

# Volumetric, Refractometric, and Excess Properties of Glycylglycine in Aqueous FeCl<sub>2</sub> Solution at Temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$

M. S. Santosh, D. Krishna Bhat,\* and Aarti S. Bhatt

Physical Chemistry Division, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India

Densities and refractive indices have been measured for glycylglycine in aqueous FeCl<sub>2</sub> solution as a function of concentration at  $T = (288.15 \text{ to } 318.15) \text{ K}$ . The apparent molar volumes and partial molar volumes were obtained from these density data. The limited partial molar expansivities have been calculated from the temperature dependence of the partial molar volume. The molar refractions were calculated from the experimental refractive index values for the studied mixture. The excess volumes and molar refractions were also calculated. The results are discussed in terms of molecular interactions.

## Introduction

Density and refractive index measurements are expected to shed some light on both solute–solute and solute–solvent interactions.<sup>1–3</sup> Salt solutions have large effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes. In the literature, there are some reports about the effect of various neutral salts on the transition temperature of proteins and enzymes.<sup>4–6</sup> Owing to the complexities arising from a direct thermodynamic study on proteins, investigations on the behavior of model compounds of protein-like amino acids and peptides in aqueous and mixed aqueous solvents have been carried out, which make it easy to understand the factors governing the stability of biopolymers.<sup>7</sup> The solution structure is of great importance in understanding the nature of bioactive molecules in the body.<sup>8–11</sup> Most of the previous studies<sup>12–16</sup> on amino acids have been carried out in different solvents and aqueous solutions at a given temperature, but interesting results have been obtained when they were studied under various temperatures and pressures in water, not only because it is used in chemistry and other related fields to control factors such as the solubility, reactivity, and stability of the system but also for the fact that biological molecules are ultimately found in water.<sup>17</sup> Studies on amino acids and biomolecules have been carried out in pure and mixed aqueous solvents by many researchers, but such investigations in the presence of metal ions which play a vital role in the functioning of living organisms are scant. Transition metal ions play an important role in plant growth, lipid metabolism, and regulation of physiological systems. Hence, as a continuation of our earlier work,<sup>18</sup> it is of interest to study the dynamics of dipeptide/transition metal salt solution systems which would fill the gap and may provide new insights and better understanding of this field of science. Through this paper, we make an attempt to present variations occurring under diverse conditions. Accordingly, this paper presents a systematic study of the densities, refractive indices, apparent molar volumes, partial molar volumes, expansibilities at infinite dilution, molar refractions, excess molar volumes, and excess

molar refractions for glycylglycine in aqueous FeCl<sub>2</sub> solution as a function of concentration and temperature over wide ranges to understand molecular behavior and the nature of solute–solvent and solute–solute interactions.

## Experimental Section

**Materials.** Glycylglycine and FeCl<sub>2</sub>·4H<sub>2</sub>O of mass fraction purity 0.99 were used in our studies and obtained from Sigma-Aldrich Germany, Ltd. Commercially available glycylglycine of the highest purity was used without further purification. FeCl<sub>2</sub>·4H<sub>2</sub>O 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  $1.29 \cdot 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$  was used for the preparation of all solutions. The solutions were prepared on weight basis using a Mettler balance with a precision of  $\pm 0.01 \text{ mg}$ . The temperature of water was controlled within  $\pm 0.01 \text{ K}$  using a thermostat. In our experiments, the concentration of FeCl<sub>2</sub> was kept constant at  $0.25 \text{ mol} \cdot \text{kg}^{-1}$  with the concentration of glycylglycine being varied. To prevent the formation of air bubbles, all solutions were preheated in sealed Eppendorf tubes to 5 K above the measurement temperature before filling the densimetric cell.

**Methods.** Densities were measured using the (Mettler Toledo) density 30PX digital densitometer with an uncertainty of  $\pm 3 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ . Refractive indices were measured using a (Mettler Toledo) Refracto 30Gs digital refractometer, and its uncertainty was found to be  $\pm 0.0005 \%$ . The densitometer and refractometer were calibrated using double-distilled water. The pressure of the measurements was about 0.1 MPa. The densities and refractive indices for glycylglycine in aqueous FeCl<sub>2</sub> solution were measured at temperatures of (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. Each measurement was repeated thrice, and the reported values are an average of all three trials.

## Results and Discussion

The experimental densities and refractive indices for glycylglycine in aqueous FeCl<sub>2</sub> solution are given as a function of concentration at  $T = (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, \text{ and } 318.15) \text{ K}$  in Tables 1 and 2, respectively.

\* Corresponding author. E-mail: denthajekb@gmail.com. Fax: 0824-2474033.

