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Physico-chemical, acoustic and excess properties of glycylglycine–$MnCl_2$ in aqueous ethanol mixtures at different temperatures

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ABSTRACT

Volumetric, acoustic, refractometric, excess and deviation properties of glycylglycine–$MnCl_2$ in aqueous ethanol mixtures have been reported at T = (288.15 to 318.15) K. Redlich–Kister equation was used to fit the derivate properties. The experimental data of the constituent binaries were analyzed to discuss the nature and strengths of intermolecular interactions. The interdependence of L_f and u has been evolved from Eyring and Kincaid model. The variations in specific acoustic impedance revealed that hydrogen bonding was predominant in the studied binary mixtures. Solvation number indicated structure-breaking tendency of the solute and weakening of local solvent structure.

1. Introduction

The stability and solubility of biological molecules has been the subject of intense interest in both experimental and theoretical science for some time [1–5]. Enough experimental work has now been done, particularly on proteins and peptides in solvent mixtures, that the overall trends in the results have given rise to several general principles, as well as clarifying the thermodynamic quantities that exhibit them. Most stability and solubility phenomena have been codified by Timasheff and collaborators [4–6] in terms of the complex balance between cosolvent exclusion from a region around a protein and specific interactions between the cosolvent and specific sites on the surface of the protein.

Since salt solutions form the natural environments for biological macromolecules, it is perhaps not surprising that many important biological processes are sensitive to changes in the concentration and nature of dissolved ions [7–9]. It is reasonably well understood that salts can affect electrostatic interactions either through indirect screening of charge–charge interactions [10] or by direct binding and neutralization of charged groups [11]. Viscosity, an important property of liquid mixtures required for the design of flow systems is widely used in engineering applications, especially in heat exchangers as well as in mass transfer equipment. In addition, it is believed that the knowledge of the dependence of viscosity on temperature and composition may provide better insight into the structure of liquids. This has motivated many researchers to investigate the dependence of viscosity of binary mixtures on composition. In addition to this, measurements of ultrasonic velocity (u) and density (ρ) values of amino acids and peptides in aqueous ethanol mixtures are of interest with a view to improve the comprehension about the stability of native proteins and the equilibrium process between "folded" versus "unfolded" forms of proteins. As the amino acid and peptide molecules contain functional groups similar to those existing in the more complex proteins, they are expected to mimic some common features of proteins. A number of authors have made contributions in the ultrasonic velocity and density measurements of binary mixtures [12–15]. In our present study we report viscosity, ultrasonic velocity, density, and refractive index for glycylglycine–$MnCl_2$ aqueous ethanol mixtures at temperatures T = (288.15 to 318.15) K. Using the ultrasonic velocity and density data, the isentropic compressibility (κ_S) and excess isentropic compressibility (κ_S^E) values have been evaluated along with viscosity deviations ($\Delta\eta$), molar refraction (R_m), excess molar volume (V_m^E), ultrasonic velocity deviation (Δu), refractive index deviation (Δn_D), intermolecular free length (L_f), specific acoustic impedance (Z) and solvation number (S_n) with a view to investigate the molecular interactions operative in the above said system.

2. Experimental

2.1. Materials

Glycylglycine and $MnCl_2 \cdot 4H_2O$ of 99% purity were purchased from Sigma–Aldrich, Germany. $MnCl_2$ was used after drying for

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72 h in a vacuum desiccator at room temperature. Deionized, doubly distilled degassed water with a specific conductance less than $1.29 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ was used for the preparation of all solutions. Ethanol of analytical grade purity 99.9% was provided by Changshu Yanguan Chemicals, China. Binary mixtures were prepared by mass in air tight stoppered glass bottles. The masses were recorded on a Mettler balance with a stated precision of $\pm 1 \times 10^{-4}$ g. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was $<1 \times 10^{-4}$.

