

Molar volume, compressibility and excess properties of glycylglycine in aqueous NiCl₂ solutions

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ARTICLE INFO

Article history:

Received 9 July 2010

Received in revised form 30 August 2010

Accepted 4 September 2010

Available online 21 September 2010

Keywords:

Molar volume
Compressibility
Glycylglycine
NiCl₂

ABSTRACT

Volumetric and acoustical parameters are reported for glycylglycine in aqueous NiCl₂ solution at $T=(288.15\text{--}318.15)\text{K}$. The apparent molar volumes and isentropic compressibilities were calculated from the experimental data of ultrasonic velocity and density. Together with these, excess isentropic compressibility (κ_S^E), excess free volume (V_f^E), excess intermolecular free length (L_f^E) and deviations of ultrasonic velocity (Δu) were obtained. The results are interpreted in terms of molecular interactions. The results show that the cation and anion play a significant role in influencing the behavior of glycylglycine in aqueous solutions. These effects were also attributed to the doubly charged behavior of glycylglycine and to the formation of physically bonded ion-pairs between charged groups of glycylglycine and cation and anion of the electrolyte.

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1. Introduction

The interactions between charged biomolecules and ions can highly influence their behavior and conformation in aqueous solutions. The study of these interactions provides an insight into the conformational stability and unfolding behavior of biomolecules such as proteins. This study also has application in the development and design of separation processes containing electrolytes, such as electrolyte-induced precipitation of biomolecules. However, the complex structure of most biomolecules makes it difficult to study the effect of different factors influencing their behavior. Dipeptides are the simplest biomolecules, which are the building blocks of other more complex biomolecules, such as proteins and peptides. Thus, they can be used as a model compound for the study of the behavior of complex biomolecules [1–3].

Among the volumetric, acoustic and excess properties which represent the interactions in a system, partial molar volume, isentropic compressibility (κ_S), excess isentropic compressibility (κ_S^E), excess intermolecular free length (L_f^E), excess free volume (V_f^E) and deviation in ultrasonic velocity (Δu) are particularly important [4,5]. These parameters provide useful and important information regarding the type of interaction and behavior of molecules in solutions. Measurement of the partial molar vol-

ume and isentropic compressibility of dipeptides in aqueous solutions without the presence of an electrolyte has been the subject of several studies [6–11]. Some studies have also been conducted to calculate the properties of complex biomolecules from the properties of their constituent dipeptides. For example, Iqbal and Verrall [6] showed that the partial specific volumes of some proteins could be calculated, with a reasonable accuracy, from the partial specific volume of their constituent dipeptides.

Further, it is important to note that transition metal ions play an important role in plant growth, lipid metabolism and regulation of physiological systems. Hence, it is of interest to study the dynamics of dipeptide–transition metal salt solution systems which may provide new insights and better understanding of this field of science.

Thus, we thought it worthwhile to study the interactions of a simple dipeptide glycylglycine with transition metal ions in aqueous and non aqueous solutions. The studies on solution properties and interactions of glycylglycine with MnCl₂ [12,13], Mn(COOCH₃)₂ [14], FeCl₂ [15], CoCl₂ [16], NiCl₂ [17] in varied media have already been reported from our lab. The study of volumetric, acoustic, refractometric properties of glycylglycine–metal salt solutions, their excess and deviation properties and evaluation of molecular interactions present in these systems were the focus of these reports. Thus, as a part of our ongoing research program, we report herein, the compressibilities, molar volumes, excess and deviation properties of glycylglycine in aqueous NiCl₂ solutions at temperatures $T=(288.15\text{--}318.15)\text{K}$. These properties have been calculated from the measured ultrasonic velocity, density and vis-

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Table 1
Ultrasonic velocity, u , density, ρ , and viscosity, η , for glycylglycine in aqueous NiCl₂ solution at $T=(288.15\text{--}318.15)\text{K}$.