**Table 1. Density,  $\rho$ , of Glycylglycine (1) in Aqueous FeCl<sub>2</sub> (2) Solution<sup>a</sup> at Different Temperatures  $T$  and Molality  $m$** 

$m$ mol·kg <sup>-1</sup>	$\rho/\text{g}\cdot\text{cm}^{-3}$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.000	0.9989	0.9982	0.9970	0.9960	0.9950	0.9945	0.9938
0.005	0.9999	0.9997	0.9978	0.9972	0.9961	0.9954	0.9950
0.007	1.0006	1.0005	0.9986	0.9981	0.9968	0.9963	0.9957
0.010	1.0014	1.0012	0.9995	0.9990	0.9975	0.9972	0.9964
0.020	1.0023	1.0020	1.0006	0.9999	0.9983	0.9981	0.9972
0.030	1.0031	1.0027	1.0015	1.0008	0.9991	0.9990	0.9980
0.050	1.0038	1.0035	1.0024	1.0017	0.9999	0.9999	0.9988
0.10	1.0046	1.0043	1.0034	1.0027	1.0007	1.0009	0.9996

<sup>a</sup> Molality of FeCl<sub>2</sub> = 0.25 mol·kg<sup>-1</sup>.**Table 2. Refractive Indices,  $n_D$ , of Glycylglycine (1) in Aqueous FeCl<sub>2</sub> (2) Solution<sup>a</sup> at Different Temperatures  $T$  and Molality  $m$** 

$m$ mol·kg <sup>-1</sup>	$n_D$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.000	1.3375	1.3468	1.3559	1.3661	1.3768	1.3874	1.3980
0.005	1.3449	1.3543	1.3641	1.3739	1.3833	1.3931	1.4016
0.007	1.3482	1.3594	1.3693	1.3789	1.3884	1.3979	1.4075
0.010	1.3528	1.3641	1.3741	1.3842	1.3935	1.4042	1.4123
0.020	1.3591	1.3694	1.3787	1.3886	1.3986	1.4094	1.4186
0.030	1.3635	1.3742	1.3845	1.3935	1.4037	1.4154	1.4229
0.050	1.3681	1.3784	1.3898	1.3992	1.4088	1.4186	1.4294
0.10	1.3718	1.3813	1.3947	1.4016	1.4139	1.4231	1.4300

<sup>a</sup> Molality of FeCl<sub>2</sub> = 0.25 mol·kg<sup>-1</sup>.

**Volumetric Studies.** The apparent molar volumes  $V_\varphi$  were calculated from the densities of the solutions using the following expression<sup>19</sup>

$$V_\varphi/\text{cm}^3 \cdot \text{mol}^{-1} = \frac{10^3(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M_2}{\rho} \quad (1)$$

where  $V_\varphi$  is the apparent molar volume,  $m$  is the molality of glycylglycine in the solution,  $M_2$  is the molar mass of the electrolyte, and  $\rho_0$  and  $\rho$  are the densities of solvent and that of solution, respectively. The molar volume results are presented in Table 3. The resulting solute  $V_\varphi$  values are reported in Table 4. The positive values of  $V_\varphi$  for glycylglycine in aqueous FeCl<sub>2</sub> solution indicate strong solute–solvent interactions. These interactions are strengthened with increasing concentration at a particular temperature but are weakened by a rise in temperature at a constant solute concentration. The apparent molar volume of the solute at infinite dilution was calculated using a least-

squares treatment of  $V_\varphi$  against  $C^{1/2}$  using the following expression of Masson<sup>20</sup>

$$V_\varphi/\text{cm}^3 \cdot \text{mol}^{-1} = V_\varphi^0(\text{cm}^3 \cdot \text{mol}^{-1}) + S_\varphi^* C^{1/2} \quad (2)$$

where  $V_\varphi^0$  is the apparent molar volume at infinite dilution,  $S_\varphi^*$  is the experimental slope, and  $C$  is the concentration in terms of molality.

The calculated values of  $V_\varphi^0$  and  $S_\varphi^*$ , along with their standard errors, are listed in Table 5. The partial molar volume of a salt at infinite dilution reflects the effects of ion–solvent interactions, while the magnitude of slope is related to the ion–ion interactions. A careful inspection of the  $V_\varphi^0$  values at infinite dilution reveals that they decrease with rising temperature. The discussion of the influence of temperature, as well as the nature of the solvent and the electronic structure of the metal ion on the partial molar volumes of the solvated cations is only possible after splitting the partial molar volumes of FeCl<sub>2</sub> into their ionic

**Table 3. Molar Volume,  $V_m$ , of Glycylglycine (1) in Aqueous FeCl<sub>2</sub> (2) Solution at Different Temperatures  $T$  and Molality  $m$** 