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 ±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. Ultrasonic velocity measurements were carried out at a fixed frequency of 2 MHz. The capacity of the measurement cell was 7 ml. The calibration of ultrasonic interferometer was done by measuring the velocity in AR grade benzene and carbon tetrachloride. Our measured values of u agree closely with the literature values [18]. The maximum estimated error in ultrasonic velocity measurements was found to be ±0.08%. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled adequately stirred water bath (accuracy ±0.1 °C). Densities were measured using the (Mettler Toledo) Density 30PX digital densitometer having a precision of $\pm 1 \times 10^{-3}\ kg\,m^{-3}$. The densitometer was calibrated using double-distilled-deionized water and dry air. Refractive indices were measured using a (Mettler Toledo) Refracto 30PX and 30Gs digital refractometer and its uncertainty was found to be ±0.0005%. The densitometer and refractometer were calibrated using double-distilled water. The sample and reference resonator cells with minimum volumes of $0.5\ cm^3$ were thermostatted with a precision of ±0.01 K, and a previously described differential technique was employed for all measurements [16]. Throughout our experiments the concentrations of glycylglycine and $MnCl_2$ were kept constant at $0.020\ mol\ kg^{-1}$ and $0.25\ mol\ kg^{-1}$, respectively. The physical parameters for glycylglycine–$MnCl_2$ in aqueous ethanol mixtures were measured at temperatures 288.15 K, 298.15 K, 308.15 K, and 318.15 K. Based on the above mentioned physical parameters acoustical, excess and deviations properties have been calculated and interpreted in terms of molecular interactions.

3. Results

Mole fraction of ethanol, viscosity, ultrasonic velocity, density and refractive index of glycylglycine–$MnCl_2$ in aqueous ethanol mixtures at T = (298.15 to 318.15) K are listed in Table 1. Viscosity deviations, isentropic compressibility, molar refraction, and excess molar volume are listed in Table 2. Ultrasonic velocity deviation, refractive index deviation, excess isentropic compressibility and molar refraction deviation for the studied mixtures are plotted for the whole composition range and at all temperatures in Figs. 1–4.

3.1. Calculation of isentropic compressibility and molar refraction

Isentropic compressibility, κ_S, is a property that can be calculated from experimental values of density and ultrasonic velocity

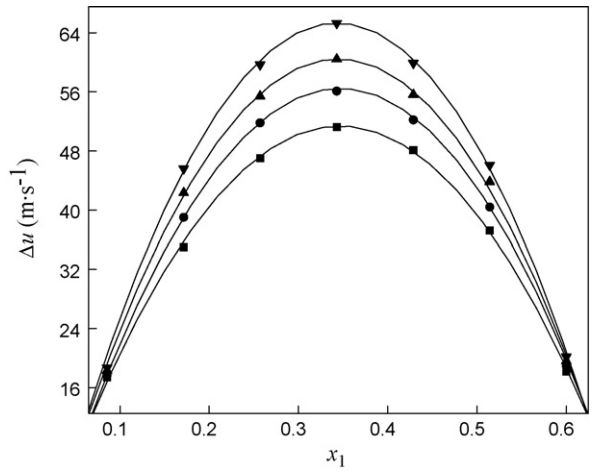

Fig. 1. Ultrasonic velocity deviation, Δu, for ($0.020\ mol\ kg^{-1}$ glycylglycine + $0.25\ mol\ kg^{-1}$ $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

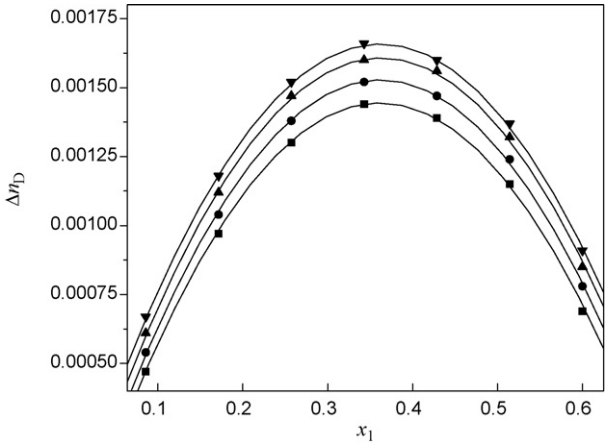

Fig. 2. Refractive index deviation, Δn_D, for ($0.020\ mol\ kg^{-1}$ glycylglycine + $0.25\ mol\ kg^{-1}$ $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

