



# Ultrasonic velocities, densities, and viscosities of glycylglycine and $\text{CoCl}_2$ in aqueous and aqueous ethanol systems at different temperatures

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## ABSTRACT

Ultrasonic velocity ( $u$ ), density ( $\rho$ ), and viscosity ( $\eta$ ) have been measured for glycylglycine and  $\text{CoCl}_2$  in aqueous and aqueous ethanol systems at  $T = (288.15 \text{ to } 318.15) \text{ K}$ . Using the experimental values, the adiabatic compressibility ( $\kappa_s$ ), molar hydration number ( $n_H$ ), apparent molar compressibility ( $K_{S\phi}$ ), apparent molar volume ( $V_\phi$ ), limiting apparent molar compressibility ( $K_{S\phi}^0$ ), limiting apparent molar volume ( $V_\phi^0$ ), their constants ( $S_K, S_V$ ), viscosity coefficients of  $A$  and  $B$  parameters of Jones–Dole equation, relative viscosity ( $\eta_r$ ), and excess Gibbs free energy of activation ( $\Delta G^{+E}$ ) were calculated and the results of all these parameters have been discussed in terms of solute–solvent and solute–solute interactions.

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## 1. Introduction

Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes with amino acids provide useful information in understanding the behaviour of liquid systems. Intermolecular and intramolecular association, complex formation, and related structural changes affect the compressibility of the system which in turn produces corresponding variation in the ultrasonic velocity. During the last two decades, ultrasonic studies have been carried out to investigate hydration of proteins through volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration [1–6]. Owing to the complexities arising from a direct thermodynamic study on proteins, investigations on the behaviour 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 biomolecules [7–12]. The investigations of volumetric and thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solvents have been the area of interest for a number of researchers [13–18]. Mixed aqueous solvents are used extensively in chemistry and other fields to control factors like reactivity and stability of systems. Since volumetric, compressibility, and viscosity studies are still scant, an attempt has been made to understand the behaviour of glycylglycine and  $\text{CoCl}_2$  in aqueous and aqueous ethanol mixtures at different temperatures and concentrations through ultrasonic velocity mea-

surements. 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 would fill the gap and may provide new insights and better understanding of this field of science. However, the ultrasonic velocity data as such do not provide significant information about the native and relative strengths of various types of intermolecular or interionic interactions between the components. Hence, their derived parameters such as adiabatic compressibility ( $\kappa_s$ ), molar hydration number ( $n_H$ ), apparent molar compressibility ( $K_{S\phi}$ ), apparent molar volume ( $V_\phi$ ), limiting apparent molar compressibility ( $K_{S\phi}^0$ ), limiting apparent molar volume ( $V_\phi^0$ ), their constants ( $S_K, S_V$ ), viscosity coefficients of  $A$  and  $B$  parameters have been obtained along with relative viscosity ( $\eta_r$ ), and excess Gibbs free energy of activation ( $\Delta G^{+E}$ ) to shed more light on such interactions. Through this paper, we make an attempt to present variations occurring under diverse conditions.

## 2. Experimental

### 2.1. Materials

Glycylglycine and cobalt(II) chloride hexahydrate, mass fraction purity of 0.99 used in our studies, were purchased from Sigma–Aldrich Germany, Ltd. and Loba Chemi Mumbai, Ltd., respectively. Commercially available glycylglycine of the highest purity was used without further purification. Cobalt(II) chloride hexahydrate was used after drying for 72 h in a vacuum desiccator at room

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temperature. Deionised, 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. Ethanol of analytical grade mass fraction purity 0.999 used after redistillation to ensure maximum purity was purchased from Changshu Yanguan Chemicals, China. The solutions were prepared on a weight basis by using a Mettler balance having a precision of  $\pm 0.01$  mg. Care was taken to avoid evaporation and contamination during mixing. The temperature of water was controlled within  $\pm 0.01$  K using a thermostat. For the aqueous solutions, system (I), the concentration of glycylglycine was kept constant at  $0.020 \text{ mol} \cdot \text{kg}^{-1}$  and that of  $\text{CoCl}_2$  was varied. In system (II), the concentration of  $\text{CoCl}_2$  was kept constant at  $0.25 \text{ mol} \cdot \text{kg}^{-1}$  and that of glycylglycine was varied. In system (III) (aqueous ethanol system), glycylglycine and  $\text{CoCl}_2$  were kept constant at (0.020 and 0.25)  $\text{mol} \cdot \text{kg}^{-1}$ , respectively, and the composition of ethanol was varied in terms of mole fraction ( $x_1$ ). The estimated uncertainty for the mole fraction of ethanol was found to be  $< 1 \cdot 10^{-4}$ . To prevent formation of air bubbles, all solutions were preheated in sealed Eppendorf tubes to 5 K above the measurement temperature before filling the ultrasonic and densimetric cells.

## 2.2. Methods

Viscosities were measured using a Brookfield DV-III Ultra Programmable Rheometer (Brookfield Engineering Laboratories, Inc., USA) which was calibrated using double distilled water and ethanol and their uncertainty was found to be  $\pm 0.5\%$  for both solutions. The 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  $7 \text{ cm}^3$ . 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. Densities were measured using the (Mettler Toledo) Density 30PX digital densitometer having a precision of  $\pm 1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and an accuracy of  $\pm 3 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ . The densitometer was calibrated using double distilled water. The sample and reference resonator cells with minimum volumes of  $0.5 \text{ cm}^3$  were thermostatted with an accuracy of  $\pm 0.01$  K, and a previously described differential technique was employed for all measurements [19]. Theoretical analyses [20] have shown that, for the type of ultrasonic cells used in our studies, the accuracy of the sound velocity measurements is about  $\pm 10^{-3}\%$  at a frequency of 2 MHz. The physical parameters for aqueous and aqueous ethanol solutions of glycylglycine– $\text{CoCl}_2$  were measured at temperatures (288.15, 298.15, 308.15, and 318.15) K. The measured viscosity and density values and their uncertainties of (0.5002, 1.0006, 3.0009 and 0.5007, 0.9999, 2.0001) M, respectively, of aqueous solutions of glycylglycine in KCl agree well with literature values [21]. Each measurement was repeated thrice and the reported values are an average of all three trials.

