solution of $MgCl_2$

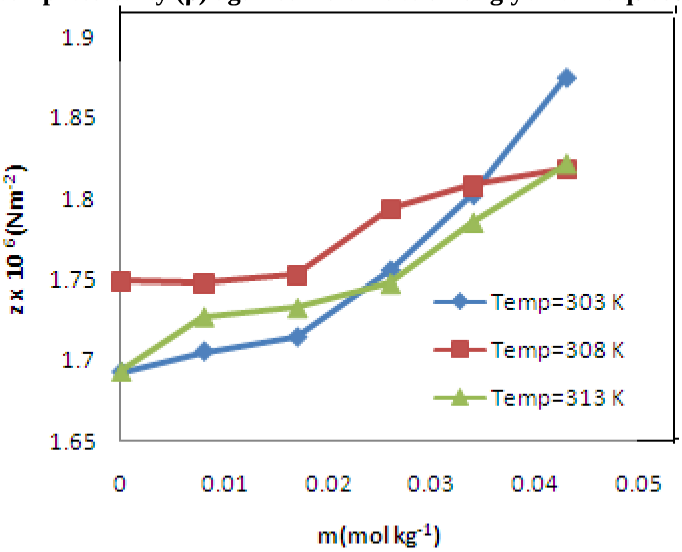


Fig 3: Acoustic impedance (Z)against mole fraction of glycine in aqueous solution of NaCl

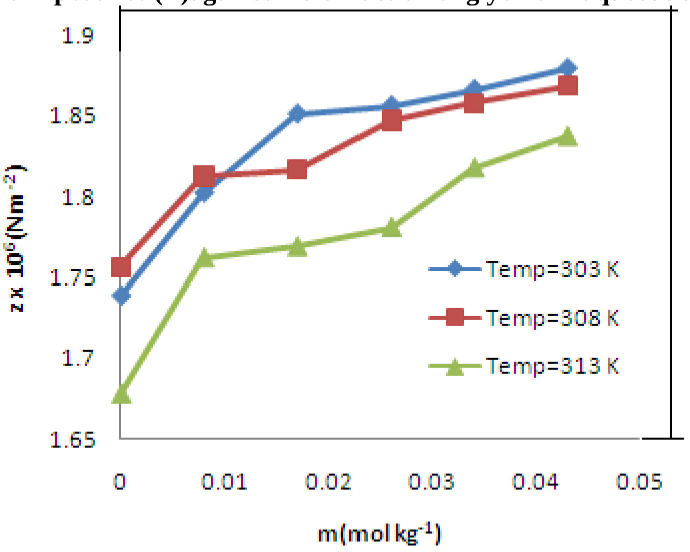


Fig 4 : Acoustic impedance (Z) against mole fraction of glycine in aqueous solution of $MgCl_2$

Adiabatic compressibility (β) decreases with increase in concentration of electrolytes, a larger portion of the water molecules are electrostatic and the amount of bulk water decreases causing the compressibility to decrease. It is well known that solutes causing electrostriction lead to decreases in the compressibility of the solution. Hydrophilic[1,2] solutes often show negative compressibility as well, due to ordering that is induced by them in water structure. In present study dβ / dc is negative which indicates the electrostriction of water molecules as depicted in Fig. 1& 2.

It is observed that the value of acoustic impendence (z) (Fig. 3 & 4) varies with increase in concentrations. The trend observed as regards the variation in ultrasonic velocity (u) with temperature is in line. This also indicates significant interactions in the systems.

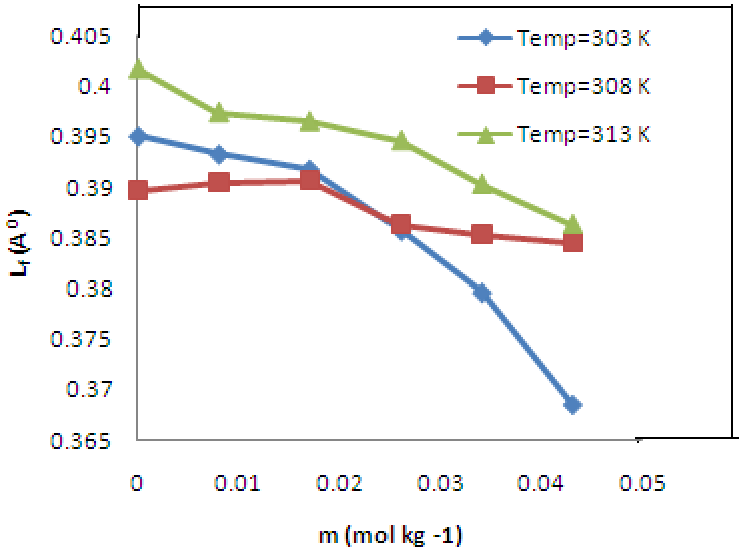


Fig 5: Intermolecular free length (L_f) against mole fraction of glycine in aqueous solution of NaCl

