



## Excess and deviation properties of {(glycylglycine + ZnCl<sub>2</sub>) in aqueous methanol} mixtures

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### ABSTRACT

The excess molar volumes ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ), deviations in isentropic compressibility ( $\Delta\kappa_S$ ) and excess molar refractivity ( $\Delta R_m^E$ ) for {(glycylglycine + ZnCl<sub>2</sub>) in aqueous methanol} mixture have been calculated from the experimental values. The bridging water molecules bend the chains into stable open ring structures together with intermolecular hydrogen bonding and interstitial accommodation leading to negative  $V^E$  values. The positive  $\Delta\eta$  values indicate a structure breaking effect of aqueous glycylglycine–ZnCl<sub>2</sub> upon contact with methanol molecules. It is also noted that chelation of zinc to glycylglycinate is through carboxylic group and not the amino group. The negative  $\Delta\kappa_S$  values suggest the formation of an open ring structure lowering the entropy of the solution. Due to weak interaction between solute and solvent, the molecular structure of individual molecule does not change significantly and leads to negative  $\Delta R_m^E$  values. Finally, the results have led to a good understanding of the thermodynamics properties of the studied liquid mixture.

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### 1. Introduction

Experimental and theoretical studies on the stability and solubility of biological molecules have been a subject of intense interest for some time [1–5]. In solvent mixtures, enough experimental work has been done, particularly on proteins and peptides. The overall trends in the results have given rise to several general principles by clarifying the thermodynamic quantities that exhibit them. Since Hofmeister's pioneering study of the hen lysozyme using different salts, the interaction of peptides and proteins has attracted many researchers [6]. Electrolyte solutions are of fundamental importance to chemistry and biology as they form a basic matrix for technological fluids and in the functioning of life. Zinc is a micro mineral in the human body which is essential for growth and development, and it acts as a cofactor for about 300 enzymes from all six enzyme classes [7,8]. It also behaves uniquely as a Lewis acid catalyst in all life processes [9]. Further, in various industrial processes, zinc is one of the most important basic materials. It offers one to seven coordination sites; in most complexes, the coordination number is four or six, in tetrahedral or octahedral arrangements [10,11]. Compared to other metal ions of biological importance like Ca<sup>2+</sup>, Mg<sup>2+</sup>, or Fe<sup>3+</sup>, which are hard cations, Zn<sup>2+</sup> is a borderline cation whereas Cu<sup>2+</sup> and Cd<sup>2+</sup> are soft cations. This has implications for the choice of ligands and for the preferred

architecture of the coordination sphere. To control factors such as reactivity and stability of the system, mixed aqueous solvents are used extensively in chemistry and other fields. In order to understand the molecular interactions between unlike molecules, knowledge of densities, excess volumes and viscosities of fluids and fluid mixtures are essential. Due to the extensive application of ultrasonic methods and their ability to characterize the physico-chemical behavior of liquid systems from absorption and velocity data, they have been used by many researchers in recent years [12–14]. It is also possible to investigate molecular packing, molecular motion and various types and extents of intermolecular interactions influenced by the size, shape, and chemical nature of the component molecules and the microscopic structures of the liquids. Earlier, the excess enthalpies of ethanol + water + ZnCl<sub>2</sub> have been reported by Zhao et al. [15]. The transport coefficients in aqueous zinc chloride solution at 25 °C have been studied by Weingartner et al. [16]. Similarly, Banipal et al. [17] have reported the volumetric studies of amino acids and zinc chloride in aqueous solutions. From the above studies, it is clear that no earlier reports on {(glycylglycine + ZnCl<sub>2</sub>) aqueous methanol} mixtures are available which can give valuable information on solute–solvent interactions and hydrogen bonding within the studied system. Hence, in continuation of our earlier works [18–24], we report in this paper the excess molar volumes ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ), deviations in isentropic compressibility ( $\Delta\kappa_S$ ) and excess molar refractive indices ( $\Delta R_m^E$ ) for {(glycylglycine + ZnCl<sub>2</sub>) in aqueous methanol} mixtures under diverse conditions.