$m$ mol·kg <sup>-1</sup>	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.005	82.146	82.328	82.531	82.845	83.218	83.476	83.793
0.007	82.793	82.990	83.194	83.492	83.855	84.119	84.454
0.010	83.445	83.651	83.857	84.139	84.492	84.762	85.115
0.020	84.097	84.312	84.520	84.786	85.129	85.405	85.776
0.030	84.742	84.974	85.183	85.433	85.766	86.048	86.438
0.050	85.390	85.636	85.846	86.080	86.403	86.691	87.101
0.10	86.049	86.289	86.514	86.728	87.027	87.335	87.756

**Table 4. Apparent Molar Volume,  $V_\varphi$ , of Glycylglycine (1) in Aqueous FeCl<sub>2</sub> (2) Solution at  $T = (288.15 \text{ to } 318.15) \text{ K}$  and Molality  $m$** 

$m$ mol·kg <sup>-1</sup>	$V_\varphi/\text{cm}^3 \cdot \text{mol}^{-1}$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.005	190.218	178.273	156.538	149.176	140.415	131.053	122.819
0.007	194.405	183.357	164.527	158.102	150.486	142.076	135.122
0.010	198.592	188.723	172.516	167.028	160.557	153.099	147.425
0.020	202.779	193.962	180.505	175.954	170.628	164.122	159.728
0.030	206.966	198.198	188.494	184.880	180.699	175.145	172.031
0.050	211.153	203.484	196.483	193.806	190.770	186.168	184.334
0.10	215.345	208.312	204.472	202.735	200.846	198.274	196.638

**Table 5. Apparent Molar Volume at Infinite Dilution  $V_{\varphi}^0$ , Experimental Slope  $S_{\varphi}^*$ , and Apparent Molar Expansibilities at Infinite Dilution  $\varphi_E^0$  of Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution at  $T = (288.15 \text{ to } 318.15) \text{ K}$** 

$T$ K	$V_{\varphi}^0$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$S_{\varphi}^*$ $\text{cm}^3 \cdot \text{mol}^{-3/2} \cdot \text{dm}^{-3/2}$	$\varphi_E^0$ $\text{cm}^3 \cdot \text{mol}^{-1}$
288.15	182.624	84.364	-7.615
293.15	172.250	98.079	-6.553
298.15	161.876	111.794	-5.491
303.15	151.502	125.509	-4.429
308.15	140.128	139.224	-3.367
313.15	130.754	152.939	-2.305
318.15	120.376	166.659	-1.238

contributions, that is, the intrinsic volume and electrostriction volume. The former is related to the size of the ion and is independent of temperature. The latter is directly related to ion–solvent interactions and is affected by temperature.  $V_{\varphi}^0$  is regarded as resulting from solute–solvent interactions as it is the apparent molar volume at infinite dilution, where by definition it is independent of solute–solute interactions. The positive values indicate the presence of strong solute–solvent interactions. These interactions are weakened by a rise in temperature.

The variation of  $V_{\varphi}^0$  with temperature can be expressed as

$$V_{\varphi}^0/\text{cm}^3 \cdot \text{mol}^{-1} = a + b(T/\text{K}) + c(T/\text{K})^2 \quad (3)$$

Values of the coefficients  $a$ ,  $b$ , and  $c$  have been estimated by least-squares fitting of the apparent molar volumes at infinite dilution. Equation 4 is thus obtained by

$$V_{\varphi}^0/\text{cm}^3 \cdot \text{mol}^{-1} = 10323.91 - 63.3495(T/\text{K}) + 0.09811(T/\text{K})^2 \quad (4)$$

The limiting apparent molar expansibilities can be obtained by differentiating eq 3 with respect to temperature:

$$\varphi_E^0/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = \left( \frac{\partial V_{\varphi}^0}{\partial T} \right)_p = b + 2c(T/\text{K}) \quad (5)$$

where  $\varphi_E^0$  is the apparent molar expansivity and  $p$  is the pressure. The values of  $\varphi_E^0$  are listed in Table 5. Negative expansivity values (i.e., decreasing volume with increasing temperature) are characteristic of aqueous solutions of a hydrophilic solute.<sup>21</sup>

**Optical Properties.** Values of molar refraction,  $R_m$ , were calculated from the measured refractive indices using the relation proposed by Lorentz and Lorenz:

$$R_m = \left[ \frac{(n^2 - 1)}{(n^2 + 2)} \right] V \quad (6)$$

The values of  $R_m$  are reported in Table 6. Increased interest in optical properties led us to measure refractive indices that are needed for calculating the molar refractions from the Lorentz–Lorenz equation.<sup>22</sup> Values of  $R_m$  increase linearly with concentration. The values of  $R_m$  are proportional to the dispersive

forces. Thus, the increasing magnitude of  $R_m$  for glycylglycine in aqueous  $\text{FeCl}_2$  solution indicates strong solute–solvent interactions.