m (mol kg ⁻¹)	x_1	u (ms ⁻¹)	u^a (ms ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$\rho^a \times 10^{-3}$ (kg m ⁻³)	η (m Pa s)	η^a (m Pa s)
T/K=288.15							
0.00000	0.00000	1636.82	1760.39	0.9980	1.2971	1.35	1.42
0.00523	0.08572	1642.90	1768.21	1.0115	1.2872	1.41	1.86
0.01072	0.17156	1648.99	1773.06	1.0250	1.2699	1.45	2.37
0.02035	0.25724	1654.08	1779.54	1.0386	1.2545	1.50	3.05
0.03014	0.34301	1660.17	1785.14	1.0520	1.2336	1.55	3.95
0.05068	0.42887	1666.25	1791.37	1.0658	1.2195	1.60	4.71
0.07543	0.51459	1672.34	1797.62	1.0795	1.1911	1.68	4.92
0.10058	0.60033	1678.42	1806.87	1.0932	1.1614	1.74	5.50
T/K=298.15							
0.00000	0.00000	1665.57	1789.56	1.0008	1.2585	1.22	1.28
0.00523	0.08572	1672.15	1796.37	1.0147	1.2420	1.27	1.60
0.01072	0.17156	1679.73	1800.42	1.0279	1.2224	1.33	2.14
0.02035	0.25724	1686.31	1804.65	1.0414	1.2031	1.37	2.75
0.03014	0.34301	1693.92	1809.73	1.0547	1.1835	1.43	3.43
0.05068	0.42887	1700.47	1815.69	1.0685	1.1642	1.48	3.99
0.07543	0.51459	1707.05	1822.22	1.0819	1.1449	1.54	4.26
0.10058	0.60033	1715.63	1829.07	1.0955	1.1128	1.60	4.74
T/K=308.15							
0.00000	0.00000	1693.36	1817.05	1.0047	1.2199	1.09	1.14
0.00523	0.08572	1699.27	1822.31	1.0179	1.1967	1.15	1.45
0.01072	0.17156	1705.18	1826.47	1.0312	1.1735	1.21	1.85
0.02035	0.25724	1711.09	1831.54	1.0443	1.1503	1.26	2.31
0.03014	0.34301	1717.03	1837.69	1.0578	1.1271	1.33	2.88
0.05068	0.42887	1723.91	1843.82	1.0710	1.1039	1.39	3.37
0.07543	0.51459	1730.82	1848.08	1.0842	1.0810	1.45	3.63
0.10058	0.60033	1737.73	1855.26	1.0975	1.0600	1.52	3.89
T/K=318.15							
0.00000	0.00000	1722.34	1848.47	1.0085	1.1813	0.94	1.03
0.00523	0.08572	1728.26	1855.06	1.0222	1.1482	0.99	1.30
0.01072	0.17156	1734.18	1861.34	1.0359	1.1151	1.03	1.60
0.02035	0.25724	1740.10	1867.81	1.0496	1.0841	1.08	1.95
0.03014	0.34301	1746.05	1873.14	1.0633	1.0504	1.15	2.48
0.05068	0.42887	1752.94	1880.53	1.0771	1.0173	1.22	2.75
0.07543	0.51459	1758.86	1886.72	1.0910	0.9842	1.28	2.94
0.10058	0.60033	1765.78	1894.88	1.1048	0.9511	1.36	3.22

x_1 = mole fraction of ethanol in Ref. [17].

u^a , ρ^a , and η^a = ultrasonic velocity, density and viscosity respectively, of glycylglycine–NiCl₂ in aqueous ethanol mixture as given in Ref. [17].

cosity data. Investigations on similar lines with other transition metal ions under diverse conditions are also under progress.

2. Experimental

2.1. Materials

Glycylglycine and Nickel (II) Chloride hexahydrate of 99% purity used in our studies were purchased from Sigma–Aldrich, Germany. Commercially available glycylglycine of the highest purity was used without further purification. NiCl₂·6H₂O was used after drying for 72 h in a vacuum desiccator at room temperature. Deionized, doubly distilled degassed water with a specific conductance less than $1.29 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ was used for the preparation of all solutions. The solutions were prepared on a weight basis by using a Mettler balance having a precision of ± 0.01 mg. Care was taken to avoid evaporation and contamination during mixing. In our studies, the concentration of NiCl₂ was kept constant at 0.25 mol kg^{-1} and the concentration of glycylglycine was varied in terms of molality (m). In order to prepare the solutions under investigation, aqueous solutions of NiCl₂ was first prepared. Different concentrations of glycylglycine were then added to the salt solution prepared in advance and stirred until a homogeneous solution was obtained. To prevent formation of air bubbles, all solutions were preheated in sealed Eppendorf tubes to 5 °C above the measurement temperature before filling the ultrasonic and densimetric cells.