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## 2. Experimental

### 2.1. Materials

Glycylglycine and zinc chloride anhydrous of mass fraction purity 0.99 were purchased from Sigma–Aldrich Germany. Commercially available glycylglycine of the highest purity was used without further purification. Zinc chloride was used after drying for 72 h in a vacuum desiccator at room temperature. Deionized, double distilled degassed water with a specific conductance of less than  $1.29 \cdot 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$  was used for the preparation of solutions. Methanol of mass fraction purity 0.998 used after distillation was also purchased from Sigma–Aldrich Germany. 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. In our studies, glycylglycine and  $\text{ZnCl}_2$  were kept constant at  $0.020 \text{ mol} \cdot \text{kg}^{-1}$  and  $0.25 \text{ mol} \cdot \text{kg}^{-1}$ , respectively, and the composition of methanol was varied in terms of mole fraction ( $x_1$ ). The estimated uncertainty for the mole fraction of methanol was found to be  $< 1 \cdot 10^{-4}$ . To prevent formation of air bubbles, all solutions were preheated in sealed Eppendorf tubes to  $5^\circ\text{C}$  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 methanol and their uncertainty was found to be  $\pm 0.5\%$  for both solutions. Ultrasonic velocities of pure components and their mixtures were measured by variable path fixed frequency interferometer supplied by Mittal Enterprises, New Delhi (Model-83). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 2 MHz. The volume of the measuring cell was 7 ml. The calibration of ultrasonic interferometer was made by measuring the velocity in AR grade benzene and methanol at 298.15 K. The maximum estimated uncertainty in ultrasonic velocity measurements was  $\pm 0.08 \text{ m} \cdot \text{s}^{-1}$ . The temperature was controlled by circulating water around the liquid cell from a thermostatically controlled adequately stirred water bath with an uncertainty of  $\pm 0.01$  K. Densities were measured using the (Mettler Toledo) Density 30PX digital densitometer having a precision of  $\pm 1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ . Refractive indices were measured using automatic digital refractometer RX-7000R, Atago Co. Ltd., Japan, having an accuracy of  $\pm 0.0001\%$ . The densitometer and refractometer were calibrated using double-distilled water. The sample and reference resonator cells with minimum volumes of  $0.5 \text{ cm}^3$  were thermostated to an accuracy of  $\pm 0.01$  K, and a previously described differential technique was employed for all measurements [25]. The physical parameters for aqueous methanol solutions of glycylglycine– $\text{ZnCl}_2$  were measured at four temperatures: (288.15, 298.15, 308.15, and 318.15) K. The measured values of viscosity and density and their uncertainties agreed well with the literature values [26]. Each measurement was repeated thrice and the reported values are an average of all three measurements.

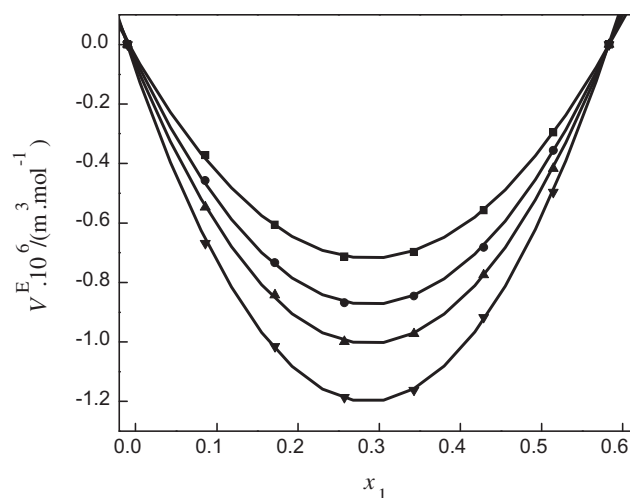
## 3. Results and discussion

The experimental viscosities ( $\eta$ ), ultrasonic velocities ( $u$ ), densities ( $\rho$ ), refractive indices ( $n_D$ ) and calculated values of isentropic compressibilities ( $\kappa_S$ ) for {(glycylglycine +  $\text{ZnCl}_2$ ) in aqueous methanol} mixtures at temperatures  $T = (288.15$  to  $318.15)$  K have been reported in table 1. From the above experimental parameters, we have calculated the excess molar volumes ( $V^E$ ), viscosity deviations ( $\Delta\eta$ ), devi-