**Excess Properties.** The excess properties of the mixtures were calculated using the following equation:

$$Y^E = Y_3 - (x_1 Y_1 + x_2 Y_2) \quad (7)$$

where  $Y^E$  represents the excess molar volume,  $V^E$ . The standard deviation of the fits,  $\sigma$ , is defined as

$$\sigma = \left[ \frac{\sum_i ((V^E)_{\text{cal}} - (V^E)_{\text{exp}i})^2}{(N - n)} \right]^{1/2} \quad (8)$$

where  $N$  is the number of experimental data points and  $n$  is the number of fitted parameters.

The excess molar volume or molar refraction deviation of water, aqueous  $\text{FeCl}_2$ , and their solution (glycylglycine dissolved in aqueous  $\text{FeCl}_2$  solution) are denoted by  $Y_1$ ,  $Y_2$ , and  $Y_3$ , respectively. The calculated excess volumes and molar refraction deviation values are reported in Tables 7 and 8, respectively.

Several methods to predict the physical properties of mixtures were applied to test their validities which were compiled by Iglesias et al.<sup>23</sup> The agreement between the experimental values of densities and refractive indices and the predicted ones is shown by standard deviation values,  $\sigma$ , calculated by eq 8 and given in Tables 9 and 10 respectively. The densities of the studied system were estimated using the following methods: Hankinson–Brobst–Thompson (HBT),<sup>24</sup> Rackett (R),<sup>25</sup> Spencer and Danner modified Rackett (SDR),<sup>26</sup> and Yen–Woods (YW).<sup>27</sup> The parameter values needed in the HBT and SDR methods can be found in Hankinson and Thompson (1979) and Munoz et al. (1999).<sup>24,28</sup> The SDR method gives the best estimation for the studied system, and HBT and YW methods present the smallest deviations. The refractive index estimation was carried out using the mixing rules proposed by Lorentz–Lorenz (LL),<sup>22</sup> Dale–Gladstone (DG),<sup>22</sup> Newton (N),<sup>29</sup> and Oster (O).<sup>30</sup> The Oster equation shows the best estimation in the studied system, whereas the lowest deviation was obtained by LL and N rules, respectively.

Many methods for the estimation of excess properties have been developed using additive binary contributions. A compilation of the equations for different methods was summarized by Munoz et al. The standard deviations between experimental and predicted methods are given in Table 11. With respect to  $V^E$ , the Tsao–Smith<sup>31</sup> and Toop<sup>32</sup> equations give the best results. The values of  $R_m$  show large differences for different equations, but for  $R_m^E$  values there are no great differences between different equations. A comparison of the above properties by implementing various methods<sup>31–36</sup> helps in analyzing the obtained results in a broader perspective. It has to be noted that the correlation equations give deviations significantly lower than those of estimated equations, especially in the case of  $V^E$ . This fact clearly shows that the use of correlation methods of excess properties

**Table 6. Molar Refraction,  $R_m$ , of Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution at Different Temperatures**

$m$ $\text{mol} \cdot \text{kg}^{-1}$	$R_m/\text{cm}^3 \cdot \text{mol}^{-1}$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.005	28.4135	28.5168	28.6793	28.3125	28.7236	28.4280	28.2923
0.007	28.8170	28.8976	29.0537	28.7302	28.9768	28.8259	28.7111
0.010	29.2205	29.2784	29.4281	29.1479	29.2300	29.2238	29.1299
0.020	29.6240	29.6592	29.8025	29.5656	29.4832	29.6217	29.5487
0.030	30.0275	30.0400	30.1769	29.9833	29.7364	30.0196	29.9675
0.050	30.4310	30.4208	30.5513	30.4010	29.9896	30.4175	30.3863
0.10	30.8346	30.8016	30.8058	30.8189	30.2432	30.8165	30.8054

**Table 7.** Excess Molar Volume,  $V^E$ , of Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution at Temperatures  $T$  and Molality  $m$ 