2.2. Methods

Ultrasonic velocity of pure components and their mixtures were measured by variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model-83). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocity were taken at a fixed frequency of 2 MHz. The capacity of the measurement cell was 7 ml. The calibration of ultrasonic interferometer was done by measuring the velocity in AR grade benzene and carbon tetrachloride. The maximum estimated error in ultrasonic velocity measurements was found to be $\pm 0.08\%$. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled adequately stirred water bath with a precision of ± 0.01 °C. Densities were measured using the (Mettler Toledo) Density 30PX digital densitometer having a precision of $\pm 1 \times 10^{-3} \text{ kg m}^{-3}$ and an accuracy of $\pm 3 \times 10^{-3} \text{ kg m}^{-3}$. Viscosities were measured using a Brookfield DV-III Ultra Programmable Rheometer (Brookfield Engineering Laboratories, Inc., USA) which was calibrated using double distilled water and its uncertainty was found to be $\pm 0.5\%$. The densitometer was calibrated using double distilled water. The sample and reference resonator cells with minimum volumes of 0.5 cm^3 were thermostated with an accuracy of ± 0.01 K, and a previously described differential technique was employed for all measurements [18]. The physical parameters for glycylglycine in aqueous NiCl₂ solutions were measured at temperatures 288.15 K, 298.15 K, 308.15 K, and 318.15 K. The measured density values and their uncertainties agree well with the literature values [19]. Each

Table 2
Isentropic compressibility, κ_S , excess isentropic compressibility, κ_S^E , apparent molar volume, V_ϕ , apparent molar isentropic compressibility, $K_{S\phi}$, and deviation of ultrasonic velocity, Δu , of glycylglycine in aqueous NiCl₂ solution at $T=(288.15\text{--}318.15)$ K.

m (mol kg ⁻¹)	$\kappa_S \times 10^{12}$ (Pa ⁻¹)	$\kappa_S^E \times 10^{12}$ (Pa ⁻¹)	$V_\phi \times 10^6$ (m ³ mol ⁻¹)	$K_{S\phi} \times 10^{15}$ (m ³ mol ⁻¹ kPa ⁻¹)	Δu (m s ⁻¹)
T/K=288.15					
0.00000	424.25	-11.60	-	-	-1.029
0.00523	404.73	-16.84	57.26	-32446.47	-1.805
0.01072	386.39	-21.48	57.59	-31089.69	-2.617
0.02035	369.57	-28.32	57.88	-29732.91	-3.738
0.03014	353.35	-32.39	58.17	-28376.13	-4.427
0.05068	337.94	-34.37	58.46	-27019.35	-4.785
0.07543	323.44	-23.23	58.75	-25662.57	-2.918
0.10058	309.77	-1.4	59.04	-24305.74	0.42
T/K=298.15					
0.00000	375.35	-9.60	-	-	-1.282
0.00523	358.87	-14.33	59.31	-28167.59	-2.163
0.01072	343.16	-17.82	59.60	-27198.08	-2.932
0.02035	328.65	-23.78	59.89	-26235.61	-4.268
0.03014	314.63	-27.78	60.18	-25273.14	-4.987
0.05068	301.63	-28.84	60.47	-24310.67	-5.321
0.07543	289.42	-19.19	60.76	-23355.20	-3.359
0.10058	277.51	-1.00	61.04	-22392.73	0.38
T/K=308.15					
0.00000	341.03	-7.22	-	-	-1.613
0.00523	326.63	-11.14	60.35	-26538.42	-2.596
0.01072	312.99	-14.08	60.63	-25724.16	-3.394
0.02035	300.17	-18.67	60.92	-24909.90	-4.724
0.03014	287.91	-21.65	61.20	-24095.64	-5.679
0.05068	276.11	-22.82	61.49	-23281.38	-6.003
0.07543	265.22	-14.49	61.77	-22467.12	-3.762
0.10058	254.88	-0.2	62.05	-21652.83	0.36
T/K=318.15					
0.00000	298.91	-6.00	-	-	-2.111
0.00523	286.68	-8.59	61.96	-24746.59	-3.111
0.01072	275.12	-11.25	62.33	-23897.13	-4.025
0.02035	264.16	-14.71	62.61	-23047.67	-5.289
0.03014	253.78	-17.18	62.89	-22198.21	-6.18
0.05068	245.06	-17.94	63.17	-21348.75	-6.444
0.07543	234.30	-11.73	63.46	-20497.29	-4.168
0.10058	225.43	0.01	63.74	-19643.78	0.34

measurement was repeated thrice and the reported values are an average of all three trials.