**TABLE 1**

Viscosity ( $\eta$ ), ultrasonic velocity ( $u$ ), density ( $\rho$ ), refractive index ( $n_D$ ) and isentropic compressibility ( $\kappa_S$ ) for {(glycylglycine +  $\text{ZnCl}_2$ ) in aqueous methanol} mixture at  $T/\text{K} = (288.15$  to  $318.15)$ , for different mole fractions,  $x_1$ , of methanol.

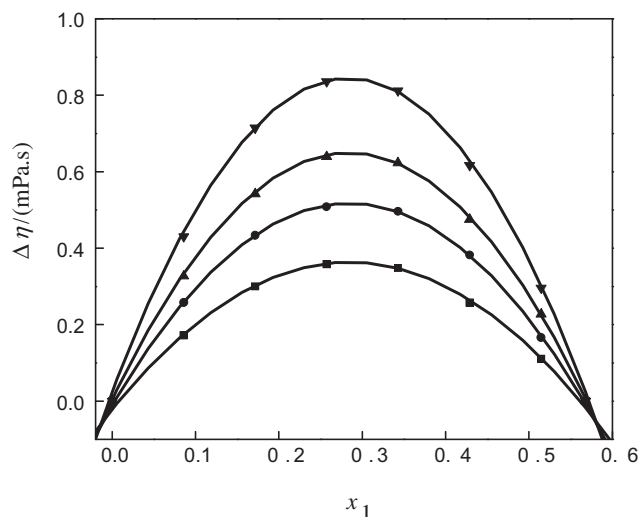
$x_1$	$\eta/(\text{mPa} \cdot \text{s})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\rho \cdot 10^{-3}/(\text{kg} \cdot \text{m}^{-3})$	$n_D$	$\kappa_S \cdot 10^{12}/(\text{Pa}^{-1})$
$T/\text{K} = 288.15$					
0.00000	1.26	1628.37	1.0232	1.3409	3.68581
0.08572	1.42	1635.01	1.0115	1.3426	3.69822
0.17156	1.48	1641.65	0.9998	1.3441	3.71130
0.25724	1.54	1648.29	0.9874	1.3473	3.72769
0.34301	1.61	1654.93	0.9711	1.3485	3.75990
0.42887	1.67	1661.57	0.9562	1.3499	3.78803
0.51459	1.73	1668.21	0.9353	1.3510	3.84191
0.60033	1.79	1674.85	0.9124	1.3527	3.90718
$T/\text{K} = 298.15$					
0.00000	1.12	1657.28	1.0350	1.3404	3.51777
0.08572	1.26	1663.75	1.0230	1.342	3.53141
0.17156	1.32	1670.23	1.0104	1.3435	3.54776
0.25724	1.38	1676.71	0.9977	1.3463	3.56520
0.34301	1.44	1683.19	0.9829	1.3474	3.59107
0.42887	1.50	1689.67	0.9681	1.3485	3.61806
0.51459	1.57	1696.15	0.9465	1.3496	3.67241
0.60033	1.64	1702.63	0.9229	1.3513	3.73770
$T/\text{K} = 308.15$					
0.00000	0.98	1685.14	1.0451	1.3398	3.36954
0.08572	1.10	1691.66	1.0339	1.3413	3.37983
0.17156	1.16	1698.18	1.0206	1.3427	3.39764
0.25724	1.22	1704.70	1.0073	1.3452	3.41622
0.34301	1.28	1711.22	0.9928	1.3462	3.43975
0.42887	1.34	1717.74	0.9765	1.3473	3.47067
0.51459	1.41	1724.26	0.9541	1.3483	3.52534
0.60033	1.47	1730.78	0.9327	1.3500	3.57910
$T/\text{K} = 318.15$					
0.00000	0.84	1714.46	1.0527	1.3393	3.23177
0.08572	0.94	1721.10	1.0423	1.3405	3.23888
0.17156	1.00	1727.74	1.0284	1.3419	3.25748
0.25724	1.07	1734.38	1.0145	1.3440	3.27687
0.34301	1.14	1741.02	0.9999	1.3449	3.29941
0.42887	1.21	1747.66	0.9841	1.3461	3.32695
0.51459	1.28	1754.30	0.9631	1.3471	3.37381
0.60033	1.34	1760.90	0.9409	1.3488	3.42758