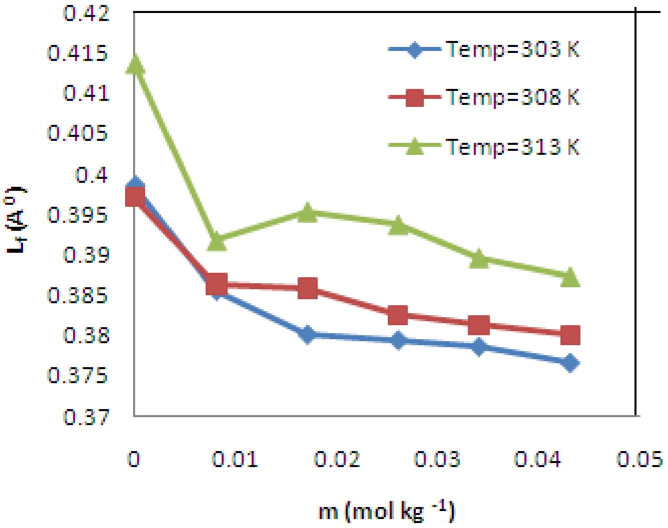


Fig 6: Intermolecular free length (L_f) against mole fraction of glycine in aqueous solution of $MgCl_2$

The variation in ultrasonic velocity depends on the intermolecular free length (L_f) on mixing. It is a predominant factor in determining the variation of ultrasonic velocity in fluids and in their solutions. It has been observed that, in the present investigation, intermolecular free length decreases with increase in glycine concentration at all temperatures. The variation of intermolecular free length (L_f) with concentration m is shown in Fig.5 & 6. The decrease in L_f

indicates that there is significant interaction between solute and co-solvent suggesting the structure promoting behavior.

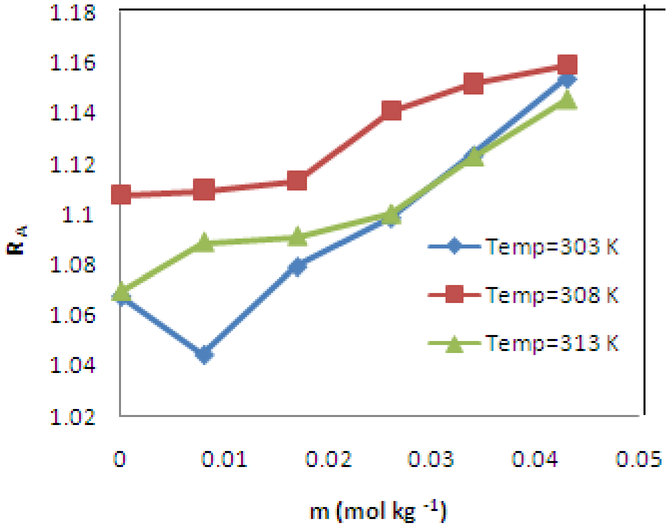


Fig 7: Relative association (R_A) against mole fraction of glycine in aqueous solution of NaCl

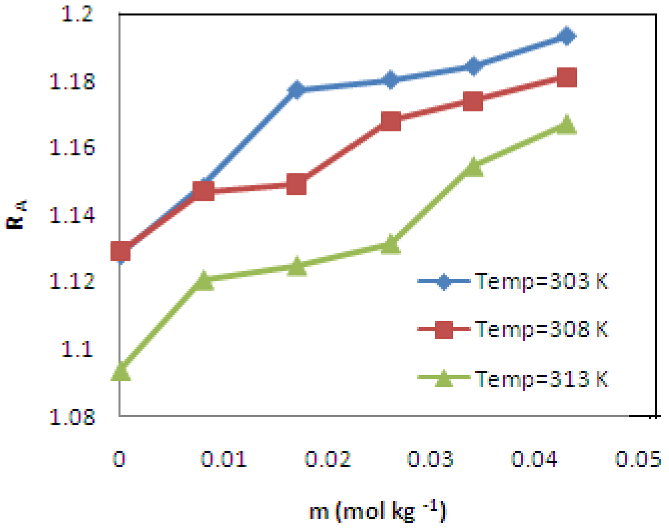


Fig 8: Relative association (R_A) against mole fraction of glycine in aqueous solution of $MgCl_2$

The variation of relative association (R_A) with concentration m is depicted in Fig 7 and 8. It is observed that R_A increases with concentration of glycine.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 thermodynamic parameters are given in Table 1, 2 and 3.

CONCLUSION

Ultrasonic velocity, density and viscosity have been measured for glycine concentrations in aqueous NaCl and $MgCl_2$ solution at 303K, 308K and 313K. The variation in ultrasonic velocity(u), density(ρ) and viscosity(η) and other related thermodynamic parameters such as adiabatic compressibility(β), acoustic impedance(z), intermolecular free length(L_f) and relative association (R_A)of glycine at various concentrations and temperatures in co- solvent of water and NaCl and $MgCl_2$ shows the variation to be non-linear. Consequently ultrasonic velocity of system increases depending on concentration of glycine solution. It is known that electrostriction leads to decrease in the compressibility of the solution.. The non linear behavior 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 the mixture as existing in the liquid systems.

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