3. Results and discussion

The experimental values of ultrasonic velocity, density and viscosity of glycylglycine in aqueous NiCl₂ solutions at different temperatures and concentrations are presented in Table 1. Table 1 also presents the values of the above experimental parameters for glycylglycine–NiCl₂ in aqueous ethanol mixture published by us earlier [17], in order to compare them with the present experimental values of the aqueous system. The values of apparent molar volumes, V_ϕ , and apparent molar isentropic compressibility, $K_{S\phi}$, were calculated using the following equations:

$$V_\phi = \frac{M}{\rho} - \frac{\rho - \rho_0}{m\rho\rho_0}, \quad (1)$$

$$K_{S\phi} = \frac{M\kappa_S}{\rho} - \frac{\kappa_S^0\rho - \kappa_S\rho_0}{m\rho\rho_0}, \quad (2)$$

Table 3
Calculated values of V_ϕ^0 , $K_{S\phi}^0$ and slopes of Eqs. (4) and (5), χ_v , χ_S along with their standard deviations (σ) obtained from the fitting of experimental data at $T=(288.15\text{--}318.15)$ K.

Parameters	T/K=288.15	T/K=298.15	T/K=308.15	T/K=318.15
$V_\phi^0 \times 10^6$ (m ³ mol ⁻¹)	57.4682	58.7235	59.1294	60.3747
$\chi_v \times 10^6$ (kg m ³ mol ⁻²)	0.6538	0.4849	0.4482	0.4212
$\sigma(V_\phi^0)$	0.0015	0.0018	0.0014	0.0017
$K_{S\phi}^0 \times 10^{15}$ (m ³ kPa ⁻¹ mol ⁻¹)	-32167.32	-28529.89	-26743.58	-23974.07
$\chi_S \times 10^{15}$ (kg m ³ kPa ⁻¹ mol ⁻²)	2957.98	2446.50	2086.34	1803.95
$\sigma(K_{S\phi}^0)$	0.0021	0.0019	0.0023	0.0022

where M denotes the molecular weight of glycylglycine, m is the molality of glycylglycine, ρ and ρ_0 are the densities of solution and solvent respectively. The terms κ_S and κ_S^0 in Eqs. (1) and (2) are isentropic compressibilities of solution and solvent respectively, calculated from ultrasonic velocity using the following relation:

$$\kappa_S = \frac{1}{u^2\rho}. \quad (3)$$

The values of κ_S , κ_S^E , V_ϕ and $K_{S\phi}$ at different temperatures and concentrations of glycylglycine are presented in Table 2. It is important to mention that for the above system containing NiCl₂ and glycylglycine, water + NiCl₂ is considered as the solvent. As the linear trends of V_ϕ and $K_{S\phi}$ experimental data with respect to glycylglycine molality suggest, their values at a fixed electrolyte molality are correlated with the molality of glycylglycine using the following relations:

$$V_\phi = V_\phi^0 + \chi_v m, \quad (4)$$

$$K_{S\phi} = K_{S\phi}^0 + \chi_S m, \quad (5)$$

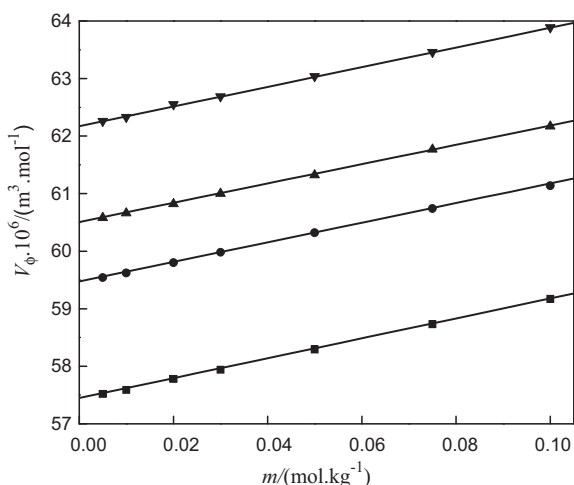


Fig. 1. Effect of concentration on V_ϕ of glycylglycine in aqueous NiCl_2 solution at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

where m is the molality of glycylglycine, V_ϕ^0 and $K_{s\phi}^0$ are respectively the apparent molar volume and apparent molar isentropic compressibility of glycylglycine at infinite dilution, χ_v and χ_s are two empirical parameters. The values of these parameters can be calculated by fitting the values of V_ϕ and $K_{s\phi}$ to the molality of glycylglycine at fixed electrolyte molality using Eqs. (4) and (5) respectively. The values of V_ϕ^0 and $K_{s\phi}^0$ together with the values of χ_v and χ_s at different temperatures are presented in Table 3.