**FIGURE 1.** Variation of excess molar volumes ( $V^E$ ) as a function of mole fraction ( $x_1$ ) for {(glycylglycine +  $\text{ZnCl}_2$ ) in aqueous methanol} mixture at different temperatures: (■), 288.15 K; (●), 298.15 K; (▲), 308.15 K; (▼), 318.15 K.

ations in isentropic compressibility ( $\Delta\kappa_S$ ) and excess molar refractive indices ( $\Delta n_m^E$ ). The variations of these excess and deviation properties over the entire composition range are depicted in figures 1 to 4, respectively.

The excess and deviation properties for {(glycylglycine +  $\text{ZnCl}_2$ ) in aqueous methanol} mixtures were fitted into Redlich–Kister polynomial equation [27] of the type:



**FIGURE 2.** Variation of viscosity deviation ( $\Delta\eta$ ) as a function of mole fraction ( $x_1$ ) for ((glycylglycine +  $\text{ZnCl}_2$ ) in aqueous methanol) mixture at different temperatures: (■), 288.15 K; (●), 298.15 K; (▲), 308.15 K; (▼), 318.15 K.

$$Y = x_1 x_2 \sum_{n=0}^K a_n (x_1 - x_2)^n, \quad (1)$$

where  $Y$  denotes the excess or deviation property. The coefficients  $a_n$  were obtained by fitting equation (7) to the experimental results using the least squares regression method as shown in table 2. In each case, the optimal number of coefficients,  $K$  was ascertained from an approximation of variation in the standard deviation. The fitted values of the coefficients along with the standard deviations are summarized in table 2. The standard deviation was calculated using the equation:

$$\sigma(Y) = \left[ \sum \frac{(Y_{\text{exp}} - Y_{\text{calc}})^2}{(N - M)} \right]^{0.5}, \quad (2)$$

where  $N$  is the number of data points and  $M$  is the number of coefficients.

### 3.1. Excess molar volume

The density values were used to calculate the excess molar volumes for the studied mixture using the following equation [28]:

$$V^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1}) = \sum_{i=1}^n x_i M_i \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right), \quad (3)$$

where  $\rho$  is the density of the mixture and  $M_i$ ,  $x_i$  and  $\rho_i$  are the molar mass, mole fraction, and density, respectively of the  $i$ th component in the mixture.

Several opposing effects contribute to the result of  $V^E$ . These may be arbitrarily divided into three types namely, physical, chemical and structural contributions. A positive contribution to  $V^E$  is made by the physical contributions which are non-specific in nature between the real species present in the mixture. In contrast, negative contributions to  $V^E$  are a result of chemical and specific intermolecular interactions leading to a decrease in volume. When methanol is added to aqueous solution, the disorder or entropy in the resulting system does not increase as expected for ideal solutions. This anomaly has traditionally been explained in terms of hydrophobic interactions involving methanol molecules that induce a static, ice-like structure in the surrounding water. The structure of liquid methanol at the studied temperatures is a combination of rings and chains, each made up of either 6 or 8 methanol molecules. When water comes in contact with methanol, the methanol chains interact with varying numbers of water molecules. These "bridging" water molecules bend the chains into open-ring structures that are stable because their glue-like hydrogen bonds are saturated. At this hydrogen bond saturation point, the methanol molecules tend to form hydrogen bonds with the already present glycylglycine molecules either partially with the C=O (carbonyl group of peptide bond) or with COOH (hydroxyl oxygen of carboxylic group) in a regular manner. Due to this interstitial accommodation and changes in free volume, structural contributions mostly lead to negative  $V^E$  values [29]. In addition, the electrostatic interaction brings about a change in the hydrogen bonding upon mixing of methanol to aqueous glycylglycine- $\text{ZnCl}_2$  solution. The values of  $V^E$  are found to be negative over the whole composition range and at all four temperatures as shown in figure 1. Packing effects and differences in the energies of interaction between molecules also contribute to negative  $V^E$  values. The disruption of ordered structure of pure component during formation of mixture leads to positive effect on excess volume, while formation of order in the mixture leads to a negative contribution. The specific interactions such as intermolecular hydrogen bonding, interstitial accommodations of mixing components because of the difference in molar volume are indicated by negative  $V^E$  values.