**TABLE 1**

Ultrasonic velocity,  $u$ , density,  $\rho$ , and viscosity,  $\eta$ , for glycylglycine and  $\text{CoCl}_2$  in aqueous solution at  $T = (288.15 \text{ to } 318.15) \text{ K}$ , keeping glycylglycine constant at  $0.020 \text{ mol} \cdot \text{kg}^{-1}$ .

$m/(\text{mol} \cdot \text{kg}^{-1})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\rho \cdot 10^{-3}/(\text{kg} \cdot \text{m}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$
<i>System I</i>			
<i>T = 288.15 K</i>			
0.000	1505.26	0.9944	1.20
0.005	1508.38	0.9969	1.23
0.010	1512.51	1.0061	1.26
0.030	1516.73	1.0153	1.29
0.050	1520.87	1.0245	1.32
0.10	1525.05	1.0337	1.35
0.25	1530.81	1.0429	1.39
0.50	1536.42	1.0522	1.50
<i>T = 298.15 K</i>			
0.000	1600.12	0.9981	0.96
0.005	1604.03	1.0070	1.00
0.010	1608.94	1.0159	1.04
0.030	1613.85	1.0248	1.09
0.050	1618.76	1.0337	1.15
0.10	1622.67	1.0426	1.20
0.25	1629.58	1.0518	1.26
0.50	1634.54	1.0613	1.37
<i>T = 308.15 K</i>			
0.000	1700.49	1.0017	0.84
0.005	1704.88	1.0106	0.87
0.010	1709.27	1.0195	0.91
0.030	1713.66	1.0285	0.95
0.050	1718.05	1.0374	1.00
0.10	1724.44	1.0464	1.06
0.25	1730.83	1.0555	1.12
0.50	1738.25	1.0653	1.23
<i>T = 318.15 K</i>			
0.000	1805.57	1.0052	0.70
0.005	1811.93	1.0146	0.74
0.010	1818.29	1.0240	0.78
0.030	1824.65	1.0334	0.82
0.050	1831.01	1.0429	0.87
0.10	1837.37	1.0524	0.93
0.25	1843.73	1.0620	0.99
0.50	1850.63	1.0714	1.10

### 3. Results

The experimental values of ultrasonic velocity ( $u$ ), density ( $\rho$ ), and viscosity ( $\eta$ ) at different concentrations and compositions of aqueous and aqueous ethanol systems containing glycylglycine–CoCl<sub>2</sub> are given in tables 1 to 3, respectively. Using the experimental results, volumetric, compressibility, transport, and Gibbs free energy parameters have been calculated with their standard relations.

Adiabatic compressibility was calculated using

$$(\kappa_s) = 1/\mu^2\rho. \quad (1)$$

Molar hydration number has been computed using the relation

$$n_H = \left(\frac{n_1}{n_2}\right) \left(1 - \frac{\kappa_s}{\kappa_s^0}\right), \quad (2)$$

where  $\kappa_s$  and  $\kappa_s^0$  are adiabatic compressibilities of solution and solvent, respectively,  $n_1$  and  $n_2$  are number of moles of solvent and solute, respectively.

The apparent molar compressibility has been calculated from the relation,

$$K_\phi = \frac{1000}{m\rho_0}(\rho_0\kappa_s - \rho\kappa_s^0) + \left(\frac{\kappa_s^0 M}{\rho_0}\right), \quad (3)$$

where  $\kappa_s$ ,  $\rho$  and  $\kappa_s^0$ ,  $\rho_0$  are the adiabatic compressibility and density of solution and solvent respectively,  $m$  is the molar concentration of the solute, and  $M$  is the molar mass of the solute. The  $K_{S\phi}$  is a func-

tion of  $m$  as obtained by Gucker [22] from Debye–Huckel theory [23] and is given by

$$K_{S\phi} = K_{S\phi}^0 + S_K m^{1/2}, \quad (4)$$

where  $K_{S\phi}^0$  is the limiting apparent molar compressibility at infinite dilution and is a constant;  $K_{S\phi}^0$  and  $S_K$  of equation (4) have been evaluated by the least squares method.

The apparent molar volume ( $V_\phi$ ) has been calculated using the relation

$$V_\phi = \left(\frac{M}{\rho}\right) - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}. \quad (5)$$

The apparent molar volume ( $V_\phi$ ) has been found to differ with concentration according to Masson's [24] empirical relation as

$$V_\phi = V_\phi^0 + S_V m^{1/2}, \quad (6)$$

where  $V_\phi^0$  is the limiting apparent molar volume at infinite dilution and  $S_V$  is a constant and these values were determined by least square method.

The viscosity  $A$  and  $B$  coefficients for glycylglycine and CoCl<sub>2</sub> in aqueous ethanol solutions were calculated from the Jones–Dole equation [25]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm, \quad (7)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent, respectively, and  $m$  is the molar concentration of the solute,  $\eta_r$  is the relative viscosity.  $A$  is determined by the ionic attraction theory

**TABLE 2**  
Ultrasonic velocity,  $u$ , density,  $\rho$ , and viscosity,  $\eta$ , for glycylglycine and CoCl<sub>2</sub> in aqueous solution at  $T = (288.15 \text{ to } 318.15) \text{ K}$ , keeping CoCl<sub>2</sub> constant at  $0.25 \text{ mol} \cdot \text{kg}^{-1}$ .

