



Molecular Solutions Interaction Studies of Glycylglycine in Aqueous NaCl and NaBr At Different Temperature

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ABSTRACT

Density and Ultrasonic velocity of Glycylglycine in aqueous NaCl and NaBr (0.5 m) solutions have been determined experimentally at 303 and 308 K. The results obtained from density and ultrasonic velocity measurement have been used to calculate the adiabatic compressibility K_s , Hydration number H_n , apparent molar volume ϕ_v , apparent molal adiabatic compressibility, ϕK_s , and partial molal volume $\phi_0 v$, transfer volume $\Delta\phi_{tr}^0$ and partial molal adiabatic compressibility, $\phi_0 K_s$ at infinite dilution. The results are interpreted in terms of solute-co- solute and solute-solvent interactions in these systems. It has been observed that there exist strong solute-solvent interaction and complex formation between in these ternary systems. The properties of this amino acid in water and water+ electrolytes solution systems are discussed in terms of the charge, size and hydrogen bonding effect.

KEYWORDS

Glycylglycine, Aqueous electrolytes, adiabatic compressibility, Hydration number, apparent molal volume, apparent molal adiabatic compressibility and transfer volume.

1. Introduction

In continuation of our earlier work (1) on the study of interaction between amino acids and electrolytes in aqueous medium, we present in this paper, the study of interaction between aqueous glycylglycine in aqueous NaCl and NaBr at 303 and 308 K. There has been an increased interest in the physicochemical properties of amino acids and carbohydrates in aqueous as well as aqueous electrolyte media to understand the role played by the biological molecules in living organism (2-6). Amino acids have zwitter-ion and are the constituents of the most important class of biopolymers, i.e. Proteins. Disarrangement water and electrolyte balance in living systems cause a wide variety of health problems. In physiological media such as blood, membranes, cellulose fluids etc., the dipolar character of amino acids (in presence of ions such as Na^+ , K^+ , Mg^{2+} and Cl^- etc., dissolved in body water) has an important bearing on their biological functions. Therefore, a knowledge of water-amino acid interaction the effects on several biological processes occurring in living organism. In recent years, a number of workers have utilized density and viscosity data to deduce the thermodynamic properties (relative viscosity, Jones-Dole coefficient and free energy of activation of viscous flow) for a number of mixtures solutions (7-9). Structural interactions of non-ionic solutes with ionic ones in different solvents are important in many fields of chemistry and bio-chemistry. Very recently, we have made systematic effort to investigate the ultrasonic and volumetric properties of amino acids in concentrated electrolytic solution (10-12). It was found that NaCl and MgCl_2 increase the apparent molar volume and decrease the adiabatic compressibility of glycine. This increase could be attributed to the interactions of the ions of the NaCl and MgCl_2 electrolytes and zwitter-ion head group of glycine, causing the transfer of hydrated water molecule to the bulk state.

In the present paper, we report densities, ρ and ultrasonic velocities, u of Glycylglycine (0.019, 0.039, 0.059, 0.079 and 0.099 m) in aqueous NaCl and NaBr (0.5m) solutions have been determined experimentally at 303 and 308K. From these experimental data a number of thermodynamic parameters namely, adiabatic compressibility K_s , Hydration number H_n , apparent molar volume ϕ_v , partial molal adiabatic compressibility, ϕK_s , and partial molal volume $\phi_0 v$, transfer volume $\Delta\phi_{tr}^0$ and partial molal adiabatic compressibility, $\phi_0 K_s$ at infinite dilution respectively have been calculated. These parameters were utilized to study various interactions taking place in the solutions of glycylglycine in aqueous NaCl and NaBr at 303 and 308K .

2 Experimental

2.1 Chemical and Preparation

Glycylglycine (99.5% purity), NaCl and NaBr (99.8% purity) were procured from Merck and S d Fine Ltd. They were used as such without further purification, after drying over calcium chloride in desiccators for more than 48 hours. The ultrasonic velocities and densities of the amino acid in aqueous electrolytes solution at various concentrations as well as in double distilled de-ionized water were measured experimentally. Aqueous solutions of NaCl and NaBr (0.5 m) were prepared and these were used as solvents to prepare glycylglycine solutions on mass basis covering the whole composition range. All the solutions were prepared by mass in dry box and were stored in special air-tight bottles and kept in dark to avoid photo chemical degradation. The weighing was done on an Afcoset ER-120A electronic balance with an accuracy ± 0.1 mg.

