Arabian Journal of Chemistry (2011) **4**, 487–490

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Ultrasonic and thermodynamic studies of glycine in aqueous electrolytes solutions at 303 K

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Received 1 June 2010; accepted 13 July 2010
Available online 17 July 2010

KEYWORDS

Amino acids;
Aqueous electrolytes;
Adiabatic compressibility;
Apparent molar volume;
Apparent molar adiabatic compressibility

Abstract Densities and ultrasonic velocities of glycine (0.01–0.09 M) in aqueous NaCl and $MgCl_2$ (0.02 and 0.06 M) solutions have been measured at 303 K. From these experimental data adiabatic compressibility K_s, apparent molar volume, ϕ_v apparent molar adiabatic compressibility, $\phi K_{s,}$ partial molar volume ϕ_v^0 and partial molar adiabatic compressibility, $\phi^0 K_s$ at infinite dilution were calculated for all the ternary systems. The data have been interpreted in terms of solute–solute and solute–solvent interactions. These results show that dipole–dipole and ion–solvent interaction are strong in glycine–aqueous $MgCl_2$ than in glycine–aqueous NaCl.

1. Introduction

In continuation of our earlier work (Akhtar, 2007) on the study of interactions between L-proline and L-glutamine in electrolytes (Cu II nitrate and Ni II chloride) in aqueous medium at 308 K, we present in this paper, the study of glycine in aqueous NaCl and $MgCl_2$ at 303 K. Ultrasonic and thermodynamic properties of these model compounds (amino acid) in aqueous electrolytes media provide information of solute–solvent and solute–solute interactions (Rai and Yan, 2003; Ali et al., 2005a; Akhtar, 2004; Badaryani, 2002). Metal ions have been reported (Akhtar, 2007; Badaryani et al., 2003; Ali et al., 2005b; Banipal and Singh, 2000; Yan et al., 2002) to play an important role in biological system and the presence of the copper amino acids complexes in human serum enhances the uptake of copper by liver tissue. Nickel, an integral component of enzyme urease may be involved in the action of hydroganise. In physiological media such as blood, membranes, and cellulose fluids, the dipolar character of amino acids (in the presence of ions such as Na^+, K^+, Mg^{+2} and Cl^- dissolved in body water) has an important bearing on their biological functions. Therefore, a knowledge of water–amino acid interaction and the effect of inorganic ions on such interaction is necessary to understand several biological processes occurring in living organisms. Very recently, we have made systematic effort to investigate the volumetric, viscometric and thermodynamic properties of l-alanine, d-serine, dl-threonine, l-histidine, glycine and glycylglycine in water and in aqueous concentrated

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Peer-review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.07.009

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electrolytes solution and l-serine and l-threonine in aqueous sodium and magnesium acetate solutions at 298.15 K. There has been an increased interest in physicochemical properties of amino acids in aqueous and aqueous electrolytes media (Yan et al., 2004; Pinho, 2008). Amino acids have zwitter–ion and are the constituents of the most important class of biopolymers, i.e. proteins. Derangement of water and electrolyte balance in living systems causes a wide variety of health problems.

In the present paper, we report that densities, ρ, and ultrasonic velocities, u, of ternary systems of glycine (0.10–9.0 M) in aqueous NaCl/$MgCl_2$ (0.02 and 0.06 M) were measured at 303 K. From these experimental data, a number of thermodynamic parameters namely, adiabatic compressibility K_s, apparent molar volume, ϕ_v, apparent molar adiabatic compressibility, ϕK_s, partial molar volume ϕ_v^0 and partial molar adiabatic compressibility ϕK_s^0 at infinite dilution respectively have been calculated. These parameters were utilized to study various interactions taking place in the solutions of electrolytes (NaCl and $MgCl_2$) and the amino acid (glycine).