$m$ mol·kg <sup>-1</sup>	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.005	-0.2124	-0.2636	-0.3228	-0.3739	-0.4087	-0.4615	-0.4977
0.007	-0.2859	-0.3605	-0.2275	-0.4651	-0.4994	-0.5477	-0.5814
0.010	-0.3594	-0.4574	-0.3228	-0.5563	-0.5901	-0.6339	-0.6651
0.020	-0.4330	-0.5543	-0.4181	-0.6475	-0.6808	-0.7201	-0.7488
0.030	-0.5065	-0.6512	-0.5134	-0.7387	-0.7715	-0.8063	-0.8325
0.050	-0.5798	-0.7481	-0.6087	-0.8299	-0.8622	-0.8925	-0.9162
0.10	-0.6537	-0.8453	-0.8947	-0.9216	-0.9529	-0.9788	-0.9999

**Table 8.** Molar Refraction Deviation,  $R_m^E$ , of Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution at Different Temperatures

$m$ mol·kg <sup>-1</sup>	$R_m^E/\text{cm}^3\cdot\text{mol}^{-1}$						
	$T/\text{K} = 288.15$	$T/\text{K} = 293.15$	$T/\text{K} = 298.15$	$T/\text{K} = 303.15$	$T/\text{K} = 308.15$	$T/\text{K} = 313.15$	$T/\text{K} = 318.15$
0.005	0.07	0.1057	0.1476	0.0416	0.0528	0.0627	0.0704
0.007	0.1112	0.1364	0.1624	0.0715	0.0774	0.0911	0.1027
0.010	0.1492	0.1671	0.1772	0.1015	0.1020	0.1195	0.1350
0.020	0.1873	0.1978	0.1920	0.1316	0.1266	0.1480	0.1673
0.030	0.2254	0.2285	0.2068	0.1614	0.1511	0.1765	0.1997
0.050	0.2636	0.2592	0.2216	0.1917	0.1757	0.2051	0.2322
0.10	0.3015	0.2899	0.2367	0.2219	0.2002	0.2338	0.2645

**Table 9.** Standard Deviations,  $\sigma$ , of the Experimental Results for Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution from Those Estimated for Density ( $\rho/\text{g}\cdot\text{cm}^{-3}$ )

$T/\text{K}$	HBT	R	SDR	YW
288.15	0.0068	0.0652	0.0356	0.0084
293.15	0.0187	0.0518	0.0270	0.0076
298.15	0.0073	0.0375	0.0218	0.0062
303.15	0.0192	0.0427	0.0329	0.0050
308.15	0.0123	0.0549	0.0264	0.0067
313.15	0.0145	0.0286	0.0197	0.0042
318.15	0.0097	0.0344	0.0314	0.0059

**Table 10.** Standard Deviations,  $\sigma$ , of the Experimental Results for Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution from Those Estimated for the Refractive Index

$T/\text{K}$	LL	DG	NW	O
288.15	0.0004	0.0004	0.0014	0.0017
293.15	0.0006	0.0012	0.0005	0.0010
298.15	0.0015	0.0004	0.0026	0.0017
303.15	0.0012	0.0021	0.0017	0.0009
308.15	0.0008	0.0013	0.0029	0.0015
313.15	0.0017	0.0032	0.0038	0.0012
318.15	0.0022	0.0009	0.0031	0.0016

**Table 11.** Standard Deviations,  $\sigma$ , of the Experimental Results for Glycylglycine (1) in Aqueous  $\text{FeCl}_2$  (2) Solution from Those Estimated for Different Empirical Equations

empirical equation	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$R_m$
Kohler <sup>33</sup>	0.033	0.0123
Jacob-Fitzner <sup>34</sup>	0.047	0.0236
Colinet <sup>35</sup>	0.030	0.0312
Tsao-Smith <sup>31</sup>	0.023	0.0417
Toop <sup>32</sup>	0.025	0.0389
Scatchard <sup>36</sup>	0.036	0.0257

is more convenient than the use of methods for direct estimation of these properties, since the correlation methods fit the experimental results better.

We speculate that the large negative  $V^E$  values indicate the following features might arise from specific interaction that occurs between solution components of the following:

(a) Interaction leads to H-bonding between water and glycylglycine that is assumed to be quite strong.

(b) Accommodation of one component into the structural network of the other component occurs. This effect largely depends on the size difference between the component molecules. In the studied system the ratio of the molar volume of glycylglycine/aqueous  $\text{FeCl}_2$  solution indicates that the size

difference is not very large, and therefore its contribution to the volume contraction does not seem to be of much significance.