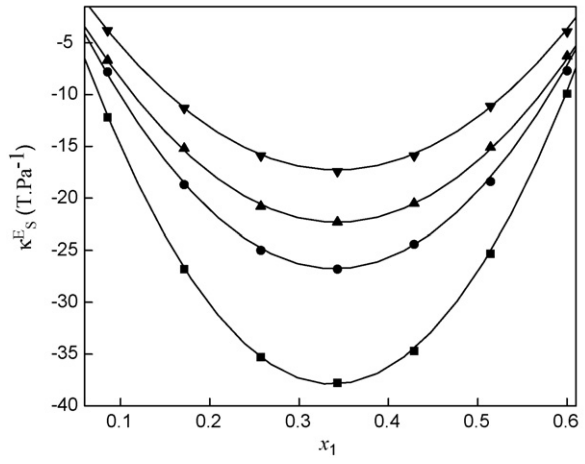

Fig. 3. Excess isentropic compressibility, κ_S^E, for ($0.020\ mol\ kg^{-1}$ glycylglycine + $0.25\ mol\ kg^{-1}$ $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

Table 1
Viscosity, η, ultrasonic velocity, u, density, ρ, and refractive index, n_D, for glygylglycine[a]–$MnCl_2$[b] in aqueous ethanol mixture at T = (288.15 to 318.15) K.

x_1	η (m Pa s)	u (m s^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	n_D
T/K = 288.15				
0.0857	1.04	1100.00	1.0033	1.3315
0.1715	1.15	1200.06	0.9919	1.3361
0.2572	1.24	1300.01	0.9805	1.3407
0.3430	1.35	1400.04	0.9691	1.3453
0.4288	1.47	1500.06	0.9577	1.3499
0.5145	1.58	1600.10	0.9463	1.3545
0.6003	1.69	1700.02	0.9349	1.3591
T/K = 298.15				
0.0857	1.01	1310.06	1.0023	1.3382
0.1715	1.11	1400.00	0.9908	1.3428
0.2572	1.21	1510.05	0.9794	1.3474
0.3430	1.31	1610.00	0.9677	1.3520
0.4288	1.42	1700.05	0.9565	1.3566
0.5145	1.53	1810.07	0.9451	1.3612
0.6003	1.65	1900.10	0.9338	1.3658
T/K = 308.15				
0.0857	0.92	1510.00	1.0014	1.3437
0.1715	1.01	1600.05	0.9896	1.3482
0.2572	1.11	1700.03	0.9782	1.3533
0.3430	1.20	1800.10	0.9663	1.3576
0.4288	1.29	1900.06	0.9553	1.3620
0.5145	1.40	2000.00	0.9438	1.3668
0.6003	1.51	2110.04	0.9326	1.3711
T/K = 318.15				
0.0857	0.83	1700.10	1.0005	1.3516
0.1715	0.92	1800.02	0.9884	1.3562
0.2572	1.00	1900.00	0.9769	1.3608
0.3430	1.09	2000.03	0.9648	1.3654
0.4288	1.16	2100.10	0.9540	1.3701
0.5145	1.25	2200.01	0.9424	1.3747
0.6003	1.37	2300.09	0.9315	1.3793

[a] Glycylglycine = 0.020 mol kg^{-1}.
[b] $MnCl_2$ = 0.25 mol kg^{-1}.

through the equation

$$\kappa_S = \frac{1}{u^2\rho}, \tag{1}$$

where u is the ultrasonic velocity and ρ is the density. The uncertainty of κ_S is 0.1 T Pa^{-1}.