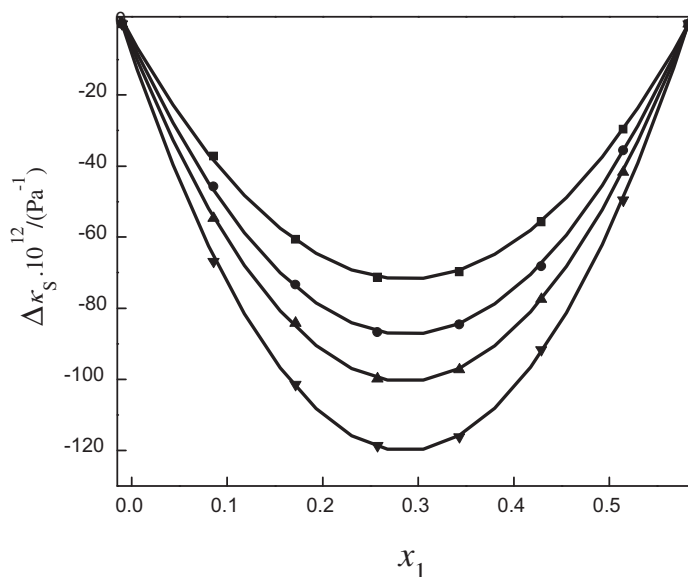
### 3.2. Viscosity deviations

The viscosity deviations ( $\Delta\eta$ ) for the studied system are depicted in figure 2. The  $\Delta\eta$  values from a linear dependence for ((glycylglycine +  $\text{ZnCl}_2$ ) aqueous methanol) mixture were calculated from the following equation:

$$\Delta\eta / (\text{m} \cdot \text{Pas}) = \eta - \sum_{i=1}^n x_i \eta_i, \quad (4)$$

where  $\eta$  is the viscosity of the mixture and  $x_i$  and  $\eta_i$  are the mole fraction and viscosity, respectively, of pure components  $i$ .

The  $\Delta\eta$  values were found to be positive over the entire composition range and at all four temperatures. The addition of  $\text{ZnCl}_2$  to aqueous solution containing glycylglycine in the dipolar form causes the reaction ( $G^\pm + \text{Zn}^{2+} = G\text{Zn}^{2+} + \text{H}^+$ ) (where  $G$  = Glycylglycine) to take place, with the release of the hydrogen ion. If the  $\text{NH}_2$  (amino) group of glycylglycine would have been the site for  $\text{Zn}^{2+}$  (metal ion) binding, then the viscosity values would have shifted to the negative region upon



**FIGURE 3.** Plot of deviation in isentropic compressibility ( $\Delta\kappa_s$ ) as a function of mole fraction ( $x_1$ ) for ((glycylglycine +  $\text{ZnCl}_2$ ) in aqueous methanol) mixture at different temperatures: (■), 288.15 K; (●), 298.15 K; (▲), 308.15 K; (▼), 318.15 K.