It is plausible that the positive values are due to the predominance of dispersive forces between unlike molecules and intermolecular dipolar interactions of the molecules which favor structure-making effects.<sup>37</sup>

**Relationships between Refractive Index and Density Based on Empirically and Theoretically Derived Equations.** Two empirical linear equations are discussed in this study: (1) Gladstone-Dale<sup>22</sup> formula

$$\frac{\bar{n} - 1}{\rho(\text{g}\cdot\text{cm}^{-3})} = R_1 = \text{constant} \quad (9)$$

and the more general linear eq 2 which includes eq 9 as a special case with  $c_2 = 1$

$$\frac{\bar{n} - c_2}{\rho(\text{g}\cdot\text{cm}^{-3})} = R_2 = \text{constant} \quad (10)$$

$$\bar{n} = R_2(\rho/\text{g}\cdot\text{cm}^{-3}) + c_2 \quad (10a)$$

$$\bar{n} = 0.194(\rho/\text{g}\cdot\text{cm}^{-3}) + 1.0321 \quad (10b)$$

In addition to these empirical equations, one theoretically derived equation is also considered. Anderson and Schreiber<sup>38</sup> suggested the general refractivity formula (eq 11) for near-neighbor interactions into consideration:

$$\frac{\bar{n}^2 - 1}{[4\pi + b(\bar{n}^2 - 1)\rho(\text{g}\cdot\text{cm}^{-3})]} = \frac{\alpha}{M} = R_3 = \text{constant} \quad (11)$$

with the electronic parameter  $b = 4\pi/3 - \gamma$ , where  $\gamma$  is a substrate-dependent constant.

The constant  $b$  has a certain value for each material and can be obtained from  $\bar{n}$  and  $\rho$  data sets by linear regression since eq 11 can be written in the form:

$$\frac{4\pi}{\bar{n}^2 - 1} = \frac{1}{R_3\rho(\text{g}\cdot\text{cm}^{-3})} - b \quad (11a)$$

with the two adjustable constants  $R_3$  and  $b$ . Linear regression analysis<sup>39</sup> was performed to obtain the best fit of the empirical formula (eq 10) and the theoretically derived general refractivity formula (eq 11). When transformed to eqs 10a and 11a,



**Table 12. Results of Regression Analysis<sup>a</sup>**

parameter	eq 10b	eq 11b
<i>a</i>	0.1957 ( <i>R</i> <sub>2</sub> )	25.7731 (1/ <i>R</i> <sub>3</sub> ; <i>R</i> <sub>3</sub> = 0.0388)
se( <i>a</i> )	0.0017	0.3145
<i>c</i>	1.0321 ( <i>c</i> <sub>2</sub> )	-1.1912 (- <i>b</i> ); [ <i>b</i> = 1.2 (1)]
se( <i>c</i> )	0.0037	0.1510
<i>I</i> <sub>sig</sub>	> 99	> 99
<i>r</i> <sup>2</sup>	99.6 %	99.8 %

<sup>a</sup> *a* = regression coefficient; *c* = regression constant; se(*a*) = standard error of *a*; se(*c*) = standard error of *c*; *r*<sup>2</sup> = percentage of total variation about the mean value of  $\bar{n}$  explained by the regression; *I*<sub>sig</sub> = level of significance in percent.

respectively, both formulae are of general type  $y = ax + c$  with the regression coefficient, *a*, and the regression constant, *c*. Skinner and Fahey<sup>40</sup> reported a least-squares equation for the relations between mean refractive index and density:

$$\bar{n} = 0.189(\rho/g \cdot \text{cm}^{-3}) + 1.047 \quad (12)$$

To represent the linear relationship between refractive index and density, a linear regression is applied: Equation 10b differs slightly from eq 12. However, the constant *c*<sub>2</sub> = 1.0321 differs significantly from unity, indicating that the empirical Gladstone–Dale relation (eq 9) is less suitable for the description of the relationship between density and refractive index.

As can be seen from the *r*<sup>2</sup> value (see Table 12), the empirical linear eq 10b describes the relationship between density and refractive index of glycylglycine in aqueous FeCl<sub>2</sub> solution. From the *r*<sup>2</sup> value it follows that 99.6 % of the variation of  $\bar{n}$  can be explained by the regression equation obtained. Moreover, empirical eqs 9 and 10b fail to account for the molecular polarizability. This is considered in the general refractivity formula (eq 11). The regression analysis yields eq 11b:

$$\frac{\bar{n}^2 - 1}{[4\pi + 1.2(\bar{n}^2 - 1)](\rho/g \cdot \text{cm}^{-3})} = 0.0298 = R_3 \quad (11b)$$

Finally, in this case, 99.8 % of the variation of  $\bar{n}$  can be explained by the regression equation method.

## Conclusions

Using density and refractive indices data, the partial molar volumes, apparent molar expansibilities at infinite dilution, molar refraction, and the excess property *V*<sup>E</sup> have been computed. The behavior of the excess parameters suggests strong solute–solvent interaction. The negative *V*<sup>E</sup> values suggest that glycylglycine acts as a structure maker in water through hydrogen bonding and large dispersive forces. The experimental and calculated values are in good agreement with each other.