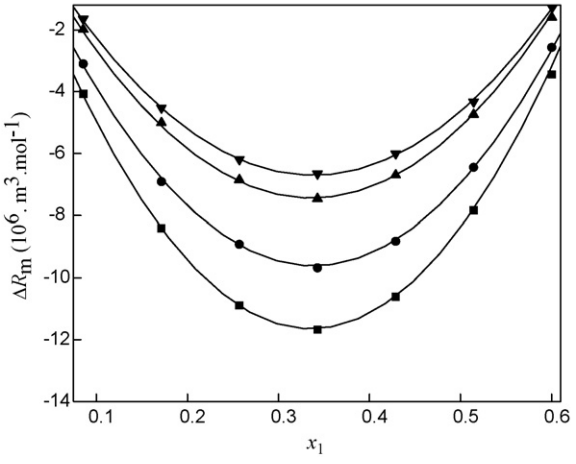

Fig. 4. Molar refraction deviation, ΔR_m, for (0.020 mol kg^{-1} glycylglycine + 0.25 mol kg^{-1} $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

For a given pure component i, the molar refraction $R_{m,i}$, is defined as

$$R_{m,i} = \frac{(n_{D,i}^2 - 1)(x_i M_i)}{[(n_{D,i}^2 + 2)\rho_i]} = \frac{V_{m,i}(n_{D,i}^2 - 1)}{(n_{D,i}^2 + 2)}, \tag{2}$$

where ρ_i, $n_{D,i}$ and $V_{m,i}$ are density, refractive index and molar volume of the ith component.

Also, the molar refraction is related with the mean electronic polarizability of a real system (either pure species or mixed components) [17] by the relation:

$$R_m = \frac{N_A \alpha_e}{3\varepsilon_0}, \tag{3}$$

where α_e is the mean electronic polarizability, N_A is Avogadro's constant and ε_0 is the permittivity of free space. Molar refraction is known to be proportional to the dispersion forces [17,18].

The molar refraction, R_m, for the binary mixture has been obtained from the measured refractive indices by means of Lorentz–Lorentz equation as follows [19]:

$$R_m = \frac{(n_D^2 - 1)(x_1 M_1 + x_2 M_2)}{[(n_D^2 + 2)\rho]} = \frac{V_m(n_D^2 - 1)}{(n_D^2 + 2)}, \tag{4}$$

where ρ is the density, n_D is the refractive index, both measured for the binary mixture, V_m represents the real molar volume of the mixture and x_i and M_i are the mole fraction and molar mass of the ith component, respectively. Uncertainty associated with R_m is $\pm 1 \times 10^{-8}$ m^3 mol^{-1}.

3.2. Calculation of excess and deviation properties

The excess molar volumes and the deviations of ultrasonic velocity, refractive index and molar refraction were calculated through the expression

$$Y_m^E \text{ or } \Delta Y = Y - \zeta_1 Y_1 - \zeta_2 Y_2, \tag{5}$$

where Y_m^E is the excess property and ΔY is the deviation of the property, Y is the property of the mixture, Y_i is the property of the pure component i and ζ_i is the mole fraction of the component i. The corresponding excess isentropic compressibility, κ_S^E, was calculated from the definition

$$\kappa_S^E = \kappa_S - \kappa_S^{id}, \tag{6}$$

where κ_S^{id} stands for isentropic compressibility for the ideal mixture [20]. The uncertainty of κ_S^E is ± 0.6 T Pa^{-1}.

The viscosity deviations, $\Delta\eta$, were calculated from the equation

$$\Delta\eta = \eta - [(1 - x) \cdot \eta_1 + x\eta_2], \tag{7}$$

where η_1 and η_2 are the viscosities of pure and mixed solvents, respectively, x is the mole fraction of ethanol.