$m/(\text{mol} \cdot \text{kg}^{-1})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\rho \cdot 10^{-3}/(\text{kg} \cdot \text{m}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$
System II			
$T = 288.15 \text{ K}$			
0.000	1510.07	0.9968	1.24
0.005	1514.18	1.0083	1.27
0.007	1519.34	1.0198	1.30
0.010	1525.26	1.0314	1.34
0.020	1530.81	1.0429	1.39
0.030	1536.57	1.0543	1.44
0.050	1542.79	1.0660	1.50
0.10	1550.18	1.0775	1.57
$T = 298.15 \text{ K}$			
0.000	1604.37	0.9999	1.02
0.005	1610.69	1.0128	1.07
0.007	1617.01	1.0257	1.13
0.010	1623.33	1.0386	1.19
0.020	1629.58	1.0518	1.26
0.030	1635.97	1.0644	1.32
0.050	1642.29	1.0773	1.38
0.10	1648.61	1.0902	1.44
$T = 308.15 \text{ K}$			
0.000	1708.62	1.0042	0.90
0.005	1714.17	1.0170	0.95
0.007	1719.72	1.0298	1.01
0.010	1725.28	1.0426	1.06
0.020	1730.83	1.0555	1.12
0.030	1736.39	1.0682	1.18
0.050	1741.92	1.0810	1.25
0.10	1747.47	1.0939	1.33
$T = 318.15 \text{ K}$			
0.000	1814.38	1.0070	0.74
0.005	1821.71	1.0206	0.79
0.007	1829.04	1.0344	0.85
0.010	1836.37	1.0481	0.92
0.020	1843.73	1.0620	0.99
0.030	1851.00	1.0756	1.06
0.050	1858.33	1.0893	1.12
0.10	1865.63	1.1029	1.18

of Falkenhagen–Vernon and therefore, also called Falkenhagen coefficient [26],  $B$  or Jones–Dole coefficient is an empirical constant determined by ion–solvent interactions.

The excess Gibbs free energy of activation ( $\Delta G^E$ ) was determined by the following equation:

$$\Delta G^E = RT \left[ \ln \left( \frac{\eta V_m}{\eta_2 V_{m2}} \right) - x_1 \ln \left( \frac{\eta_1 V_{m1}}{\eta_2 V_{m2}} \right) \right], \quad (8)$$

where  $\eta_i$ ,  $V_{mi}$ ,  $x_i$ , respectively, represent viscosity, molar volume, and mole fraction of the  $i$ th component ( $i = 1, 2$  for binary mixtures),  $\eta$  and  $V_m$  are viscosity and molar volume of the mixture, respectively,  $R$  is the universal gas constant, and  $T$  is the absolute temperature.

The values of the excess Gibbs free energy of activation has been fitted into Redlich–Kister polynomial equation [27]

$$Y^E = x_1(1 - x_1) \sum_{i=1}^5 a_i(2x_1 - 1)^{i-1}. \quad (9)$$

The values of the coefficient  $a_i$  were calculated by method of least squares along with the standard deviation  $\sigma(Y^E)$ . The coefficients are adjustable parameters for a better fit of the excess functions.

The standard deviation values were obtained from

$$\sigma(Y^E) = \left[ \frac{\sum_{i=1}^n (Y_{\text{expt}}^E - Y_{\text{cal}}^E)^2}{n - p} \right]^{1/2}, \quad (10)$$

where  $n$  is the number of experimental points,  $p$  is the number of parameters,  $Y_{\text{expt}}$  and  $Y_{\text{cal}}$  are the experimental and calculated parameters, respectively.

#### 4. Discussion

The values of adiabatic compressibility, hydration number, apparent molar compressibility, apparent molar volume, limiting apparent molar compressibility, limiting apparent molar volume, constants  $S_K$  and  $S_V$ , and viscosity coefficients of  $A$  and  $B$  parameters of Jones–Dole equations are given in tables 4 to 7, respectively. In systems I and II, the values of density and ultrasonic velocity increases with increase in molar concentration of  $\text{CoCl}_2$  and glycylglycine, respectively. But in system III (aqueous ethanol mixture), there is a decrease in the density values. The increasing trend in aqueous solutions suggests that a molecular interaction exists between solute and solvent molecules. Also, molecular association is mainly responsible for the observed increase in ultrasonic velocity in the above mixture. The increase in ultrasonic velocity in the above systems may be attributed to the cohesion brought about by the ionic hydration. The decreasing trend in density values for aqueous ethanol mixture may be due to the high molecular aggregation of solute components in the solution. Ethanol is an interesting non-aqueous solvent, in particular because it is strongly self associated through hydrogen bonding despite its low dipole moment and dielectric constant. The O–H bond is weaker in primary alcohols as the electron density increases between the O–H bond and the hydrogen tends to separate as a proton. Thus, primary alcohols are most reactive when there is cleavage of O–H bond. The effect of alcohol on the solubility of dipeptides can be attributed to the hydrophobic and electrostatic interactions of the solute. The promoted hydrophobicity of the solute with an increased amount of alcohol in the mixture destabilizes the intra-

TABLE 3

Ultrasonic velocity,  $u$ , density,  $\rho$ , and viscosity,  $\eta$ , for glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol solution at  $T = (288.15 \text{ to } 318.15) \text{ K}$ , against mole fraction,  $x_1$ , of ethanol.

$x_1$	$u/(\text{m} \cdot \text{s}^{-1})$	$\rho \cdot 10^{-3}/(\text{kg} \cdot \text{m}^{-3})$	$\eta/(\text{mPa} \cdot \text{s})$
System III			
$T = 288.15 \text{ K}$			
0.0000	1626.24	1.0253	1.29
0.0857	1750.18	1.0237	1.44
0.1715	1756.25	1.0026	2.51
0.2572	1762.73	0.9927	3.34
0.3430	1768.17	0.9794	3.98
0.4288	1775.39	0.9618	4.26
0.5145	1783.41	0.9537	4.74
0.6003	1791.92	0.9452	5.30
$T = 298.15 \text{ K}$			
0.0000	1744.12	1.0237	1.02
0.0857	1791.33	1.0213	1.20
0.1715	1795.76	1.0008	1.65
0.2572	1800.04	0.9909	1.98
0.3430	1806.45	0.9777	2.39
0.4288	1812.27	0.9600	2.76
0.5145	1818.58	0.9518	3.02
0.6003	1825.86	0.9426	3.41
$T = 308.15 \text{ K}$			
0.0000	1848.43	1.0211	0.81
0.0857	1891.36	1.0185	0.99
0.1715	1894.72	0.9983	1.17
0.2572	1898.95	0.9880	1.36
0.3430	1902.27	0.9754	1.78
0.4288	1906.13	0.9572	2.05
0.5145	1910.44	0.9490	2.28
0.6003	1915.58	0.9396	2.64
$T = 318.15 \text{ K}$			
0.0000	1943.62	1.0187	0.68
0.0857	1995.07	1.0152	0.81
0.1715	1999.15	0.9949	0.99
0.2572	2004.84	0.9850	1.23
0.3430	2009.77	0.9733	1.47
0.4288	2015.69	0.9541	1.69
0.5145	2021.26	0.9460	1.92
0.6003	2028.53	0.9358	2.28