2. Experimental

2.1. Chemicals and preparation

Glycine (Sigma Chemicals Co.), NaCl and $MgCl_2$ (A R grade) were of highest commercially available purity and were used as such without further purification, after drying over calcium chloride in a desiccator for more than 48 h. Aqueous solutions of NaCl and $MgCl_2$ (0.02 and 0.06 M) were prepared and these were used as solvents to prepare the glycine solutions on mass basis covering the whole composition range. All the solutions were prepared in a dry box and stored in special air tight bottles. The weighing was done on an Afcoset ER-120A electronic balance with a precision of ±0.1 mg. The densities of solvents (aq. NaCl and aq. $MgCl_2$) and ternary mixture (glycine + aq. NaCl/aq. $MgCl_2$) were measured using a single-capillary pycnometer (made of Borosil glass) of bulb capacity of $8 \times 10^{-6}\,m^3$. The marks of the stems were calibrated using double distilled water at 303 K. The pycnometer was kept for about 30 min 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 3 MHz. The temperature of the test solutions was maintained at 303 ± 0.2 K in an electronically controlled thermostatic water bath. The velocity and density data were found to be accurate within ±0.01% and ±0.02%, respectively.

3. Results and discussion

The densities and ultrasonic velocities of the NaCl, $MgCl_2$ and their ternary mixtures with glycine as a third component were determined at 303 K and are recorded in Table 1. The values of u and ρ increase with increase in concentration of amino acids in all the ternary systems under investigation, which appear to be due to hydrophobic properties of solutes i.e. H-bond forming the variation of ultrasonic velocity with the concentration of glycine (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:

Table 1 Densities (ρ) and ultrasonic velocity (u) of glycine + aqueous NaCl and glycine + aqueous $MgCl_2$ at 303 K.

C (mol^1)	0.02 M		0.06 M	
	ρ (kg m^3)	u (ms^{-1})	ρ (kg m^3)	u (ms^{-1})
Glycine + aqueous NaCl				
0.00	1020.6	1513.5	1003.8	1509.4
0.10	1021.3	1515.1	1004.6	1512.0
0.20	1024.1	1517.3	1005.1	1514.1
0.30	1028.9	1552.6	1007.3	1522.3
0.40	1029.4	1560.3	1009.1	1524.4
0.50	1031.2	1645.9	1011.8	1537.3
0.60	1032.9	1683.3	1019.1	1543.2
0.70	1035.7	1724.2	1020.6	1545.9
0.80	1038.1	1765.3	1020.9	1550.6
0.90	1041.3	1783.5	1024.7	1557.4
Glycine + aqueous $MgCl_2$				
0.00	998.7	1512.0	1006.2	1511.6
0.10	1004.0	1521.9	1006.4	1512.3
0.20	1010.0	1525.3	1014.3	1525.7
0.30	1013.4	1530.4	1015.7	1525.9
0.40	1017.2	1538.6	1016.7	1526.4
0.50	1024.9	1545.4	1017.5	1527.0
0.60	1027.1	1574.0	1019.8	1535.1
0.70	1034.2	1594.2	1020.9	1546.7
0.80	1035.6	1686.0	1024.9	1549.7
0.90	1038.5	1733.1	1025.3	1553.1

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

The quantity $(1/\rho)$ $(d\rho/dc)$ is positive while $(1/K_s)(dK_s/dc)$ is negative and the net value is negative. This makes du/dc positive, showing that u increases with the concentration of glycine in both the systems glycine + NaCl + water and glycine $MgCl_2$ + water which is in good agreement with the results reported for adenosine mono-, di- and tri-phosphates + dixane–H_2O (Mishra and Gautum, 2001).