2.2. Measurement of density and ultrasonic velocity

The densities were measured with a single capillary pycnometer (made of Borosil glass) of bulb capacity of $8 \times 10^{-6} \text{ m}^3$. The marks of the stems were calibrated using double distilled water at 303 and 308 K. The pycnometer was kept for about 30 minutes in a thermostatic water bath so that the thermal fluctuation in density was minimized. The ultrasonic velocities in solutions were measured using a single crystal variable path interferometer at 3MHz. The temperature of the test solutions was maintained at 303 and $308 \pm 0.02\% \text{ K}$ in an electronically controlled thermostatic water bath. The velocity and density data were found to be accurate with in $\pm 0.10\%$ and $\pm 0.01\%$ respectively.

3. Results and discussion

The densities, ρ and ultrasonic velocities, u of Glycylglycine (0.019, 0.039, 0.059, 0.079 and 0.099 m) in aqueous NaCl and NaBr (0.5m) solutions have been determined experimentally at 303 and 308K are presented in Table 1. It is observed from Table 1 that densities and ultrasonic velocities for all the ternary systems increase with increase in molalities of glycylglycine. The values of ρ and u increase with increase in concentration of amino acid in all the ternary systems under investigation, which appear to be due to hydrophobic properties of solutes i.e. H-bond forming. This may be attributed to the formation of clusters by the amino acids and strong intermolecular forces in the solute. The changes in structure of solvent or solution as a result of H-bond formation lead to decrease in intermolecular free length (13). Solute may occupy the interstitial spaces in solvent or get solvated forming new weaker

bonds. It was suggested [14-16] that what is experimentally observed for any system, reflects the compromise between the tendency for the ion and the peptide to interact with each other and inclination of the solutes to associate with the solvent. The variation of ultrasonic velocity with the concentration of glycylglycine, (du/dc) can be shown to depend upon the concentration derivations of the density and adiabatic compressibility of the system investigated.

Thus in the relation:

$$du/dc = -u/2 [1/\rho (d\rho/dc) + (1/K_s)(dK_s/dc)] \quad (1)$$

The quantity $(1/\rho)(d\rho/dc)$ is negative while $(1/K_s)(dK_s/dc)$ is positive and the net value is negative. This makes du/dc positive, showing that u increases with the concentration of the ternary systems.

3.1 Adiabatic Compressibility

The adiabatic compressibility of the glycylglycine + water + NaCl and NaBr were determined at 303 and 308K from the density and velocity data. The adiabatic compressibility was calculated by this relation

$$K_s = 1/u^2\rho \quad (2)$$

The per usual of Table 1 exhibits the values of the adiabatic compressibility K_s are found to be decrease with increase the concentration of solute glycylglycine in all the ternary systems. Such a decrease in adiabatic compressibility observed in the ternary systems (glycylglycine + water + electrolytes) clearly confirms the conclusion drawn from the ultrasonic velocity data. It is well known fact that when a solute dissolves in a solvent. Since the solvent molecules are oriented in ionic field i.e. electrostatic field of ions of glycylglycine. The solvent molecules are more compactly packed in the primary solvation shells. This is the reason, why solvent is compressed by the introduction of the ions. Thus the electrostatic field of the ions causes the compression of the medium giving rise to phenomenon called 'Electrostriction'. Since the water molecules are compressed, they do not respond to a further application of pressure. So the solutions become harder to compress. This will lead to the decrease in compressibility values. This may further ascribed that such a decrease in adiabatic compressibility, K_s is attributed to the influence of the electrostatic field of the ions on the accompanying molecules. The increasing electrostrictive compression of water around the molecules results in a large decrease in compressibility of solutions. It may be inferred that the weakening of hydrogen bond strength formed by the solute and solvent molecules and maximum complex formation may also be the reason for decrease in compressibility. Thus is in accordance with the view proposed by others [17 & 18].