molecular interaction between the solute and the water thereby reducing the solubility. It is known that both aqueous and aqueous ethanol mixtures of glycylglycine and  $\text{CoCl}_2$  contains an electrically neutral molecule, *i.e.*, zwitterionic state of glycylglycine. When glycylglycine is dissolved in aqueous solutions, the cations  $\text{NH}_3^+$  and anions  $\text{COO}^-$  are formed. The water molecules are attached to the ions strongly by the electrostatic forces, which induce a greater cohesion in the solution. Thus, the cohesion increases with the increase of glycylglycine concentration in the solution. The increased association, observed in these solutions, may also be due to water structure enhancement brought about by the increase in electrostriction effect which brings about the shrinkage in the volume of solvent, caused by the zwitterionic portion of glycylglycine. This is greater in aqueous ethanol mixture as compared to that in aqueous solution. This effect is similar to the results of Dash [28] and Ragouramane [29]. From table 4, it was observed that the adiabatic compressibility values are larger in aqueous solutions compared to aqueous ethanol system which shows that molecular association/interaction is greater in aqueous solutions than that of the aqueous ethanol system. Dipeptide molecules in the neutral solution exist in the dipolar form, and thus have stronger interaction with the surrounding water molecules. The increasing electrostrictive compression of water around the molecules results in a large decrease in the compressibility of solutions. The decrease in compressibility implies that there is an enhanced molecular association in the above system upon increase in solute content, as the new entities

(formed due to molecular association) become compact and less compressible.

The interaction between the solute and the water molecules in the solvent is termed as hydration. The positive values of hydration number increases as appreciable solvation of solutes [30]. This is a supporting feature for the structure promoting nature of the solutes as well as the presence of dipolar interaction between solute and water molecules. This also suggests that compressibility of the solution will be less than that of the solvent. As a result, solutes will gain greater mobility and the probability of contact with solvent molecules will be more. This may enhance the interaction between solute and solvent molecules. From tables 4 to 6, it is observed that the values of hydration number increases with increase in concentration of the solute in aqueous solution and decreases with increase in the concentration of ethanol in aqueous ethanol system. This indicates that glycylglycine and  $\text{CoCl}_2$  together has less dehydration effect in aqueous solutions (figures 1a and 1b) and has more dehydration effect in aqueous ethanol mixture (figure 1c). Hence, the following observations have been made on  $K_{S\phi}$  and  $V_\phi$  in tables 4 to 6 for glycylglycine and  $\text{CoCl}_2$  in aqueous and aqueous ethanol mixtures.

- The values of  $K_{S\phi}$  and  $V_\phi$  are negative over the entire concentration range.
- $K_{S\phi}$  values increase with increase in concentration of solute in the systems studied.

TABLE 4

Adiabatic compressibility,  $\kappa_s$ , hydration number,  $n_H$ , apparent molar compressibility,  $K_{S\phi}$ , and apparent molar volume,  $V_\phi$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping glycylglycine constant at different temperatures.

$m/(\text{mol} \cdot \text{kg}^{-1})$	$\kappa_s \cdot 10^{-10}/(\text{m}^2 \cdot \text{N}^{-1})$	$n_H$	$-K_{S\phi} \cdot 10^{13}/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{N}^{-1})$	$-V_\phi \cdot 10^{-3}/(\text{m}^3 \cdot \text{mol}^{-1})$
System I				
T = 288.15 K				
0.000	4.4382			
0.005	4.4088	28.17	42.87	38.46
0.010	4.3447	31.10	40.10	35.09
0.030	4.2814	34.01	37.33	31.72
0.050	4.2199	36.92	34.56	28.35
0.10	4.1594	39.83	31.79	24.98
0.25	4.0918	42.74	29.02	21.61
0.50	4.0260	45.65	26.24	18.24
T = 298.15 K				
0.000	3.9130			
0.005	3.8596	26.39	40.13	40.87
0.010	3.8025	28.19	37.77	37.56
0.030	3.7465	30.38	35.41	34.20
0.050	3.6918	32.57	33.05	30.98
0.10	3.6426	34.76	30.69	27.67
0.25	3.5802	36.95	28.33	24.36
0.50	3.5267	39.14	25.92	21.05
T = 308.15 K				
0.000	3.4523			
0.005	3.4043	23.28	37.16	43.02
0.010	3.3573	25.32	34.71	39.94
0.030	3.3109	27.35	32.26	36.82
0.050	3.2657	29.38	29.82	33.70
0.10	3.2137	31.41	27.35	30.58
0.25	3.1625	33.44	24.90	27.47
0.50	3.1067	35.47	22.43	24.36
T = 318.15 K				
0.000	3.0515			
0.005	3.0020	18.76	33.75	45.98
0.010	2.9537	20.93	31.47	43.09
0.030	2.9065	23.06	29.19	40.22
0.050	2.8600	25.19	26.91	37.35
0.10	2.8146	27.32	24.63	34.48
0.25	2.7700	29.45	22.35	31.61
0.50	2.7252	31.58	20.03	28.74

- (c)  $V_\phi$  values decrease with increase in concentration for aqueous ethanol solution whereas, a reverse trend was obtained in aqueous solutions.
- (d) The maximum value of  $V_\phi$  obtained in the system studied is in the sequence system I > system II > system III.