3.1. Adiabatic compressibility

The adiabatic compressibility of the Gly + NaCl + water and Gly + $MgCl_2$ + water mixture was determined at 303 K from the density and velocity data. The adiabatic compressibilities were calculated by this relation

$$K_s = 1/u2\rho \quad (2)$$

The observed values of the adiabatic compressibility, K_s Table 2 are found to decrease with the concentration of glycine in all the ternary systems. However, the decrease in K_s is more marked in 0.02 M electrolyte solution and become less so as the 0.06 M concentration of the electrolyte in the solution. This clearly suggested that the strength of interaction (hydration of the glycine molecules) in both the systems decreases with increasing concentration of electrolyte in the solution (Yu et al., 2002). The compressibility behavior of glycine molecules in the present systems can be explained by considering the strong electrostrictive compression of the solvent produced by NH_3^+ and COO^- ends of the glycine dipolar molecules (Ogawa et al., 1984). As the concentration of electrolyte in solution increases, the interaction between NH_3^+ and Cl^- and between COO^- and Na^+/Mg^{+2} become increasingly strong, there by, reducing the electrostrictive effect of NH_3^+ and COO^- ends of glycine molecules. Consequently,

Table 2 Adiabatic compressibility (K_s), apparent molar volume (ϕ_v) and apparent molar adiabatic compressibility (ϕ_{K_s}) of Glycine + aqueous NaCl and Glycine + aqueous $MgCl_2$ at 303 K.

C (mol l^{-1})	K_s (10^{-10} m^2 N^{-1})	ϕ_v (10^{-5} m^{-3} mol^{-1})	ϕ_{K_s} (10^{-14} m^{-5} N^{-1} mol^{-1})
Glycine + water 0.02 M NaCl			
0.00	4.2774		
0.10	4.2654	6.3980	1.5412
0.20	4.2415	5.4927	0.5523
0.30	4.0319	5.5428	−6.2407
0.40	3.9902	5.1223	−4.9878
0.50	3.5797	5.2156	−11.7220
0.60	3.4168	5.2943	−12.0790
0.70	3.2478	5.1966	−12.4860
0.80	3.0912	5.1724	−12.6150
0.90	3.0191	5.0665	−11.8140
Glycine + water 0.06 M NaCl			
0.00	4.3726		
0.10	4.3541	6.0589	0.7998
0.20	4.3371	6.4478	1.0399
0.30	4.2839	6.0395	−0.3168
0.40	4.2645	5.9420	−0.1054
0.50	4.1820	5.7067	−1.3168
0.60	4.1204	5.7873	−2.1109
0.70	4.1000	5.9566	−1.7279
0.80	4.0740	5.2333	−1.4452
0.90	4.0235	5.0614	−1.6663
Glycine + water 0.02 M $MgCl_2$			
0.00	4.3799		
0.10	4.3003	4.3500	−6.0566
0.20	4.2557	3.0268	−4.8840
0.30	4.2132	3.4129	−4.0618
0.40	4.1528	3.4972	−4.1448
0.50	4.0854	2.7638	−4.6785
0.60	3.9299	3.1915	−6.1022
0.70	3.8046	2.7954	−6.9937
0.80	3.3970	3.2115	−10.880
0.90	3.2059	3.3679	−11.569
Glycine + water 0.06 M $MgCl_2$			
0.00	4.3495		
0.10	4.3446	6.0413	4.7485
0.20	4.2354	6.3769	−2.9323
0.30	4.2285	6.4378	−1.2354
0.40	4.2215	6.5143	−0.3663
0.50	4.2149	6.5802	−0.1690
0.60	4.1611	6.3667	−0.3707
0.70	4.0945	6.3799	−0.8678
0.80	4.0628	6.0268	−0.9630
0.90	4.0434	6.1482	−0.7269

these polar end groups would be able to cause more electrostrictive contraction of neighboring water molecules in 0.02 M – electrolyte solution than in 0.06 M electrolyte solution. This account for the sharp decreases in K_s in 0.02 M electrolytes solutions than 0.06 M electrolyte solution. This is in accordance with the view proposed by others (Mallick et al., 1986).

