

## Viscometric studies of $\alpha$ -amino acid in aqueous NaCl and MgCl<sub>2</sub> at 303 K

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**Abstract** : Densities, and viscosities of glycine in aqueous solutions of 0.02, 0.06 and 0.10 M NaCl and MgCl<sub>2</sub> as a function of glycine concentration are measured at 303 K. The viscosity data have been analyzed by means of Jones-Dole equation to calculate *A* and *B* coefficients. The activation parameters of viscous flow, namely, free energies of activation of viscous flow, per mole of solvent and solute were obtained by the application of transition state theory. The results show the presence of weak solute-solute and strong solute-solvent interactions and also that both solutes act as structure-makers in aqueous glycine.

**Keywords** : Glycine, viscosity, molecular interactions.

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### 1. Introduction

In recent years, there has been an increased interest in the physico-chemical properties of amino acids in aqueous as well as aqueous-electrolyte media [1–3]. However, data on the state of these biomolecules in aqueous electrolyte medium are scarce. Amino acids have dipolar character and are the constituents of the most important class of biopolymers, *i.e.* proteins. Derangement of water and electrolyte balance in living systems may cause a wide variety of health problems. In physiological media such as blood, membranes, cellular fluids *etc.*, the dipolar character of amino acids (in presence of ions such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> *etc.*, 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.

In this work, an attempt has been made to study the interaction of glycine molecules with water in presence of Na<sup>+</sup>, Mg<sup>2+</sup>, and Cl<sup>-</sup> ions. For this purpose, densities  $\rho$

and viscosities  $\eta$  of the binary mixtures of aqueous NaCl/MgCl<sub>2</sub> (0.02, 0.06 and 0.10 M) and the ternary mixtures of glycine (0.10M to 0.90 M) in aqueous NaCl/MgCl<sub>2</sub> (0.02, 0.06 and 0.10 M), were measured at 303 K. Several thermodynamic parameters such as Jones-Dole coefficient *B* [4], Falkenhagen coefficient *A* [5], free energy of activation per mole of solvent  $\Delta\mu_1^{0\#}$  and free energy of activation per mole of solute  $\Delta\mu_2^{0\#}$ , were computed from the experimental data. These parameters were utilized to study various interactions taking place in the solutions of electrolytes (NaCl and MgCl<sub>2</sub>) and the bioactive molecules (glycine).

### 2. Materials and method

Glycine (Sigma Chemicals Co.), NaCl and MgCl<sub>2</sub> (AR 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 hours. Aqueous solutions of NaCl and MgCl<sub>2</sub> (0.02, 0.06 and 0.10 M) were prepared and these were used as solvents to prepare glycine solutions on mass basis covering the whole composition range. The

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weighings were done on an Afcoset-ER-120A electronic balance with a precision of  $\pm 0.1$  mg.

The densities of solvents (aq. NaCl/aq. MgCl<sub>2</sub>) and the ternary mixtures (glycine + aq. NaCl/aq. MgCl<sub>2</sub>) were measured using a single-capillary pycnometer having bulb capacity of  $8 \times 10^{-3}$  dm<sup>3</sup>. The marks on the stem were calibrated using deionized triple-distilled water. Viscosity measurements were carried out by Ubbelohde-type suspended level viscometer. The viscometer was allowed to stand in an electronically controlled water bath for 20 minutes to minimize thermal fluctuation. The temperature of the water bath was maintained at  $303 \pm 0.2$  K. The accuracies in density and viscosity measurements were found to be  $\pm 0.01$  kg m<sup>-3</sup> and  $\pm 3 \times 10^{-6}$  N m<sup>-2</sup>s, respectively.

### 3. Results and discussion

Densities and viscosities of aqueous NaCl, MgCl<sub>2</sub> and their ternary mixtures with glycine as third component were determined at 303 K and are presented in Table 1. The viscosity data were used to calculate relative viscosity using Jones-Dole equation [4]

$$\eta_r = \eta/\eta_0 = [1 + Am^{1/2} + Bm], \quad (1)$$

where  $\eta_r$  is the relative viscosity of the solutions,  $A$  is the Falkenhagen coefficient [5] which takes into account ionic interactions and  $B$ , the Jones-Dole coefficient [4] is related to size of the ions and the different ion-solvent or solute-solvent interactions. The  $A$  and  $B$  coefficients were obtained from the intercepts and slopes of the curves and their values are given in Table 2.

It is observed from Table 1 that  $\rho$  and  $\eta$  for all ternary systems increase non-linearly with increase in molarities of glycine. Such changes in  $\rho$  and  $\eta$  can be correlated to hydrophobic (hydrogen bond forming or structure making) or hydrophilic (hydrogen bond disrupting or structure breaking) character of solute. Solutes may occupy the interstitial spaces in solvent or get solvated forming new weaker bonds. It was suggested [6–8] 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.