The values of hydration number H_n of these ternary systems (glycylglycine + water + electrolytes) were calculated by the following relation and are reported in Table 1.

$$H_n = (n_1/n_2) (1 - K_s/K_s) \quad (3)$$

Further it is observed that the values of H_n increase with increase of temperature which indicates solute-solvent interaction are strong and they behave as structure makers are shown in Table 1. The interaction between the solute and the water molecules in the solvent is term as hydration. The positive value of hydration number of indicates an appreciable solvation of solutes. This is added support for the structure promoting nature of solute as well as the presence of appreciable dipole-dipole interaction between solute and water molecules.

3.2 Apparent molal volume

The apparent molal volume, ϕ_v were calculated from measured density data of Glycylglycine in aqueous metal halides namely NaCl and NaBr solution at different molalities at 303 and 308 K using the following equation :

$$\phi_v = [1000 (\rho^0 - \rho) / m\rho \rho^0] + M/\rho \quad (4)$$

Where M is the molecular mass of the solutes, ρ^0 and ρ are densities of solvent and solution. The calculated values of ϕ_v of these ternary systems are given in Table 2. In these cases where molality dependence of ϕ_v , having definite trend points, The ϕ_v values increase due to reduction in the electrostriction effect at terminals, whereas it decreases due to disruption of side group hydration by that of the charged end.

The partial molal volume at infinite dilution ϕ_v^0 was calculated by taking an average data points. The linear variation is obtained by least square fitting to the following equation.

$$\Phi_v = \phi_v^0 + S_v m^{1/2} \quad (5)$$

The intercept which is the limiting apparent molal volume at infinite dilution ϕ_v^0 is the experimental slope, S_v which is considered to be volumetric pair wise coefficient. The derived values ϕ_v^0 of along with S_v are summarized in Table 3. Table 3 shows that the values of ϕ_v^0 are positive of these ternary systems which indicate ion-solvent interactions are strong. The positive value of ϕ_v^0 with electrolyte concentration of water molecules as a result of shielding of polar terminal groups of Glycylglycine molecules is due to increased interaction between these polar ends and ions of electrolytes. They have estimated the contraction of water around the appositively charge group is caused by electrostatic ion-solvent interaction and is called electrostriction. A mutual comparison of these electrolytes shows the values of ϕ_v^0 are larger in case of NaCl than in NaBr. The Cl^- and Br^- ions have the same charge, but Br^- ions has the biggest ionic radius than Cl^- ion. Due to this interaction of Br^- ions with glycylglycine are weak and hydration of NaCl (Solute - solvent interaction) will be much more than that of NaBr which is in good agreement with the results reported in Glycine - Electrolytes - water mixture [13]. The ϕ_v^0 are decreases with rise in temperature due to the increase in the electrostriction affect at the terminal also it makes disruption of side group hydration by that of charge end. The S_v values (Table -3) NaCl are found to be negative and positive for NaBr. The negative values indicates ion-ion interactions are weak in NaCl but in case of NaBr ion-ion interactions are strong.

The types of interactions occurring between the charge centre of glycylglycine and ions (Na^+ , Cl^- and Br^-) can be classified as follows:

Ions of co-solutes (Na^+ , Cl^- and Br^-) and hydrophilic part of charged centre of glycylglycine and

The terminal groups of zwitter ions of amino acid $-\text{NH}_3^+$ and COO^- are hydrated in electrostatic manner.

The electrostriction of NH_3^+ group is greater than the COO^- by a factor of 10.

The overlap of hydration co spheres of terminal groups (NH_3^+ and COO^-) and of adjacent groups results in volume change.

Ions of co-solutes (Na^+ , Cl^- and Br^-) and hydrophobic part of non-polar side group of glycylglycine.

3.3 Transfer volume of solute at infinite dilution

The transfer volume of glycylglycine at infinite dilution from aqueous NaCl and NaBr to aqueous solution were calculated using the following equation

$$\Phi_{v(\text{tr})}^0 = \phi_v^0(\text{aq. Electrolyte}) - \phi_v^0(\text{aq}) \quad (6)$$