Fig. 1 depicts the effect of glycylglycine concentration on its apparent molar volume at different temperatures. As shown in this figure, the value of V_ϕ of glycylglycine increases as the concentration of glycylglycine increases. This indicates that glycylglycine molecules are larger in volume in solutions of the studied system. It can also be seen that for a fixed electrolyte concentration the nature of both cation and anion of the electrolyte affect the value of V_ϕ of glycylglycine. These effects can be explained by the fact that amino and carboxyl groups of glycylglycine in aqueous solutions dissociate and become positively and negatively charged respectively. In the presence of an electrolyte, this leads to the formation of physically bonded ion-pairs between the charged groups of glycylglycine and cation and anion of the electrolyte. This leads to decrease in hydration number of glycylglycine and the interaction between glycylglycine and water. It should be mentioned that the bonds forming the ion-pairs are physical and non-covalent in nature. The formation of ion-pairs also decreases the hydrophobicity of glycylglycine molecules arising from hydrocarbon backbone of glycylglycine with water molecules. This results in a more favorable interaction between glycylglycine and water molecules, which in turn decreases the hydration number of glycylglycine. The increasing values of V_ϕ^0 at all four temperatures are presented in Table 3. The formation of ion-pairs between charged dipeptide and ions have been shown and discussed in several previous investigations. A complete review of these investigations is published by Collins [20]. The results of these studies in general agree on the formation of ion-pairs and the fact that the presence of an electrolyte in an aqueous solution of a dipeptide results in the condensation of the cation and the anion of electrolyte on the charged groups of dipeptide and thereby their neutralization. It has also been shown that this phenomenon is the reason for the influence of electrolytes on the solubility of dipeptides [20,21] in aqueous solutions. The effect of cation and anion of the electrolyte on the value of V_ϕ can also be attributed to the formation of ion-pairs. These effects reflect from a study made by us [17] where flexibility of ethanol molecules increases upon weakening of dipole-induced dipole of O–H group.

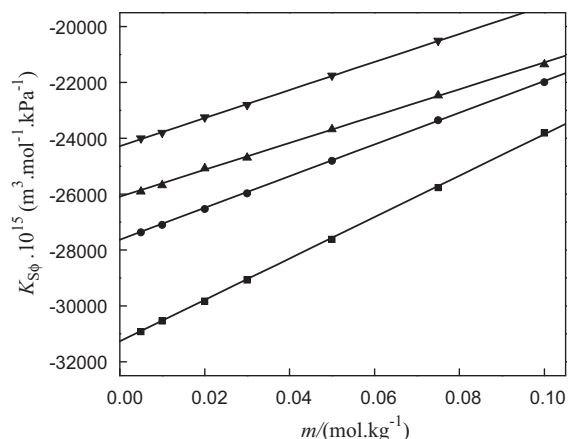


Fig. 2. Effect of concentration on $K_{s\phi}$ of glycylglycine in aqueous NiCl_2 solution at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

Nevertheless, in coordination with the metal ion, the peptide linkage acts as acidic group and supports hydrogen bonding between peptide and solvent. Further, it can be seen from Table 3 that V_ϕ^0 increases as the temperature increases. It can also be seen that for a fixed electrolyte concentration, V_ϕ^0 of glycylglycine depends on the constituent ion of the electrolyte present in the solution. It is important to mention that the presence of an electrolyte can change the protonation behavior of glycylglycine, which in turn may result in the formation of singly charged forms of glycylglycine in solution. The effect of electrolyte on the first and second dissociation constants of glycylglycine [22,23] show that in the absence of a strong proton donor or acceptor, the presence of an electrolyte does not result in the formation of singly charged glycylglycine molecules.

Fig. 2 depicts the effect of glycylglycine concentration on its isentropic compressibility at different temperatures. From Fig. 2 it can be seen that the value of $K_{s\phi}$ of glycylglycine is negative throughout the range of glycylglycine concentration studied and it increases as the concentration of glycylglycine increases. The experimental results show that at low electrolyte concentration that we have used $K_{s\phi}$ of glycylglycine is less affected by the cation or the anion of the electrolyte. From the negative values of $K_{s\phi}$ and $K_{s\phi}^0$, presented in Tables 2 and 3, it can be deduced that the water molecules around glycylglycine molecules are less compressible than the water molecules in the bulk solution. It should be mentioned that $K_{s\phi}$ reflects the interactions between the solute and solvent, which in turn can be related to the hydration of molecules. Hydration phenomenon plays an important role in the interactions among water + dipeptide + electrolyte systems. This is owing to the doubly charged behavior of glycylglycine in aqueous solutions, which influences the structure of water molecules in the vicinity of the glycylglycine molecules and this phenomenon is called electrostriction. As a result of mass action law, the charges on more glycylglycine molecules are neutralized and the electrostatic interactions between glycylglycine and water molecules are suppressed and therefore the water molecules become more compressible [24,25].