The data of the excess properties (namely isentropic compressibilities) and also those of ultrasonic velocity, refractive index and molar refraction deviations were fitted to the Redlich–Kister equation, Eq. (8).

$$Y_m^E \text{ or } \Delta Y = \zeta_1(1 - \zeta_1)\sum_{i=0}^{N} A_i(2\zeta_1 - 1)^i. \tag{8}$$

The symbol Y_m^E or ΔY denotes the properties $\kappa_S^E/(\text{T Pa}^{-1})$, $\Delta u/(\text{m s}^{-1})$, Δn_D or $\Delta R_m/(10^6\ \text{m}^3\ \text{mol}^{-1})$ and ζ_i is the x_i, the mole fraction of component i, and A_i are adjustable coefficients. Uncertainty for Δu and Δn_D are ± 0.5 m s^{-1} and 5×10^{-5}, respectively. The fitting was carried out by using a Levenberg–Marquardt algorithm. The adjusting coefficients are listed in Table 3 along with the

Table 2
Viscosity deviations, $\Delta\eta$, isentropic compressibility, κ_S, molar refraction, R_m, excess molar volume, V_m^E, for glygylglycine[a]–$MnCl_2$[b] in aqueous ethanol mixture at T = (288.15 to 318.15) K.

x_1	$\Delta\eta$ (mPa s)	κ_S (TPa^{-1})	$R_m \times 10^6$ (m^3 mol^{-1})	$V_m^E \times 10^6$ (m^3 mol^{-1})
T/K = 288.15				
0.0857	7.56	823.72	10.87	−0.3952
0.1715	13.28	700.04	12.49	−0.5199
0.2572	18.31	603.47	14.11	−0.6446
0.3430	19.42	526.44	15.74	−0.6940
0.4288	18.24	464.03	17.37	−0.6546
0.5145	13.86	412.74	19.01	−0.5297
0.6003	6.17	370.10	20.65	−0.4052
T/K = 298.15				
0.0857	5.39	581.32	10.92	−0.4216
0.1715	10.21	514.94	12.54	−0.5463
0.2572	13.43	447.77	14.16	−0.6710
0.3430	14.56	398.66	15.79	−0.7204
0.4288	13.39	361.73	17.42	−0.6807
0.5145	10.74	322.94	19.06	−0.5563
0.6003	5.28	296.61	20.71	−0.4316
T/K = 308.15				
0.0857	3.82	437.96	10.98	−0.4783
0.1715	9.16	394.70	12.61	−0.6030
0.2572	12.54	353.71	14.24	−0.7277
0.3430	13.63	319.37	15.88	−0.7771
0.4288	12.92	289.95	17.52	−0.9380
0.5145	9.47	264.88	19.16	−0.6130
0.6003	4.68	240.83	20.81	−0.4883
T/K = 318.15				
0.0857	2.78	345.80	11.05	−0.4937
0.1715	8.69	312.25	12.68	−0.6184
0.2572	11.48	283.55	14.31	−0.7431
0.3430	12.85	259.11	15.94	−0.7925
0.4288	11.77	237.66	17.58	−0.9528
0.5145	8.46	219.23	19.22	−0.6285
0.6003	3.62	202.92	20.87	−0.5037

[a] Glycylglycine = 0.020 mol kg^{-1}.
[b] $MnCl_2$ = 0.25 mol kg^{-1}.

Table 3
Redlich–Kister fitting coefficients for excess isentropic compressibility, κ_S^E, molar refraction deviation, ΔR_m, ultrasonic velocity deviation, Δu, refractive index deviation, Δn_D, for glygylglycine[a]–$MnCl_2$[b] in aqueous ethanol mixture at T = (288.15 to 318.15) K.

Functions	κ_S^E (TPa^{-1})	$\Delta R_m \times 10^6$ (m^3)	Δu (m s^{-1})	Δn_D
T/K = 288.15				
A_0	−110.7	−26.96	156.38	0.0057
A_1	72.4	11.2	−86.7	0.0036
A_2	−161	−6.17	61.2	0.0020
A_3	152	3.32	−17.9	0.0014
σ	0.6	0.01	0.4	0.00001
T/K = 298.15				
A_0	130.3	−26.79	145.64	0.0052
A_1	93.6	11.1	−81.2	0.0030
A_2	−128.9	−6.30	60.7	0.0039
A_3	103.4	3.30	−13.5	0.0021
σ	0.4	0.01	0.4	0.00001
T/K = 308.15				
A_0	−152.2	−26.62	133.73	0.0046
A_1	115.8	10.9	−76.4	0.0024
A_2	−98.7	−6.45	60.1	0.0057
A_3	80.6	3.27	−9.3	0.0028
σ	0.3	0.01	0.4	0.00001
T/K = 318.15				
A_0	−175.1	−26.50	121.68	0.0040
A_1	137.8	10.8	−72.2	0.0018
A_2	−75.4	−6.62	59.6	0.0075
A_3	62.9	3.25	−5.8	0.0035
σ	0.2	0.01	0.4	0.00001