A perusal of Table 2 shows that the values of  $A$  coefficients are negative or small positive and those of  $B$  coefficients are large positive for all the ternary systems under investigation, thereby suggesting that solute-solute interactions are weak and solute-solvent interactions are strong.

**Table 1.** Densities ( $\rho$ ) and viscosities ( $\eta$ ) of glycine + aqueous NaCl and glycine + aqueous MgCl<sub>2</sub> at 303 K.

C (mol <sup>-1</sup> )	$\rho$ (kg m <sup>-3</sup> )	$\eta$ ( $\times 10^{-3}$ N m <sup>-2</sup> s)	$\rho$ (kg m <sup>-3</sup> )	$\eta$ ( $\times 10^{-3}$ N m <sup>-2</sup> s)	$\rho$ (kg m <sup>-3</sup> )	$\eta$ ( $\times 10^{-3}$ N m <sup>-2</sup> s)
Glycine + aqueous NaCl						
	0.02 M		0.06 M		0.10 M	
0.00	1020.6	0.843	1003.8	0.862	1002.7	0.858
0.10	1021.3	0.847	1004.6	0.866	1002.9	0.860
0.20	1024.1	0.904	1005.1	0.871	1003.5	0.864
0.30	1028.9	0.912	1007.3	0.890	1006.6	0.877
0.40	1029.4	0.914	1009.1	0.902	1012.2	0.885
0.50	1031.2	0.918	1011.8	0.913	1017.6	0.895
0.60	1032.9	0.926	1019.1	0.935	1019.6	0.906
0.70	1035.7	0.931	1020.6	0.942	1022.3	0.919
0.80	1038.1	0.941	1020.9	0.946	1025.4	0.932
0.90	1041.3	0.959	1024.7	0.967	1029.8	0.941
Glycine + aqueous NaCl <sub>2</sub>						
	0.02 M		0.06 M		0.10 M	
0.00	998.7	0.825	1006.2	0.903	1007.3	0.901
0.10	1004.0	0.876	1006.4	0.916	1011.8	0.918
0.20	1010.0	0.905	1014.3	0.943	1012.3	0.927
0.30	1013.4	0.914	1015.7	0.960	1018.8	0.938
0.40	1017.2	0.938	1016.7	0.967	1019.4	0.973
0.50	1024.9	0.991	1017.5	0.989	1024.3	0.979
0.60	1027.1	1.002	1019.8	1.007	1025.1	0.984
0.70	1034.2	1.027	1020.9	1.014	1025.5	1.011
0.80	1035.6	1.050	1024.9	1.045	1033.1	1.047
0.90	1038.5	1.180	1025.3	1.062	1033.7	1.06

**Table 2.** Falkenhagen coefficient,  $A$  and Jones-Dole coefficient,  $B$  of glycine + aqueous NaCl and glycine + aqueous MgCl<sub>2</sub> at 303 K.

	0.02 M	0.06 M	0.10 M
Glycine + aqueous NaCl			
$A$ ( $10^{-2}$ dm <sup>3/2</sup> mol <sup>-1/2</sup> )	5.926	-4.726	-4.774
$B$ ( $10^{-1}$ dm <sup>3</sup> mol <sup>-1</sup> )	0.958	1.858	1.575
Glycine + aqueous MgCl <sub>2</sub>			
$A$ ( $10^{-2}$ dm <sup>3/2</sup> mol <sup>-1/2</sup> )	-6.290	-0.321	-2.597
$B$ ( $10^{-1}$ dm <sup>3</sup> mol <sup>-1</sup> )	4.304	1.950	2.170

A mutual comparison of the two electrolytes shows that values of  $A$  and  $B$  coefficients are larger in case of MgCl<sub>2</sub> than in NaCl. Mg<sup>2+</sup> ion being smaller in size, has an intense force field and hence a strong hydration cosphere around it. Therefore, hydration of MgCl<sub>2</sub> (solute-solvent interaction) will be much more than that of NaCl.

Further to this effect is superimposed the effect of interaction of cations (Na<sup>+</sup> and Mg<sup>2+</sup>) and anion (Cl<sup>-</sup>) with negative and positive charge centers of glycine respectively (solute-solute interaction). The double charge on Mg<sup>2+</sup> ion results in intense electric field and thus, the possibility of interaction with glycine is larger in case of glycine + aq. MgCl<sub>2</sub> ternary system. These two effects result in larger values of *A* and *B* coefficients for MgCl<sub>2</sub> than for NaCl. However, the *B* values do not show a regular trend with concentration of electrolytes. As suggested by Ogawa *et al* [9], sometimes there seems exist no regularity concerning the effects of salts on *t*. *B* coefficient of amino acids. Such anomalous behaviour of *B* has also been observed by Kapadi and coworkers [10]. Stronger interactions have been reported in L-cystine + aq. MgCl<sub>2</sub> than in L-cystine + aq. NaCl by Yu *et al* [11].