The variations of ultrasonic velocity as a function of molality (m) of glycylglycine were fitted to a polynomial of the type [21,22]:

$$u(m) = \sum_{j=0}^4 \alpha_j \cdot m^j, \quad (6)$$

by the method of least-squares with each point weighted equally. The values of coefficients α_j and standard deviations $\sigma(u)$ are summarized in Table 4.

Table 4
Coefficients a_j and standard deviation $\sigma(u)$ of Eq. (6) for glycyglycine in aqueous NiCl_2 solution at $T=(288.15\text{--}318.15)$ K.

Coefficients	$T/K=288.15$	$T/K=298.15$	$T/K=308.15$	$T/K=318.15$
$a_0 \times 10^{-2}$	18.2367	17.2189	18.4337	17.9193
$a_1 \times 10^{-2}$	-5.4178	-4.8235	-4.8812	-4.9227
$a_2 \times 10^{-2}$	0.0020	0.3536	-0.7245	-0.2674
$a_3 \times 10^{-2}$	0.0165	-0.1348	1.7388	-0.8293
$a_4 \times 10^{-2}$	0.2007	0.2217	-0.7224	-0.3556
$\sigma(u)$ (m s^{-1})	0.03	0.32	0.33	0.31

The deviations in ultrasonic velocity from a linear dependence on the average of molality (m_i) have been calculated from the relationship [23]:

$$\Delta u = u - \sum_{i=1}^2 u_i \cdot m_i, \quad (7)$$

where u_1 , u_2 and u are the ultrasonic velocities of water, aqueous NiCl_2 and the mixture (glycyglycine in aqueous NiCl_2 solution), m_i is the molality of the component i .

The values of Δu calculated by using Eq. (7) are listed in Table 2.

The values of Δu also show similar trend as observed in κ_S^E (negative). These negative values may be due to specific forces between molecules such as making and breaking of hydrogen bonds, physical intermolecular forces including electrostatic forces between charged particles and between a permanent dipole and induced dipole and forces of attraction and repulsion between non-polar molecules. Together with the above factors, structural characteristics of the components arising from geometrical fitting of one component into the other due to differences in shape and size of the components also lead to negative values (Fig. 3).

The excess isentropic compressibilities (κ_S^E) were calculated from the relation [23]:

$$\kappa_S^E = \kappa_S - \kappa_S^{\text{ideal}} = \kappa_S - \sum_{i=1}^2 \kappa_{S,i}^0 \cdot m_i, \quad (8)$$

where ($\kappa_{S,i}^0$) is the isentropic compressibility of the pure component i and m_i is the molality of the component i . The values of κ_S^E calculated using Eq. (8) are also listed in Table 2. The values of κ_S^E are negative over the entire composition range for the studied mixture (see Fig. 4). The estimated uncertainty for κ_S^E is $\pm 0.2 \text{ Pa}^{-1}$. The negative values of κ_S^E indicate the formation of molecular order

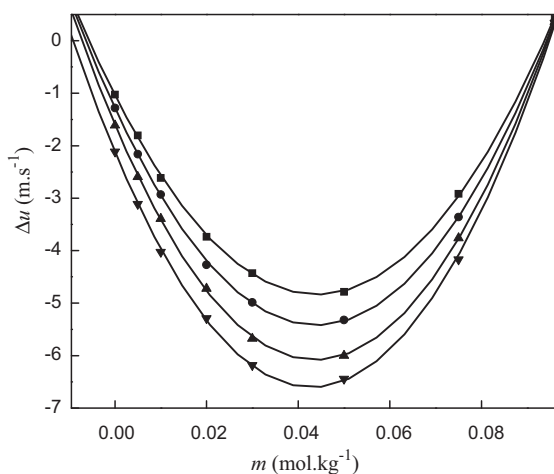


Fig. 3. Plot of deviation of ultrasonic velocity (Δu) against molality (m) for glycyglycine in aqueous NiCl_2 solution at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