[a] Glycylglycine = 0.020 mol kg^{-1}.
[b] $MnCl_2$ = 0.25 mol kg^{-1}.

corresponding standard deviations defined by

$$\sigma = \left[\frac{\sum_{j=1}^{m}\{(Y_j^E/\Delta Y)^{\exp} - (Y_j^E/\Delta Y)^{\mathrm{cal}}\}^2}{m-n}\right]^{1/2}, \quad (9)$$

where the superscript exp and cal are the experimental and calculated values, m is the number of experimental points, and n is the number of coefficients used in the fitting equation. Their graphic representations of the corresponding fitted curves are shown in Figs. 1–4.

3.3. Calculation of acoustical parameters and solvation number

The variations in intermolecular free length, specific acoustic impedance and solvation numbers at different temperatures and mole fractions of ethanol have been shown in Figs. 5–7 and were calculated using the following equations:

$$L_f = k\sqrt{\kappa_S}, \quad (10)$$

$$Z = u \cdot d, \quad (11)$$

$$S_n = \frac{M_1}{M_2}[1 - \kappa_S/\kappa_s^0]\left[100 - \frac{X}{X}\right], \quad (12)$$

where k is the Jacobson constant [21] which is different for different temperatures; X is the number of grams of solute in 100 g of the solution; M_1 and M_2 are the molecular weights of solvent and solute, κ_S and κ_s^0 are the adiabatic compressibilities of solvent and solute, respectively.

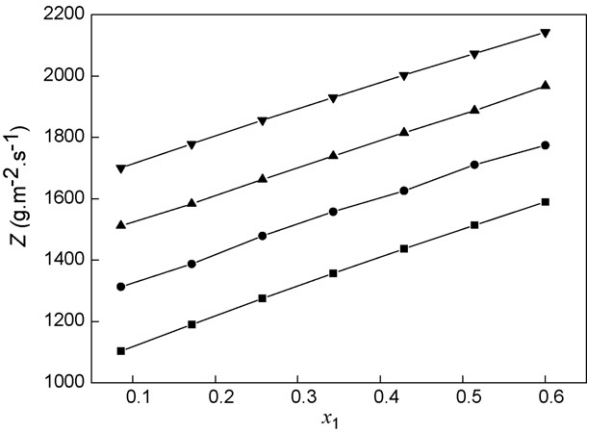

Fig. 5. Variation of intermolecular free length, L_f, as a function of mole fraction of ethanol for (0.020 mol kg^{-1} glycylglycine + 0.25 mol kg^{-1} $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

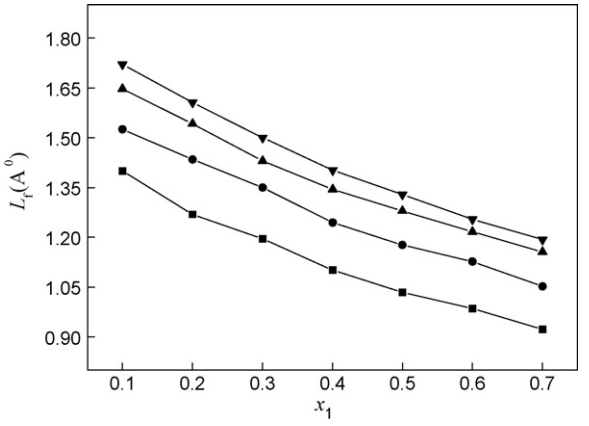

Fig. 6. Variation of acoustic impedance, Z, as a function of mole fraction of ethanol for (0.020 mol kg^{-1} glycylglycine + 0.25 mol kg^{-1} $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