The above observations, clearly suggest that the negative values of  $K_{S\phi}$  indicate ionic, dipolar, and hydrophobic interactions occurring in these system. The increasing values of  $K_{S\phi}$  in the system reveal that strengthening the solute–solvent interactions is very low in the mixture (figures 2a, 2b, 2c). Further, the negative values of  $V_\phi$  in the system indicate greater presence of solute–solvent interactions and electrostrictive solvation of ions (figures 3a, 3b, 3c). The decrease in  $V_\phi$  is due to strong ion–solvent interaction and vice-versa. The limiting apparent molar compressibility due to  $K_{S\phi}^0$  has been computed using the least square method. The  $K_{S\phi}^0$  and  $S_K$  provide information regarding the solute–solvent and solute–solute interactions in the mixture, respectively. Appreciable negative values of  $K_{S\phi}^0$  for the above system strongly confirms the existence of solute–solvent interactions. The positive values of  $S_K$  indicate the presence of ion–ion or solute–solute interaction in the system. Based on the behaviour of  $V_\phi^0$  in table 7, following types of interactions are possible:

- (1) Ion–solvent interactions between zwitterionic centres of glycylglycine and polar parts of aqueous ethanol.

- (2) Hydrophilic–hydrophilic interactions between polar head groups of glycylglycine and polar parts of aqueous ethanol.
- (3) Hydrophilic–polar interaction between polar parts of glycylglycine and polar part of water.

The first and the second type of interactions results in positive contribution whereas the third type results in negative contribution. Therefore, the obtained positive values for aqueous solutions show that the first and second types of interactions dominate over the third type.

It is evident from table 7 that the negative values of  $S_V$  in the aqueous solutions indicate the presence of weak solute–solute interaction whereas the positive values of  $S_V$  in aqueous ethanol solution indicate strong solute–solute interaction. In order to shed more light on this, the role of viscosity  $B$ -coefficient has also been obtained. Figure 4 shows the composition dependence of relative viscosity as a function of mole fraction of ethanol. From table 7, it is observed that the values of  $A$  are negative in all systems studied and  $B$ -coefficient are positive. Since  $A$  is a measure of ionic interaction, it is evident that there is a weak ion–ion interaction in the dipeptide studied which is indicated by the smaller magnitude of  $A$  values. The  $B$ -coefficient is also known as a measure of order or disorder introduced by the solute in to the solvent. It is also a measure of solute–solvent interaction and the relative size of the solute and solvent molecules. The behaviour of  $B$ -coefficient in the systems studied suggests the existence of strong ion–solvent interaction. The larger value of  $B$  indicates structure making capac-

**TABLE 5**

Adiabatic compressibility,  $\kappa_s$ , hydration number,  $n_H$ , apparent molar compressibility,  $K_{S\phi}$ , and apparent molar volume,  $V_\phi$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping  $\text{CoCl}_2$  constant at different temperatures.

$m/(\text{mol} \cdot \text{kg}^{-1})$	$\kappa_s \cdot 10^{-10}/(\text{m}^2 \cdot \text{N}^{-1})$	$n_H$	$-K_{S\phi} \cdot 10^{13}/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{N}^{-1})$	$-V_\phi \cdot 10^{-3}/(\text{m}^3 \cdot \text{mol}^{-1})$
System II				
$T = 288.15 \text{ K}$				
0.000	4.3994			
0.005	4.3256	26.48	40.28	35.37
0.007	4.2479	29.27	37.61	32.39
0.010	4.1675	32.06	34.94	29.41
0.020	4.0918	34.85	32.27	26.43
0.030	4.0172	37.64	29.60	23.45
0.050	3.9412	40.43	26.93	20.47
0.10	3.8620	43.24	24.22	17.45
$T = 298.15 \text{ K}$				
0.000	3.8853			
0.005	3.8058	24.02	38.37	37.64
0.007	3.7286	26.29	35.68	34.58
0.010	3.6537	28.56	32.99	31.52
0.020	3.5802	30.83	30.30	28.46
0.030	3.5103	33.10	27.59	25.40
0.050	3.4416	35.37	24.90	22.34
0.10	3.3748	37.65	22.19	19.28
$T = 308.15 \text{ K}$				
0.000	3.4110			
0.005	3.3463	21.97	35.45	39.93
0.007	3.2834	24.11	33.02	36.75
0.010	3.2222	26.25	30.59	33.87
0.020	3.1625	28.39	28.16	30.69
0.030	3.1049	30.53	25.73	28.51
0.050	3.0487	32.67	23.30	25.23
0.10	2.9936	34.86	20.86	22.32
$T = 318.15 \text{ K}$				
0.000	3.0165			
0.005	2.9520	19.27	32.18	42.39
0.007	2.8897	21.41	29.86	39.43
0.010	2.8292	23.55	27.54	36.77
0.020	2.7700	25.69	25.22	33.81
0.030	2.7135	27.83	22.90	30.65
0.050	2.6583	29.97	20.58	27.49
0.10	2.6050	32.15	18.26	24.63

**TABLE 6**  
Adiabatic compressibility,  $\kappa_s$ , hydration number,  $n_H$ , apparent molar compressibility,  $K_{S\phi}$ , and apparent molar volume,  $V_\phi$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol solution keeping glycylglycine and  $\text{CoCl}_2$  constant at different temperatures.