The viscosity data have been analyzed on the basis of transition state theory of the relative viscosities of electrolytic solutions. The application of this treatment gives rise to the following equation :

$$B = (\bar{V}_1^0 - \bar{V}_2^0)/1000 + \bar{V}_1^0 [(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})/RT]/1000, \quad (2)$$

where  $\bar{V}_1^0$  and  $\bar{V}_2^0$  are the partial molar volumes of the solvent and solute respectively.  $\Delta\mu_2^{0*}$  is the contribution per mole of the solute to the free energy of activation of the viscous flow of the solution and  $\Delta\mu_1^{0*}$  is the free energy of activation per mole of the pure solvent. The values of  $\Delta\mu_1^{0*}$  and thereafter those of  $\Delta\mu_2^{0*}$  were calculated using the following equations :

$$\Delta\mu_1^{0*} = RT \ln(\eta_0 \bar{V}_1^0 / h N_A) \quad (3)$$

and

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + (RT/\bar{V}_1^0) [1000B - (\bar{V}_1^0 - \bar{V}_2^0)], \quad (4)$$

where *R*, *h* and *N* are the gas constant, Plank's constant and Avagadro's constant respectively and *T* is the absolute temperature. The values of  $\Delta\mu_1^{0*}$  and  $\Delta\mu_2^{0*}$  for different compositions of glycine in aqueous NaCl/MgCl<sub>2</sub> are given in Table 3. Table 3 shows that  $\Delta\mu_2^{0*}$  are larger than  $\Delta\mu_1^{0*}$  suggesting that the formation of transition state is less favoured in the presence of these electrolytes. This implies that the formation of transition state is accompanied by the breaking and distortion of the intermolecular bonds. Moreover, the greater values of  $\Delta\mu_2^{0*}$  than  $\Delta\mu_1^{0*}$  suggest that the metal chlorides under study, behave as structure makers/promoters in different

**Table 3.** Free energy of activation per mole of solvent,  $\Delta\mu_1^{0*}$ , and solute,  $\Delta\mu_2^{0*}$  of glycine + aqueous NaCl and glycine + aqueous MgCl<sub>2</sub> at 303 K.

	0.02 M	0.06 M	0.10 M
Glycine + aqueous NaCl			
$\Delta\mu_1^{0*}$ (kJ mol <sup>-1</sup> )	9.12	9.22	9.22
$\Delta\mu_2^{0*}$ (kJ mol <sup>-1</sup> )	28.39	41.86	37.85
Glycine + aqueous MgCl <sub>2</sub>			
$\Delta\mu_1^{0*}$ (kJ mol <sup>-1</sup> )	9.22	9.13	9.36
$\Delta\mu_2^{0*}$ (kJ mol <sup>-1</sup> )	37.85	72.34	46.63

concentration ranges of glycine. Greater values of  $\Delta\mu_2^{0*}$  than  $\Delta\mu_1^{0*}$  have also been reported in mixtures of Ni, Cu, Co and Zn chlorides in aqueous glycine [12].

A comparison of  $\Delta\mu_1^{0*}$  and  $\Delta\mu_2^{0*}$  values of the two solutes reveals the order of structure making ability as Mg<sup>2+</sup> > Na<sup>+</sup> which may be due to stronger solute-solvent interactions in case of MgCl<sub>2</sub> solutions. The hydration of Mg<sup>2+</sup> ion is stronger than that of Na<sup>+</sup> ion since the electric charge of Mg<sup>2+</sup> is twice that of Na<sup>+</sup> and the radius of the former is much shorter than that of latter. It may further be noted that  $\Delta\mu_2^{0*}$  has highest values at 0.06 M concentration for both the electrolytes. This suggests maximum structure making ability of the solutes at this particular concentration. Increase in concentration of electrolyte from 0.06 M to 0.1 M probably causes disruption of the intermolecular bonds of the solvent, thereby decreasing the values of  $\Delta\mu_2^{0*}$ .

Thus, the trends and magnitude of the various parameters obtained from viscosity measurement reported in this paper, and those obtained from ultrasonic studies which are reported in our earlier paper [13], support each other. Both the studies suggest that solute-solvent interactions are stronger than solute-solute interactions in the ternary systems under study and both solutes behave as the structure makers. The extent of interactions and structure making ability is greater in case of MgCl<sub>2</sub>.

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