4. Discussion

In this part, we analyze the evolution of different properties, both obtained and calculated, for the system (glycylglycine + $MnCl_2$ in aqueous ethanol) at T = (288.15 to 318.15) K. It is observed that viscosity increases with an increase in concentration and decreases with an increase in temperature. A regular change in viscosity data for different concentrations in aqueous ethanol mixture suggests that solvent–solvent interactions are more predominant than solute–solvent interactions. This phenomenon may appear due to H-bond formation and it may be attributed to the formation of intermolecular forces in the solvent. The linear behavior of ultrasonic velocity with concentration indicates the interactions between unlike molecules through hydrogen bonding (OH–O) which in turn produces displacement of electron and nuclei (Table 1). The densities decrease with increasing content of ethanol and also with increasing temperature. For glycylglycine and $MnCl_2$ in aqueous ethanol mixtures, the temperature dependence becomes distinctly linear, especially at high alcohol concentrations. The refractive index also shows an increase in its values with an increase in concentration. It may be noted that such changes are due to the electronic perturbation of the individual molecules during mixing and therefore depends very much on the nature of mixing molecules.

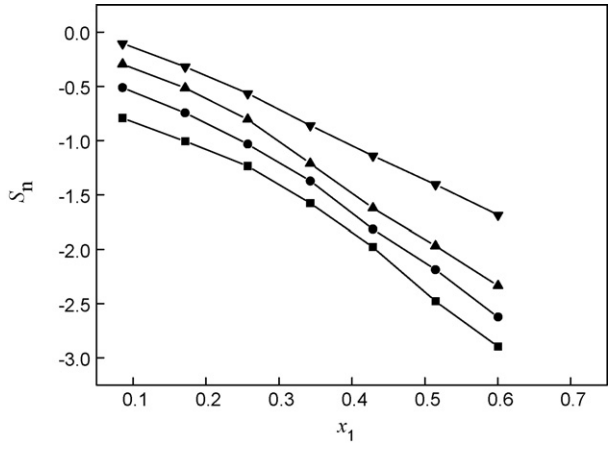

Fig. 7. Variation of solvation number, S_n, as a function of mole fraction of ethanol for (0.020 mol kg^{-1} glycylglycine + 0.25 mol kg^{-1} $MnCl_2$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

Excess molar volumes are negative on the whole composition range for the investigated mixture (Table 2). The values of excess molar volumes, V_m^E, of the mixture formed from two self-associated (H-bonded) substances are a result of number of effects which may contribute terms differing in sign. Disruption of H-bonds and other specific interactions may cause negative contributions to V_m^E. The free-volume effect, which depends on differences in the characteristic pressures and temperatures of the components, causes a negative contribution. Packing effects or conformational changes of the molecules in the mixtures are more difficult to categorize. However, interstitial accommodation and the effect of condensation give further negative contributions. The magnitude of V_m^E is the result of the following effects broadly recognized [22] as:

(a) Dissociation of ethanol structure on mixing, with a positive contribution to V_m^E.
(b) Non-specific physical interactions and unfavorable interactions between dissimilar molecules which also contribute positively to V_m^E.
(c) Specific interactions between unlike molecules (weak hydrogen bonding), with a negative contribution to V_m^E.
(d) Interstitial accommodation due to differences in molar volume and free volume between liquid components which are mostly negative.

In our case, it is evident that the negative contributions overtake the positive contributions to V_m^E in the binary mixture and these can be explained based on the following points:

(a) As the concentration of ethanol increases, a lowering in the molar volume is observed.
(b) The degree of association of the ethanol molecules with other components of the mixture decreases.
(c) Weakening of H-bond between dissimilar molecules on mixing takes place.

Table 2 reports the values of molar refraction, R_m, and its variation trend. The variations may be due to the electronic polarization of the mixtures which decrease monotonously as the composition of ethanol increases for a given mixture and this behavior is hardly influenced by temperature. The molecular structure of the individual molecules in the binary mixture does not undergo any significant change due to weak interactions between the solute and solvent components. These weak intermolecular interactions are of van der Walls type and hence, no significant changes occur in the electronic dispersion frequencies associated with the solvent components.