$x_1$	$\kappa_s \cdot 10^{-10}/(\text{m}^2 \cdot \text{N}^{-1})$	$n_H$	$-K_{S\phi} \cdot 10^{13}/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{N}^{-1})$	$-V_\phi \cdot 10^{-3}/(\text{m}^3 \cdot \text{mol}^{-1})$
System III				
T = 288.15 K				
0.0000	3.6879			
0.0857	3.1890	40.27	43.54	20.21
0.1715	3.2336	37.62	40.47	24.58
0.2572	3.2419	34.98	37.40	28.95
0.3430	3.2658	32.31	34.33	33.32
0.4288	3.2985	29.65	31.26	37.69
0.5145	3.2967	26.99	28.19	42.06
0.6003	3.2948	24.36	25.12	46.44
T = 298.15 K				
0.0000	3.2112			
0.0857	3.0513	39.65	41.78	21.75
0.1715	3.0985	37.04	38.72	26.09
0.2572	3.1146	34.43	35.66	30.43
0.3430	3.1343	31.82	32.60	34.77
0.4288	3.1716	29.21	29.55	39.11
0.5145	3.1767	26.60	26.51	43.45
0.6003	3.1822	23.94	23.43	47.83
T = 308.15 K				
0.0000	2.8663			
0.0857	2.7446	38.76	39.63	23.02
0.1715	2.7902	36.12	36.54	27.26
0.2572	2.8068	33.48	33.45	31.50
0.3430	2.8331	30.84	30.36	35.76
0.4288	2.8753	28.20	27.27	40.02
0.5145	2.8871	25.56	24.19	44.28
0.6003	2.9003	22.88	21.07	48.54
T = 318.15 K				
0.0000	2.5985			
0.0857	2.4745	37.59	36.96	24.72
0.1715	2.5149	34.83	33.78	28.93
0.2572	2.5258	32.07	30.60	33.14
0.3430	2.5436	29.31	27.42	37.36
0.4288	2.5796	26.55	24.24	41.57
0.5145	2.5874	23.79	21.06	45.79
0.6003	2.5968	20.98	17.84	50.03

ities of the solute. The magnitude of  $B$ -coefficient is of the order system III > system II > system I.

The values of Redlich–Kister polynomial coefficient  $a_i$  evaluated by the method of least squares along with standard deviation are given in table 8. The plot of excess Gibbs free energy of activation against mole fraction of ethanol is given in figure 5. The excess values reflect the interactions between the mixing species and mainly depend upon the composition, their different molecular size and shapes, and temperatures. The important effects, which influence the values of excess thermodynamic function, are divided into physical, chemical, and structural contributions:

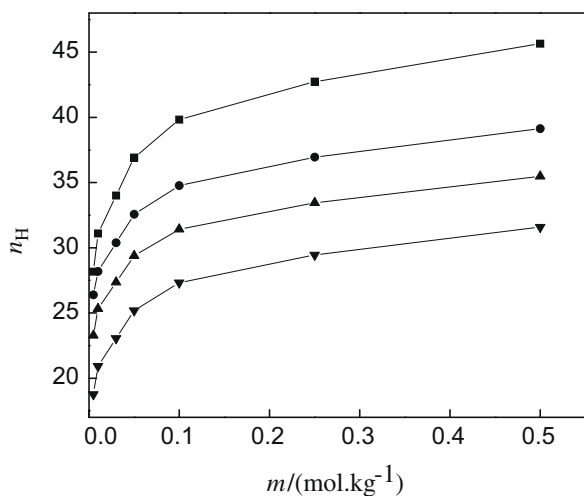
- (1) Physical contributions comprise non-specific physical interactions, e.g. dispersion forces or weak dipole–dipole interaction leading to negative contribution towards  $\Delta G^{\text{E}}$ .
- (2) Chemical effect includes charge transfer forces, formation of H-bonds and other complex forming interactions making positive contribution towards  $\Delta G^{\text{E}}$ .

- (3) Geometrical fitting of the component molecules into each other's structure and also due to difference in molar and free volumes.

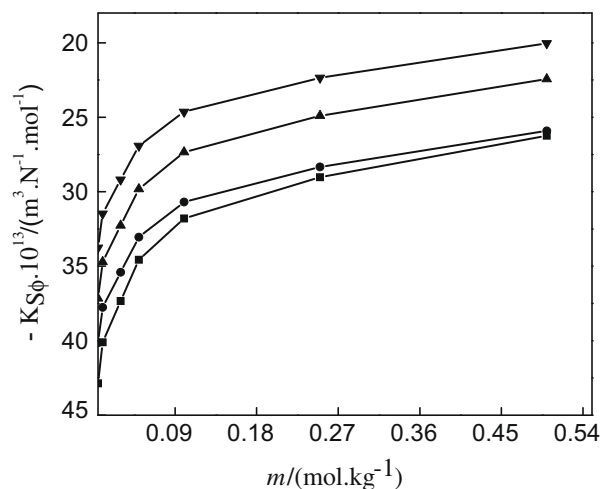
The observed positive values of  $\Delta G^{\text{E}}$  in the case of aqueous ethanol mixture containing glycylglycine and  $\text{CoCl}_2$  (figure 5) indicate that there are no strong specific interactions present between the components of this mixture. Thus, the breaking of self-association of ethanol has influences in the excess values of Gibbs free energy of activation of viscous flow, thereby suggesting that dispersive forces are operative on aqueous ethanol system exhibiting positive values of  $\Delta G^{\text{E}}$  [31]. Increase in temperature will cause rupture of more and more H-bonded self-association in ethanol molecules and also hetero association between unlike molecules which causes more deviation as temperature increases for aqueous ethanol mixture. Finally, the above studies fall in line with our previous report [18] which supports the discussion on solute-solvent interactions.

**TABLE 7**  
The values of limiting apparent molar compressibility,  $K_{S\phi}^0$ , limiting apparent molar volume,  $V_\phi^0$ , constants  $S_K$ ,  $S_V$ , and viscosity  $A$  and  $B$  coefficients of Jones–Dole equation for aqueous and aqueous ethanol systems containing glycylglycine and  $\text{CoCl}_2$  at  $T = 318.15$  K.