These values are presented in Table 3, which shows to be positive in NaCl and NaBr systems at 303 and 308 K. This tendency can also be explained using the co-sphere model [19 & 20]. The decrease in $\Phi_{v(\text{tr})}^0$ with increase in temperature which leads to be less hydrophilic- ionic interactions. The change in

values of $\Phi_{v(tr)}^0$ are interpreted on the basis of co-sphere overlap model given by Friedman and Krishnan [21]. According to this model overlap of co-sphere hydration of two terminal groups (NH_3^+ and COO^-) results in decreased electrostriction of water, which reflect increase in volume. Shahidi et al [22] have suggested eq. (6) which shows that limiting apparent molar volume of amino acids is made up of vander volume (V_{vw}), volume associated with empty space (V_v) and volume due to shrinkage (V_s), mainly due to electrostriction of solvent by the terminal charge centre of the amino acids.

$$V\Phi = V_{vw} + V_v + V_s \quad (7)$$

These tendencies can also be explained using the co-sphere overlap model [21]. According to this model, hydrophilic-ionic group interactions contribute positively, where as ionic hydrophobic group interaction contribute negatively values of $\Phi_{0v(tr)}$. The values of transfer volume of glycylglycine are positive for (0.5 m) aqueous NaCl and NaBr solution due to hydrophilic-ionic group interactions. The $\Phi_{0v(tr)}$ are small in NaBr than NaCl due to the Br- has small charge and big ionic radius and the electrostriction is weaker than NaCl.

3.3 Apparent molal adiabatic compressibility

The density and adiabatic compressibility values were employed for calculated apparent molal adiabatic compressibility, ϕK_s of glycylglycine in aqueous metal halides namely NaCl and NaBr solution at different molality and at 303 and 308 K using the

$$\phi K_s = [1000 (\rho^0 K_s - \rho K_s^0) / C \rho \rho^0] + M K_s / \rho \quad (8)$$

Table 3 shows that the less negative values of ϕK_s over the entire range of molality of the ternary systems which indicates the less negative values of ϕK_s are due to loss of structural compressibility of solvent on increase in the population of four bonded solvent molecule in the vicinity of the solute molecules.

The partial molal adiabatic compressibility, $\phi^0 K_s$ at infinite dilution are obtained from the plot of ϕK_s versus $m^{1/2}$ by least square method. The molality dependence of this parameter has been expressed in terms of the following equation

$$\phi_{K_s} = \phi_{K_s}^0 + S_{K_s} m^{1/2} \quad (9)$$

Where $\phi_{K_s}^0$ is the partial molal adiabatic compressibility at infinite dilution. It provides information regarding solute-solvent interaction and S_{K_s} is the experimental slope ion-ion interactions. The values of $\phi_{K_s}^0$ and S_{K_s} are also included in Table 3. The magnitude of negative values of $\phi_{K_s}^0$ are higher in NaCl systems suggesting that the presence of strong solute-solvent. The Cl⁻ ion is being smaller in size, than Br⁻ ion has an intense force field and hence strong hydration co-sphere around them and maximum complex ion formation. The hydration of NaCl (solute - solvent interaction) will be much more than that of NaBr. The values of S_{K_s} glycylglycine + water+ NaCl are negative which is indicating the presence of weak ion-pair interactions and with rise of temperature the ion- pair interactions gets weakened due to increase in the thermal energy of the system. From this tabulation, one can notice that the values of $\phi_{K_s}^0$ in mixed ternary system less than the pure system suggesting the weak interactions in the ternary systems by others [22].

Conclusion

The volume and compressibility data have been used to study of solute –solute and solute-solvent interaction in these ternary systems. It can be concluded that the existence of molecular interaction is in the order of NaCl > NaBr. This suggests glycylglycine in aqueous NaCl solution are strong structure maker than glycylglycine in aqueous NaBr solution. The positive value of $\Delta\Phi_{tr}^0$ of glycylglycine from water to aqueous metal halides solutions show that the interactions involving

the charged centre of peptide as well as ions are dominating. Further, with rise of temperature the ion-solvent interactions are weak of the systems.