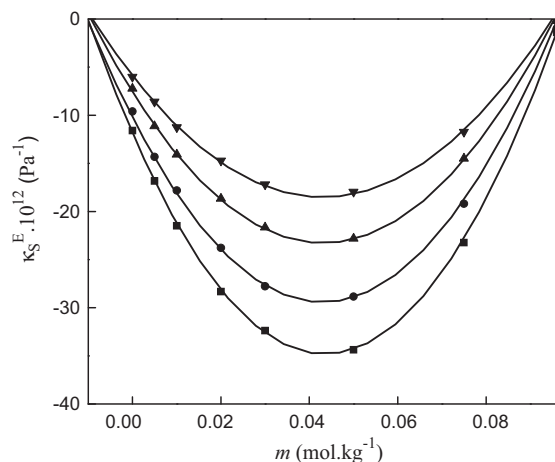


Fig. 4. Plot of excess isentropic compressibility (κ_S^E) against molality (m) for glycyglycine in aqueous NiCl_2 solution at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

in the studied mixture due to dipole–dipole interactions between the molecules. The more easily the molecules fit into each other's structure, κ_S^E values become more and more negative.

A review of literature shows that the deviations of analyzed function provide experimental evidence for the formation of intermolecular complexes, and provide a valuable aid for determining their stoichiometry and relative stability [23,25]. In a typical example [17], formation of strong hydrogen bonds between water and ethanol leads to more compact hydration layer and the water structure collapses as the ethanol molecules are introduced into the aqueous system. As a result, increase in ethanol molecules disturbs the cage-like structure of water leading to an increase in ultrasonic velocity and a decrease in compressibility of the solution. However, negative κ_S^E and Δu values indicate the presence of strong intermolecular bonding between the components in the mixture. In the present system, at least four different effects can be identified which contribute to Δu and κ_S^E values: (1) the breaking of liquid order on mixing; (2) favorable interactions between polar groups (OH and O) of unlike molecules; (3) geometrical fitting of one component into other; and (4) hydrophobic interactions between OH group of water and CH_2 group of glycyglycine.

The free volume (V_f) of the mixture is calculated from the relation [23]:

$$V_f = [M \cdot u \cdot K \cdot \eta]^{3/2}, \quad (9)$$

where M and η are the molar mass and viscosity of the mixture, respectively and K is a dimensionless constant having value of 4.28×10^9 , independent of temperature and the nature of liquid system.

The viscosities (η) required to calculate free volumes are given in Table 1.

The corresponding excess free volumes (V_f^E) were calculated from the relation [23,25]:

$$V_f^E = V_f - \sum_{i=1}^2 V_{f,i} \cdot m_i, \quad (10)$$

where $V_{f,i}$ is the free volume of the pure component i , V_f is the free volume of the mixture, and m_i is the molality of the component i .

The excess intermolecular free length (L_f^E) were calculated from the relation [22,23]:

$$L_f^E = L_f - \sum_{i=1}^2 x_i \cdot L_{f,i}, \quad (11)$$

Table 5

Coefficients a_j and standard deviation σ (Δu , κ_S^E , V_f^E and L_f^E) of Eq. (12) for glycyglycine in aqueous NiCl_2 solution at $T = 318.15$ K.

Coefficients	Δu (m s^{-1})	$\kappa_S^E \times 10^{12}$ (Pa^{-1})	V_f^E (m^3)	L_f^E (\AA)
a_0	-46.429	-87.429	-35.826	-0.0104
a_1	-12.321	-3.124	-31.532	-0.0362
a_2	23.442	-2.103	-6.379	-0.0107
a_3	-27.567	24.728	22.734	-0.0062
a_4	-41.213	26.092	18.473	-0.0023
σ	0.16	0.25	0.12	0.0002

where $L_f = K/u \cdot \rho^{1/2}$, $K = (93.875 + 0.375T) \times 10^{-8}$, K is the temperature dependent constant [24].

The values of Δu , κ_S^E , V_f^E and L_f^E were fitted to Redlich–Kister polynomial regression of the type:

$$F = m_1 \cdot (1 - m_1) \sum_{j=0}^4 a_j \cdot (2m_1 - 1)^j,$$

where $F = (\Delta u, \kappa_S^E, V_f^E \text{ and } L_f^E)$. (12)

The parameter a_j in Eq. (12) was evaluated by the least squares method. The values of these parameters with standard deviation σ (Δu , κ_S^E , V_f^E and L_f^E), are summarized in Table 5.