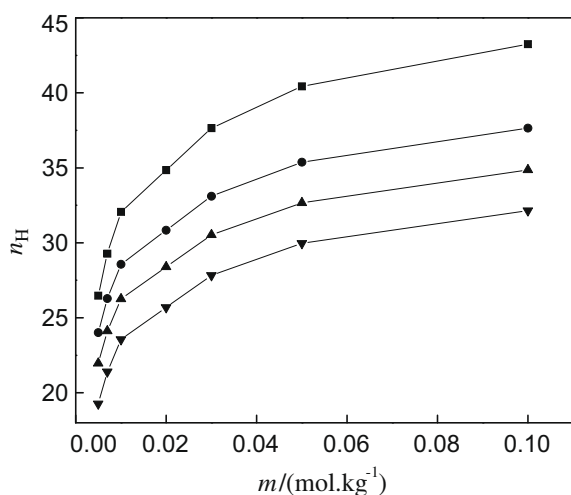
System	$-K_{S\phi}^0 \cdot 10^{13}/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{N}^{-1})$	$S_K \cdot 10^{-8}/(\text{N}^{-1} \cdot \text{m}^{-1} \cdot \text{mol}^{-1})$	$V_\phi^0/(\text{m}^3 \cdot \text{mol}^{-1})$	$S_V/(\text{m}^3 \cdot \text{lt}^{1/2} \cdot \text{mol}^{-3/2})$	$A/(\text{dm}^{3/2} \cdot \text{mol}^{-1/2})$	$B/(\text{dm}^3 \cdot \text{mol}^{-1})$
System I	62.27	78.21	22.64	−178.40	−0.6234	1.8534
System II	58.48	86.92	26.93	−195.87	−0.1456	2.9237
System III	61.76	77.48	−154.36	398.49	−0.4598	3.9562



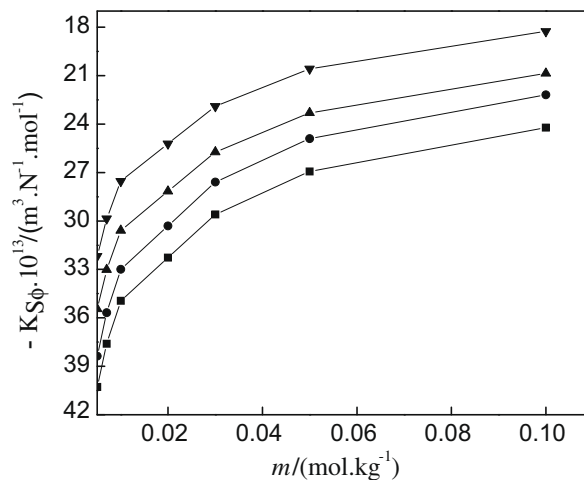
**FIGURE 1a.** Plot of hydration number,  $n_H$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping glycylglycine constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.



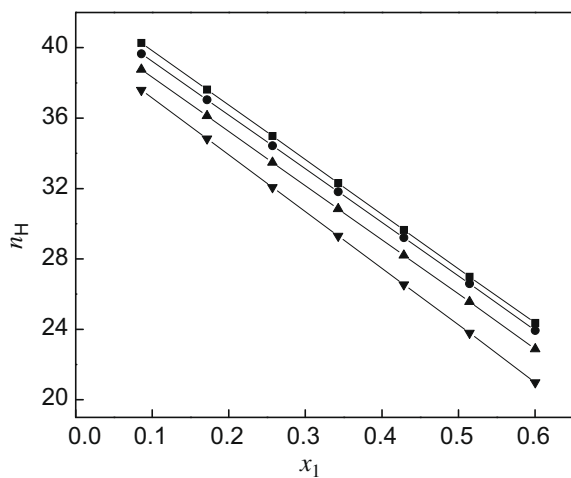
**FIGURE 2a.** Plot of apparent molar compressibility,  $K_{S\phi}$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping glycylglycine constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.



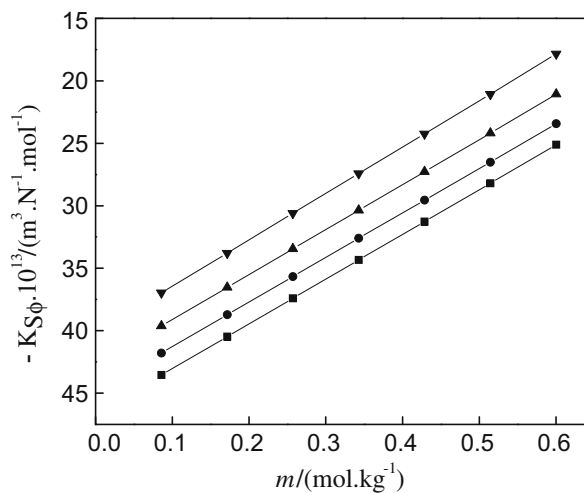
**FIGURE 1b.** Plot of hydration number,  $n_H$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping  $\text{CoCl}_2$  constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.



**FIGURE 2b.** Plot of apparent molar compressibility,  $K_{S\phi}$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping  $\text{CoCl}_2$  constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.

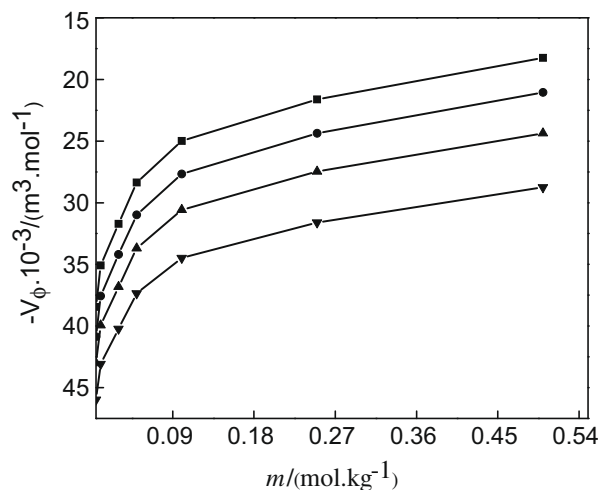


**FIGURE 1c.** Plot of hydration number,  $n_H$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol solution keeping glycylglycine and  $\text{CoCl}_2$  constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.