## Literature Cited

- Moody, G. J.; Thomas, J. D. R. *Dipole Moments in Inorganic Chemistry*; Edward Arnold: London, 1971.
- Nath, J. Speeds of sound in and isentropic compressibilities of (n-butanol + n-pentane, or n-hexane, or n-heptane, or 2,2,4-trimethylpentane) at T = 288.15 K, (n-hexanol + n-pentane or n-hexane) at T = 298.15 K, and (n-hexanol + n-heptane or n-octane) at T = 298.15 K and T = 303.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 1857–1872.
- Mehta, S. K.; Sharma, A. K.; Bhasin, K. K.; Prakash, R. Physico-chemical properties in mixtures of hexamethylphosphoramide with 2,2,2-trichloroethanol or 2,2,2-trifluoroethanol or 1,1,1,3,3,3-hexafluoropropan-2-ol. *Fluid Phase Equilib.* **2002**, *201*, 203–216.
- Riyazuddeen; Bansal, G. K. Intermolecular/interionic interactions in l-leucine-, l-asparagine- and glycylglycine-aqueous electrolyte systems. *Thermochim. Acta* **2006**, *445*, 40–48.
- Banipal, T. S.; Kaur, D.; Banipal, P. K. Effect of magnesium acetate on the volumetric and transport behavior of some amino acids in aqueous solutions at 298.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 1214–1226.
- Sinha, A.; Roy, M. N. Densities, Viscosities, and Sound Speeds of Some Acetate Salts in Binary Mixtures of Tetrahydrofuran and Methanol at (303.15, 313.15, and 323.15) K. *J. Chem. Eng. Data* **2006**, *51*, 1415–1423.
- Rialdi, G. *International Review of Science, Physical Chemistry Series 2*; Skinner, H. A., Ed.; Butterworths: London, 1975.
- Zarei, H. A.; Iloukhani, H. Excess molar enthalpies of methyl isobutyl ketone (MIBK) with alkan-1-ols (C<sub>1</sub>–C<sub>6</sub>) and their correlations at 298.15 K. *Thermochim. Acta* **2005**, *427*, 201–205.
- Zarei, H. A.; Iloukhani, H. Excess molar enthalpies of formamide + some alkan-1-ols (C<sub>1</sub>–C<sub>6</sub>) and their correlations at 298.15 K. *Thermochim. Acta* **2003**, *405*, 123–128.
- Iloukhani, H.; Zarei, H. A. Excess Molar Enthalpies of *N,N*-Dimethylformamide + Alkan-1-ols (C<sub>1</sub>–C<sub>6</sub>) at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 195–197.
- Lowen, B.; Schulz, S. Excess molar enthalpies of acetone + water, cyclohexane, methanol, 1-propanol, 2-propanol, 1-butanol and 1-pentanol at 283.15, 298.15, 323.15, 343.15 and 363.15 K. *Thermochim. Acta* **1995**, *262*, 69–82.
- Millero, F. J.; Surdo, A. L.; Shin, C. The Apparent Molal Volumes and Adiabatic Compressibilities of Aqueous Amino Acids at 25 °C. *J. Phys. Chem.* **1978**, *82*, 784–792.
- Bhat, R.; Ahluwalia, J. C. Partial Molar Heat Capacities and Volumes of Transfer of Some Amino Acids and Peptides from Water to Aqueous Sodium Chloride Solutions at 298.15 K. *J. Phys. Chem.* **1985**, *89*, 1099–1105.
- Kharakoz, D. P. Volumetric Properties of Proteins and Their Analogues in DiMed Water Solutions. 2. Partial Adiabatic Compressibilities of Amino Acids at 15–70 °C. *J. Phys. Chem.* **1991**, *95*, 5634–5642.
- Hedwig, G. R.; Häckel, M.; Hin, H. J. Thermodynamic properties of peptide solutions 8. Isentropic pressure coefficients ( $\partial V_2/\partial p$ )<sub>s</sub> of the apparent molar volume *V*<sub>2</sub> for each of the aqueous solutes: diglycine, triglycine, and tetraglycine. *J. Chem. Thermodyn.* **1991**, *23*, 1029–1035.
- Chalikian, T. V.; Sarvazyan, A. P.; Breslauer, K. J. Partial Molar Volumes, Expansibilities, and Compressibilities of  $\alpha,\omega$ -Aminocarboxylic Acids in Aqueous Solutions between 18 and 55 °C. *J. Phys. Chem.* **1993**, *97*, 13017–13026.
- Ali, A.; Nain, A. K.; Kamil, M. Physico-chemical studies of non-aqueous binary liquid mixtures at various temperatures. *Thermochim. Acta* **1996**, *274*, 209–221.
- Santosh, M. S.; Bhat, D. K.; Bhatt, A. S. Molecular Interactions in Glycylglycine-MnCl<sub>2</sub> Aqueous Solutions at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K. *J. Chem. Eng. Data* **2009**, *54*, 2813–2818.
- Klotz, I.; Rosenberg, R. M. *Chemical Thermodynamics, Basic Theory and Methods*, 3rd ed.; Benjamin Cummings: Upper Saddle River, NJ, 1972.
- Masson, D. O. Solute Molecular Volumes in Relation to Solvation and Ionization. *Philos. Mag.* **1929**, *8*, 218–235.
- Franks, F. The hydrophobic interaction. In *Water: Aqueous Solution of Amphiphiles and Macromolecules*; Franks, F., Ed.; Plenum Press: London, 1975.
- Tasic, A. Z.; Djordjevic, B. D.; Grozdanic, D. K. Use of mixing rules in predicting refractive indices and specific refractivities for some binary liquid mixtures. *J. Chem. Eng. Data* **1992**, *37*, 310–313.
- Iglesias, M.; Orge, B.; Tojo, J. Refractive Indices, Densities, and Derived Excess Properties on Mixing of the Systems Acetone + Methanol + Water and Acetone + Methanol + 1-Butanol at 298.15 K. *Fluid Phase Equilib.* **1996**, *126*, 203–223.
- Hankinson, R. W.; Thompson, G. H. A New Correlation for Saturated Densities of Liquids and Their Mixtures. *AIChE J.* **1979**, *25*, 653–663.
- Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data* **1970**, *15*, 514–517.
- Spencer, C. F.; Danner, R. P. Improved equation for prediction of saturated liquid density. *J. Chem. Eng. Data* **1972**, *17*, 236–241.
- Yen, L. C.; Woods, S. S. A generalized equation for computer calculation of liquid densities. *AIChE J.* **1966**, *12*, 95–99.
- Munoz, R.; Burguet, M. C.; Martínez-Soria, V.; de Araújo, R. N. Densities, Refractive Indices, and Derived Excess Properties of *tert*-Butyl Alcohol + Toluene, + Methylcyclohexane, and + Isooctane and Toluene + Methylcyclohexane, and the ternary System *tert*-Butyl Alcohol + Toluene + Methylcyclohexane at 298.15 K. *Fluid Phase Equilib.* **1999**, *167*, 99–111.
- Kurtz, S. S., Jr.; Ward, A. L. Refractivity intercept and the specific refraction equation of Newton: I. Development of refractivity intercept