3.2. Apparent molar volume

The apparent molar volumes, ϕ_v were calculated from measurement density data using the following equation

$$\phi_v = 1000(\rho^0 - \rho/C\rho^0) + M/\rho^0 \quad (3)$$

where M is the molar mass of the solute, C is the molarity of the solutions, ρ and ρ^0 are the densities of solution and solvent, respectively. The positive values of ϕ_v (Table 1) for both glycine + NaCl + water and glycine + $MgCl_2$ + water systems indicate the presence of strong solute–solvent interactions. The partial molar volume at infinite dilution ϕ_v^0 was evaluated by taking an average of all the data points, standard deviation pertaining to the mean value (Cabani et al., 1981; Singh et al., 2004). In all other cases, the standard partial molar volume was obtained by least square fitting method to the following equation

$$\phi_v = \phi_v^0 + S_v C^{1/2} \quad (4)$$

ϕ_v^0, which is the limiting apparent molar volume (equal to partial molar volume at infinite dilution) and S_v, which is the experimental slope are considered to be volumetric pairwise interaction coefficient and are summarized in Table 3 which shows the values of ϕ_v^0 in both the electrolytes (NaCl and $MgCl_2$) as positive and increase as the concentration of these salt increases to 0.02 and 0.06 M. An increase in ϕ_v^0 with electrolyte concentration of water molecules as a result of shielding of polar terminal groups of glycine molecules is due to increased interaction between these polar ends and ions of the electrolytes. Baddin and Tyunina (2008), Banipal et al. (2007), Fereiara et al. (2009), Waris et al. (2001), Yuan et al. (2006) have estimated that the contraction of water around the appositively charged group is caused by electrostatic solute–solvent interaction and is called electrostriction. A mutual comparison of the two electrolytes shows that values of ϕ_v^0 are larger in case of $MgCl_2$ than in NaCl. Mg^{+2} ion being smaller in size has an intense force field and hence a strong hydration co sphere around it. Therefore hydration of $MgCl_2$ (solute–solvent interactions) will be much more than that of NaCl. Further to this effect is superimposed the effect of interaction of cations (Na^+ and Mg^{+2}) and anion (Cl^-) with negative and positive charge centers of glycine, respectively (solute–solute interactions). The double charge on Mg^{+2} results in intense electric field and thus the possibility of interaction with glycine is larger in case of glycine + aq. $MgCl_2$ ternary systems. The hydration behavior of amino acids considered the following interaction (Ali and Akhtar, 2003; Mishra and Gautum, 2001; Yu et al., 2002) as the terminal groups of Zwitter ions of amino acids, $-NH_3^+$ and COO^- are hydrated in electrostatic manner whereas, hydration of intervening backbone depends on its nature which may be hydrophobic, hydrophilic or amphiphilic, (b) electrostriction of NH_3^+ group is greater than the COO^- by a factor of 10, (c) the overlap of hydration groups co spheres of terminal (NH_3^+ and COO^-) and of adjacent groups result in volume change. Table 3 shows that the values of S_v of amino acids are found to be less negative suggesting strong solute–solute interactions. The values of S_v indicating the solute–solvent interactions are greater than the solute–solute interactions.

3.3. Apparent molar adiabatic compressibility

The density and adiabatic compressibility values were employed for calculating apparent molar adiabatic compressibility, ϕK_s of solutes in aqueous electrolytes solutions at different concentration using the equation

Table 3 Partial molar volume (ϕ_v^0), its experimental slope, (S_v), partial molar adiabatic compressibility (ϕ_{Ks}^0) and its experimental slope, (S_{K_s}), of Glycine + aqueous NaCl and Glycine + aqueous $MgCl_2$ at 303 K.

C (mol l^{-1})	ϕ_v^0 (10^{-6} m^{-3} mol^{-1})	S_v (10^{-6} m^{-3} $mol^{-3/2}$ $l^{-1/2}$)	ϕ_{K_s} (10^{-14} m^{-5} N^{-1} mol^{-1})	S_{K_s} (10^{14} m^5 N^{-1} $mol^{-3/2}$ $l^{-1/2}$)
Glycine + water NaCl				
0.02	56.78	−16.02	1.61	−3.80
0.06	64.94	−36.51	1.08	−7.40
Glycine + water $MgCl_2$				
0.02	37.00	−16.38	2.60	−16.00
0.06	90.60	−82.95	0.99	−5.10

$$\phi K_s = [1000(\rho_{K_s}^0 - \rho_{K_s})/C\rho\rho^0] + M_{K_s}/\rho \qquad (5)$$