The standard deviation values were obtained from:

$$\sigma = \left[\frac{\sum (X_{\text{expt}} - X_{\text{calc}})^2}{N - p} \right]^{1/2}, \quad (13)$$

where N is the number of experimental points, p is the number of parameters, X_{expt} and X_{calc} are the experimental and calculated properties, respectively. These values provide valuable information about the interactions between glycyglycine and the solvent (water + electrolyte), as at infinite dilution the interactions between glycyglycine molecules are negligible.

Fig. 5 shows that the excess free volume (V_f^E) in the studied mixture becomes more negative when Δu and κ_S^E decrease. The plot of this function indicates that the excess free volume created in the mixture is not available for compression. This means that the interstitial accommodation plays an important role by influencing Δu and κ_S^E of the liquid mixture. It also indicates that the molecular size and shape of the components are important factors in the studied mixture [26–28]. The course of changes in L_f^E also confirms these

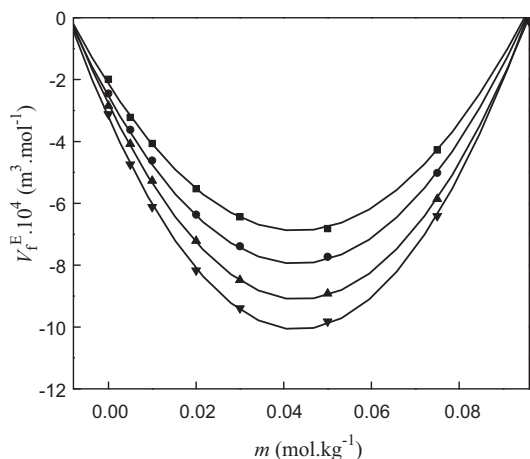


Fig. 5. Plot of excess free volume (V_f^E) against molality (m) for glycyglycine in aqueous NiCl_2 solution at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

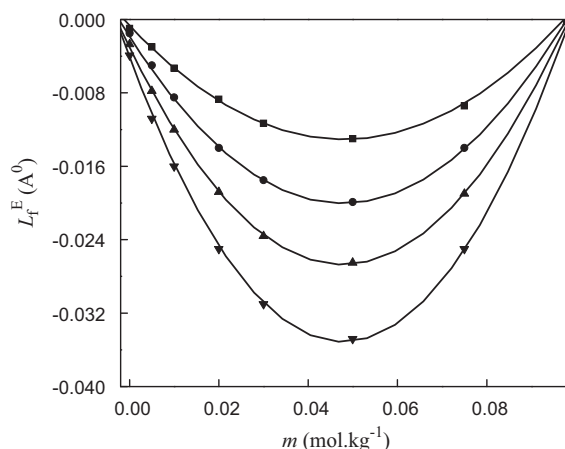


Fig. 6. Plot of excess intermolecular free length (L_f^E) against molality (m) for glycyglycine in aqueous NiCl_2 solution at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

conclusions (see Fig. 6), because L_f^E is generally more negative when the structure has high rigidity.

4. Conclusions

The experimental data of ultrasonic velocity, density and viscosity for glycyglycine in aqueous NiCl_2 solutions have been reported at four different temperatures. The values of apparent molar volume and isentropic compressibility were calculated from the experimental data. The results indicated that the interactions between glycyglycine and NiCl_2 influence its properties in aqueous solution. The results also showed that both cation and anion of the electrolyte play an important role in the interactions between NiCl_2 and glycyglycine. For the system studied, it was found that these interactions result in a positive volume transfer. It was also found that the value of $K_{S\phi}$ of glycyglycine is negative for the entire range of concentration. Various excess properties (Δu , κ_S^E , V_f^E and L_f^E) support that there exists intermolecular hydrogen bonding between the components of the mixture and the interstitial accommodation also plays an important role in analyzing their behavior. The negative values implied that the water molecules around glycyglycine were less compressible than the water molecules in the bulk solution. These effects were attributed to the doubly charged behavior of glycyglycine and the formation of ion-pairs with weak non-covalent bonds between the charged groups of glycyglycine and the ions present in the solution. The above conclusions are drawn after comparing the studied system of glycyglycine– NiCl_2 in both aqueous and aqueous ethanol mixture. The results are found to be in good accordance with each other and give a clear picture of the interactions between various molecules in solution.

Acknowledgement

The authors thank the DRDO, Govt. of India for their financial support in the form of an R & D project grant.

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