addition of the metal salt. On the other hand, as the carboxylate anion of glycylglycine is the binding site for  $Zn^{2+}$  in the studied system, the viscosity deviations showed a positive trend. The  $GZn^{2+}$  complex formation may take place due to high stability and weak solute–solvent interactions. When  $GZn^{2+}$  complex comes in contact with methanol molecules, the highly associated aqueous  $GZn^{2+}$  undergoes a structure breaking effect due to intermolecular hydrogen bonding between glycylglycine and methanol molecules. However, making and breaking of hydrogen bonds between water and methanol [26,30,31] is quite significant reflecting solvent–solvent interactions. Concluding from the above discussion, it is clear that amino group is not involved in metal–ligand complex formation and hence, it may be postulated as a binary  $ZnG^+$  complex in which zinc is chelated to glycylglycinate through the carboxylate group.

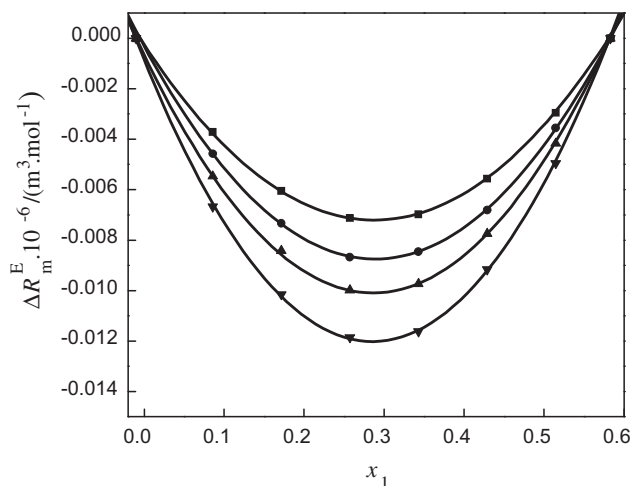
### 3.3. Deviation in isentropic compressibility

Isentropic compressibility ( $\kappa_S$ ) and deviations in isentropic compressibility ( $\Delta\kappa_S$ ) for {(glycylglycine +  $ZnCl_2$ ) in aqueous methanol} mixtures were calculated using the following relations:

$$\kappa_S = 1/u^2 \rho, \quad (5)$$

$$\Delta\kappa_S \cdot 10^{12}/(\text{Pa}^{-1}) = \kappa_S - \sum_{i=1}^n x_i \kappa_{S,i}, \quad (6)$$

where  $u$  and  $\kappa_S$  are the ultrasonic velocity and isentropic compressibility, respectively, for the mixture and  $x_i$  and  $\kappa_{S,i}$  are the mole fraction and isentropic compressibility, respectively, for the  $i$ th component in the mixture.



**FIGURE 4.** Plot of excess molar refractivity ( $\Delta R_m^E$ ) as a function of mole fraction ( $x_1$ ) for {(glycylglycine +  $ZnCl_2$ ) in aqueous methanol} mixture at different temperatures: (■), 288.15 K; (●), 298.15 K; (▲), 308.15 K; (▼), 318.15 K.

**TABLE 2**

Redlich–Kister coefficients ( $a_n$ ) and standard deviations ( $\sigma$ ) for {(glycylglycine +  $ZnCl_2$ ) in aqueous methanol} mixture at  $T = (288.15 \text{ to } 318.15) \text{ K}$ .

Property	$T/\text{K}$	$a_0$	$a_1$	$a_2$	$\sigma$
$V^E \cdot 10^6/(\text{m}^3 \cdot \text{mol}^{-1})$	288.15	-2.2342	1.5223	-1.1117	0.001
	298.15	-2.3105	1.5842	-1.1631	0.001
	308.15	-2.3350	1.6785	-1.2236	0.0012
	318.15	-2.3499	1.7338	-1.2842	0.001
	$\Delta\eta/(\text{mPa} \cdot \text{s})$	288.15	-1.4406	-1.3428	-0.248
	298.15	-1.3603	-1.3408	-0.534	0.002
	308.15	-1.2847	-1.3012	-0.892	0.0018
	318.15	-1.2098	-1.2829	0.1084	0.002
$\Delta\kappa_S \cdot 10^{12}/(\text{Pa}^{-1})$	288.15	-1.3716	1.1123	347.78	0.002
	298.15	-1.3987	1.1232	7.34	0.0022
	308.15	-1.4122	1.1406	56.38	0.003
	318.15	-1.4398	1.1539	14.82	0.0031
	$\delta R_m^E \cdot 10^{-6}/(\text{m}^3 \cdot \text{mol}^{-1})$	288.15	-0.4857	1.0432	0.0879
298.15		-0.4428	1.4418	-0.0745	0.004
308.15		-0.3982	1.4507	-0.0626	0.0012
318.15		-0.3473	1.4598	0.0519	0.0021