Table -1

Densities (ρ) and ultrasonic velocity (u) of Glycylglycine +aqueous NaCl and Glycylglycine + aqueous NaBr at 303 and 308 K

m (mol.dm ⁻³)	ρ (kg m ⁻³)	u (m s ⁻¹)	ρ (kg m ⁻³)	u (m s ⁻¹)
Glycylglycine + aqueous + NaCl (0.5 m)				
303 K				
0.000	892.8	1553.0	891.5	1554.1
0.019	894.0	1559.0	892.9	1564.1
0.039	895.8	1560.6	893.2	1567.6
0.059	898.0	1570.7	895.0	1579.7
0.079	902.4	1574.6	896.8	1580.1
0.099	912.6	1609.4	897.6	1612.7
Glycylglycine + aqueous + NaBr (0.5 m)				
303 K				
0.000	907.68	1564.1	905.51	1571.3
0.019	907.73	1588.1	906.54	1595.0
0.039	908.64	1602.0	907.93	1606.8
0.059	909.35	1621.8	908.26	1627.2
0.079	911.08	1633.8	910.85	1638.1
0.099	913.87	1642.1	911.29	1650.0

Table-2

Adiabatic compressibility (K_s), hydration number (H_n), apparent molal volume (Φ_v), apparent molal adiabatic compressibility (Φ_{K_s}) of Glycylglycine + aqueous NaCl and Glycylglycine + aqueous NaBr at 303 and 308 K

m (mol.dm ⁻³)	K_s (10 ⁻¹⁰ m ² N ⁻²)	H_n	Φ_v (10 ⁻³ m ³ mol ⁻¹)	$-\Phi_{K_s}$ (10 ⁻⁹ m ² N ⁻²)
Glycylglycine + aqueous + NaCl (0.5 m)				
303 K				
0.000	4.6434	-	-	-
0.019	4.6010	23.60	81.35	24.57
0.039	4.5818	17.26	96.81	19.42
0.059	4.5081	25.30	128.66	27.91
0.079	4.4684	24.50	150.40	28.17
0.099	4.3007	41.81	244.14	44.60
Glycylglycine + aqueous + NaCl (0.5 m)				
308 K				
0.000	4.6430	-	-	-
0.019	4.5767	36.91	87.84	36.79
0.039	4.5543	24.90	53.30	24.40
0.059	4.4767	31.09	73.07	30.73
0.079	4.4649	24.91	82.77	25.69
0.099	4.2825	43.98	76.15	39.21
Glycylglycine + aqueous + NaBr (0.5 m)				
303 K				
0.00	4.5026	-	-	-
0.019	4.3675	67.02	59.54	67.54

0.039	4.2874	53.29	30.19	55.03
0.059	4.1801	53.16	34.20	55.14
0.079	4.1112	48.53	51.27	51.04
0.099	4.0305	44.22	74.62	47.59

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Glycylglycine + aqueous + NaBr (0.5 m)

308 K

0.00	4.4723	-	-	-
0.019	4.3356	68.27	60.79	70.81
0.039	4.2655	51.56	72.86	54.77
0.059	4.1574	19.96	56.62	53.75
0.079	4.0906	47.65	81.71	51.04
0.099	4.0305	44.17	70.62	47.59

Table -3

Limiting apparent molal volume (Φ_v^0), experimental slope (S_v), transfer volume ($\Delta\Phi_{tr}^0$), Limiting apparent molal adiabatic compressibility ($\Phi_{K_s}^0$) and experimental slope (S_{K_s}) of Glycylglycine + aqueous NaCl and Glycylglycine + aqueous NaBr at 303 and 308 K

$\Phi_v^0 \times 10^{-3}$	S_v	$\Delta\Phi_{tr}^0 \times 10^{-3}$	$-\Phi_{K_s}^0 \times 10^{-7}$	$S_{K_s} \times 10^{-8}$
($m^3 \text{ mol}^{-1}$)	($m^3 \text{ l}^{1/2} \text{ mol}^{3/2}$)	($m^3 \text{ mol}^{-1}$)	($m^2 \text{ N}^{-2} \text{ mol}^{-1}$)	($m^{-1} \text{ N}^{-2} \text{ mol}^{-1}$)
303 K Glycylglycine + aqueous + NaCl				
57.78	-83.6	18.96	4.30	-10.38
308 K Glycylglycine + aqueous + NaCl				
74.54	-3.05	2.56	30.16	-5.08
303 K Glycylglycine + aqueous + NaBr				
42.23	3.60	34.51	79.88	10.39
308 K Glycylglycine + aqueous + NaBr				
53.18	6.43	23.92	84.68	12.09

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