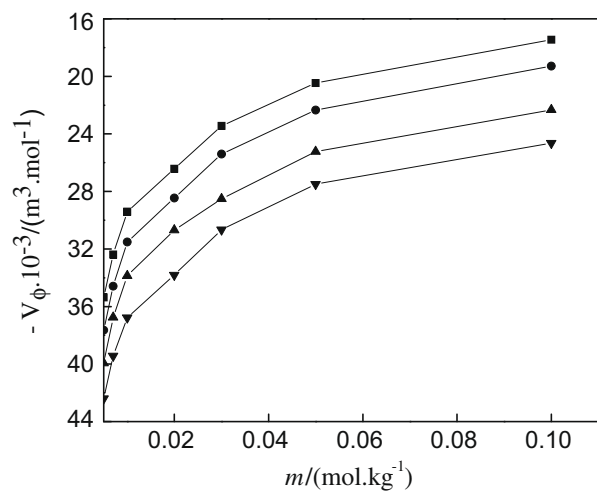


**FIGURE 2c.** Plot of apparent molar compressibility,  $K_{S\phi}$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol solution keeping glycylglycine and  $\text{CoCl}_2$  constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.

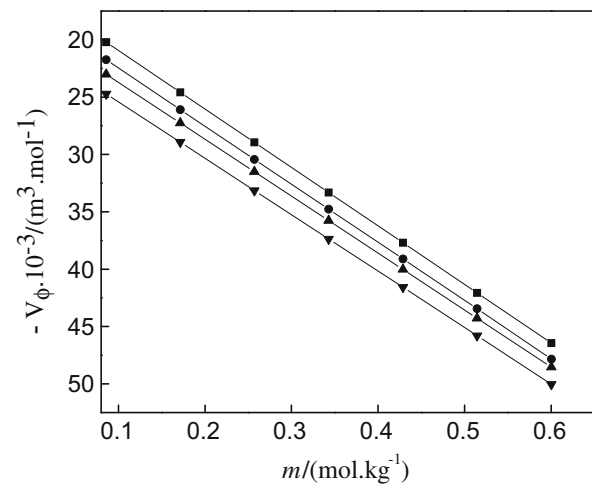




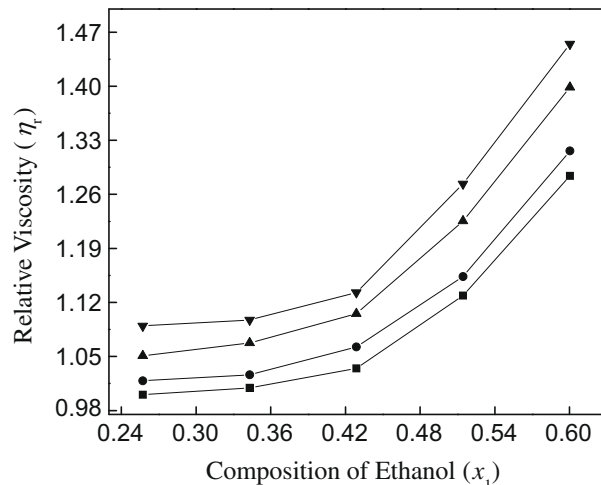
**FIGURE 3a.** Plot of apparent molar volume,  $V_\phi$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping glycylglycine constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.



**FIGURE 3b.** Plot of apparent molar volume,  $V_\phi$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous solution keeping  $\text{CoCl}_2$  constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.



**FIGURE 3c.** Plot of apparent molar volume,  $V_\phi$ , of glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol solution keeping glycylglycine and  $\text{CoCl}_2$  constant at different temperatures. (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.

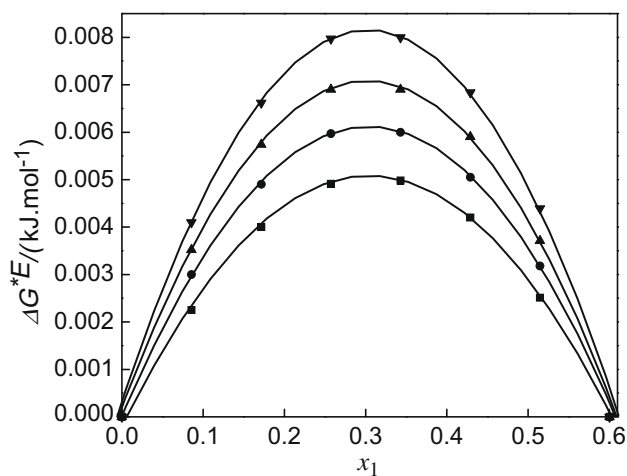


**FIGURE 4.** Composition dependence of relative viscosity,  $\eta_r$ , as a function of mole fraction,  $x_1$ , of ethanol for glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol mixture at different temperatures: (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.

**TABLE 8**

The values of coefficient  $a_i$  from equation (10) for  $\Delta G^E$  and standard deviation  $\sigma(Y^E)$  for glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol mixture at different temperatures.

Functions	$T = 288.15$ K	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
	$\Delta G^E / (\text{kJ} \cdot \text{mol}^{-1})$			
$a_1$	-1.1098	-1.9347	-2.8776	-3.2497
$a_2$	-0.1532	0.4886	0.4959	0.5432
$a_3$	2.4015	0.4002	-4.5263	-8.9760
$a_4$	2.3296	-1.9989	-3.6676	-5.4386
$a_5$	-6.1247	0.4775	9.4987	11.2384
$\sigma(Y^E)$	0.0078	0.0123	0.0058	0.0079



**FIGURE 5.** Excess Gibbs free energy of activation,  $\Delta G^*E$ , as a function of mole fraction,  $x_1$ , of ethanol for glycylglycine and  $\text{CoCl}_2$  in aqueous ethanol mixture at different temperatures: (■),  $T = 288.15$  K; (●),  $298.15$  K; (▲),  $308.15$  K; (▼),  $318.15$  K.

## 5. Conclusions

In our present study, experimental results for ultrasonic velocity, density, and viscosity are reported for glycylglycine and  $\text{CoCl}_2$  in aqueous and aqueous ethanol systems. Also, from the above val-

ues, acoustical, and excess Gibbs free energy of activation parameters have been calculated to explain the intermolecular interactions in terms of ionic, polar, and hydrophilic types. Also, the values of  $\Delta G^{\ddagger E}$  suggest that dispersive forces are highly operative in aqueous ethanol system. From the magnitude and  $B$ -coefficient, it can be concluded that the existence of strong ion–solvent interaction leads to structure making capacities of the solute.

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