Table 3 shows the less negative values of ϕK_s which indicates strong solute–solvent interactions. The apparent molar adiabatic compressibilities, ϕK_s of glycine as a function of its concentration in different $NaCl/MgCl_2$ + water solutions were calculated using Eq. (5). The values of ϕK_s were fitted to the equation:

$$\phi_{K_s} = \phi_{K_s}^0 + S_{K_s} C^{1/2} \qquad (6)$$

where $\phi_{K_s}^0$ is the limiting apparent molar compressibility (also know as partial molar compressibility at infinite dilution). It provides information regarding solute–solvent interaction. S_{K_s} is the experimental slope of the plot of ϕ_{K_s} versus $C^{1/2}$ and gives the idea of solute–solute interactions in the solution. The calculated values of $\phi_{K_s}^0$ and S_{K_s} are also included in Table 3 along with the values of ϕ_v^0 and S_v. Appreciable positive values of $\phi_{K_s}^0$ for both the systems reinforce our earlier view that strong solute–solvent interaction prevails in the present systems.

Acknowledgements

I am highly thankful to Dr. M.D. Darweish and Dr. T. Ahmad, Department of Chemistry, University of Tabuk, K.S.A for their co-operation and valuable suggestions.

References

Akhtar, Y., 2004. Indian Council Chem. 21 (2), 43.

Akhtar, Y., 2007. Fluid Phase Equilib. 258, 125–130.

Ali, A., Akhtar, Y., 2003. J. Pure Appl. Ultrason. 25, 13.

Ali, A., Hyder, S., Akhtar, Y., 2005a. Indian J. Phys. 79 (20), 157.

Ali, A., Hyder, S., Akhtar, Y., 2005b. Ind. J. Phys. 79 (2), 157–160.

Badaryani, R., Kumar, A., 2002. Fluid Phase Equilib. 338, 321–338.

Badaryani, R., Kumar, A., 2003. J. Chem. Eng. Data 48, 664–668.

Baddin, V.G., Tyunina, E.Y., 2008. Russ. J. Chem. 78 (6), 1155–1160.

Banipal, T.S., Singh, G., 2000. Indian J. Chem. 39A, 1011–1018.

Banipal, T.S., Kaur, D., Banipal, P.K., Singh, G., 2007. J. Chem. Thermodyn. 39 (3), 371–384.

Cabani, S., Conti, G., Tine, M.R., 1981. J. Chem. Soc. Faraday Trans. I 77, 2377.

Fereiara, L.A., Macedo, E.A., Pinho, S.P., 2009. J. Chem. Thermodyn. 41 (2), 193–196.

Mallick, I.N.B., Mohanty, R.K., Chakraborty, U., 1986. Indian J. Chem. 25A, 1089.

Mishra, A.P., Gautum, S.K., 2001. Indian J. Chem. 40A, 100.

Ogawa, T., Mizutani, K., Yasuda, M., 1984. Bull. Chem. Soc. Jpn. 57, 2064.

Pinho, S.P., 2008. J. Chem. Eng. Data 53 (1), 180–184.

Rai, T.C., Yan, G.B., 2003. Carbohydr. Res. 338, 2921–2927.

Singh, S.K., Kundu, A., Kishore, N., 2004. J. Chem. Thermodyn. 35, 7–18.

Waris, B.N., Hassan, U., Srivastava, N., 2001. Indian J. Chem. 40A, 1218–1222.

Yan, Z., Wang, J., Lu, J., 2002. Biol. Phys. Chem. 99, 199–207.

Yan, Z., Wang, J., Kong, W., Lu, J., 2004. Fluid Phase Equilib. 215, 150–156.

Yu, D.L.Q., Wang, Y.Y., Sun, D., 2002. Indian J. Chem. 41A, 1126.

Yuan, Q., Li, Zhi Fen, Wong, B.H., 2006. J. Chem. Thermodyn. 38 (1), 20–23.