- and comparison with specific refraction equations. *J. Franklin Inst.* **1936**, 222, 563–592.
- (30) Oster, G. The scattering of light and its application to chemistry. *Chem. Rev.* **1948**, 43, 319–365.
- (31) Tsao, C. C.; Smith, J. M. Heats of mixing of liquids. *Chem. Eng. Prog. Symp. Series* **1953**, 49, 107–117.
- (32) Toop, G. W. Predicting ternary activities using binary data. *Trans. Metall. Soc. AIME* **1965**, 223, 850–855.
- (33) Kohler, F. Estimation of thermodynamic data for a ternary system from the corresponding binary systems. *Monatsh. Chem.* **1960**, 91, 738–740.
- (34) Jacob, K. T.; Fitzner, K. The estimation of the thermodynamic properties of ternary alloys from binary data using the shortest distance composition path. *Thermochim. Acta* **1979**, 18, 197–206.
- (35) Colinet, C. Thesis, University of Grenoble, France, 1967.
- (36) Scatchard, G.; Ticknor, L. B.; Goates, J. R.; McCartney, E. R. Heats of mixing in some nonelectrolyte solutions. *J. Am. Chem. Soc.* **1952**, 74, 3721–3724.
- (37) Deetlefs, M.; Seddon, K.; Shara, M. Predicting physical properties of ionic liquids. *Phys. Chem. Chem. Phys.* **2006**, 8, 642–649.
- (38) Anderson, O. L.; Schreiber, E. The relation between refractive index and density of minerals related to the earth's mantle. *J. Geophys. Res.* **1965**, 70, 1463–1471.
- (39) Draper, N. R.; Smith, H. *Applied regression analysis*; John Wiley & Sons: New York, 1966.
- (40) Skinner, B. J.; Fahey, J. J. Observations on the inversion of Stishovite to silica glass. *J. Geophys. Res.* **1963**, 68, 5595–5604.

Received for review February 10, 2010. Accepted April 22, 2010. The authors thank the DRDO, Govt. of India for financial support in the form of an R&D project grant.

JE100151B