The isentropic compressibility values are given in table 1 and the deviations in isentropic compressibility are graphically depicted in figure 3. The  $\Delta\kappa_S$  values for the studied mixture are negative over the entire composition range and at all temperatures. These trends can be explained in terms of molecular interactions [32,33] between unlike molecules. It appears from the sign and magnitude of  $\Delta\kappa_S$  that specific interactions between the mixture components exist. These results are in excellent agreement with those for  $V^E$  discussed earlier. At the molecular level, very little mixing of methanol and water occurs in solution. Instead, chains of methanol molecules react with clusters of water molecules to form stable open-ring structures, which lower the solution's entropy. The high degree of order in these clusters reduces the overall entropy of the solution mixture. Yet entropy must either stay the same or increase in the mixture. Consequently, the presence of  $ZnCl_2$  and glycylglycine discourages the formation of too many such clusters in the liquid. Indeed, the measurements indicate that only a portion of the chains are being bridged. While the formation of clusters prevents full mixing, the existence of glycylglycine limits the degree of order in the system, suggesting a competition between increasing entropy and hydrogen bonding of clusters. The results have substantially refined both our knowledge of structure and order in aqueous methanol solutions and our understanding of the unusual thermodynamic properties of this liquid mixture.

### 3.4. Excess molar refractivity

The excess molar refractivity ( $R_m^E$ ) gives more information about the mixture phenomenon than refractive index ( $n_D$ ) because it takes into account the electronic perturbations of the molecular orbitals during the liquid mixture process. In addition,  $R_m^E$  is directly related to the dispersion forces. Due to weak interactions between solute and solvent molecules, there is no significant change in the molecular structure of the individual molecule. It can be evaluated from the Lorentz–Lorenz equation [34]:

$$R_m^E \cdot 10^{-6}/(\text{m}^3 \cdot \text{mol}^{-1}) = \left( \frac{n_D^2 - 1}{n_D^2 - 2} \right) \left( \frac{M}{\rho} \right), \quad (7)$$

where  $R_m^E$ ,  $n_D$  and  $M$  are the excess molar refractivity, refractive index and molar mass of the mixture, respectively. The deviation in excess molar refractivity was calculated using the equation:

$$\Delta R_m^E \cdot 10^{-6}/(\text{m}^3 \cdot \text{mol}^{-1}) = R_m^E - (x_1 R_{m,1}^E + x_2 R_{m,2}^E). \quad (8)$$

The values of  $n_D$  are listed in table 1 and that of ( $\Delta R_m^E$ ) for the studied mixture are shown in figure 4.

## 4. Conclusions

The experimental values of viscosity, ultrasonic velocity, density and refractive index have been used to calculate the excess and deviation properties. The negative values of  $V^E$  have been accounted for chemical and structural contributions leading to a decrease in the volume due to intermolecular interactions. The positive  $\Delta\eta$  values were due to the  $GZn^{2+}$  complex formation indicating a weak solute–solvent interaction. The negative  $\Delta\kappa_S$  values indicate molecular interactions between unlike molecules and the trends in  $\Delta\kappa_S$  are also in agreement with those of  $V^E$ . The electronic perturbations of molecular orbitals lead to negative  $R_m^E$  values. The results give a clear idea on the type of molecular interactions occurring in the studied solution mixture.

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JCT 10-319