The viscosity deviations are also reported in Table 2 which shows that they are negative over the whole composition and temperature range. Moreover, the deviations become smaller as the temperature increases. It is also observed that the negative deviations are smaller and more symmetrical for the system studied. The negative $\Delta\eta$ values suggest that intermolecular structures existing in the mixture shows smaller resistance to the viscous flow. The trend in viscosity deviation may be due to ion–dipole interaction and/or a partial hydrogen bond between carbonyl oxygen of glycylglycine and hydroxyl hydrogen of alcohol upon addition of alcohol to aqueous solution containing glycylglycine and $MnCl_2$ [23,24]. The strengthening of hydrogen bond interactions between carbonyl oxygen and hydroxyl hydrogen in the solution leads to a lower mobility of ions and a higher viscosity deviation in the mixture.

Ultrasonic velocity deviations (Fig. 1) show positive values for all mole fractions and at all temperatures. The variation can be observed with an increase in mole fraction of ethanol and lower the temperature, lower is the ultrasonic velocity deviation, which is an indicative of weak interaction involving dispersion forces [25]. This fact is consistent with an idea of a higher degree of association between the molecules at $T = 288.15$ K than at higher temperatures. The degree of association in aqueous ethanol system at lower temperature in presence of glycylglycine varies from complete dissociation into zwitterions and subsequent interaction with other components of the binary mixture. In our case, it should be plausible to deduce that in presence of ethanol the components of the mixture seem to maintain its high degree of association at lower temperature rather at higher temperature.

Refractive index deviations (Fig. 2) are also positive for all mole fractions and temperatures. As it is published [26] the sign of V_m^E which is negative in this work is opposite to the sign presented by refractive index deviation values. The variation observed in the refractive index deviations are due to the formation of a close ion pair clearly indicating the interactions between cation, anion and solvent molecules.

Excess isentropic compressibility values are negative on the whole composition range at all temperatures in Fig. 3. Negative values of κ_S^E mean that the mixture is less compressible than the ideal mixture, suggesting that there may be strong interactions between glycylglycine, $MnCl_2$ and ethanol molecules.

The molar refraction deviation values are plotted as a function of mole fraction of ethanol in Fig. 4 and are found to be negative at all compositions and temperatures. The negative values indicate that the interactions of glycylglycine and $MnCl_2$ with water molecules are relatively weak as compared to that of ethanol and present almost the same tendency as V_m^E and κ_S^E values.

Intermolecular free length is an important parameter that has association with adiabatic compressibility. Fig. 5 shows the variation of free length with mole fraction. It is clear that the intermolecular free length shows a similar variation as reflected by κ_S. The decreased compressibility brings the molecules to a closer packing resulting a decrease in the intermolecular free length. Moreover, free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. The interdependence of L_f and u has been evolved from a model for sound propagation proposed by Eyring and Kincaid [27]. According to the proposed theory, the decrease in the value of κ_S and L_f with an increase in ultrasonic velocity further strengthens the process of complex formation between solute molecules through hydrogen bonding due to which structural arrangement is considerably altered [28]. When an acoustic wave travels in a medium, there is a variation pressure from particle to particle. When a plane ultrasonic wave is setup in a liquid, the pressure and hence, density of the liquid shows a periodic variation with distance from the source along the direction of propagation. The acoustic impedance is the parameter related to the elastic properties of the medium. Therefore, it is important to examine the acoustic impedance in relation to concentration and temperature. Fig. 6 shows the variation of acoustic impedance with mole fraction. Such variations are due to intermolecular interactions owing to hydrogen bonding [29]. Solvation number decreases with an increase in mole fraction and temperature and it is negative for all concentrations. Fig. 7 shows the variation of solvation number as a function of mole fraction. The negative solvation number indicates structure-breaking tendency of the solute. This shows a decrease in the tendency of solvation of ions with decrease in dielectric constant of the solvent mixtures [30]. The negative values of solvation numbers can be understood in terms of weakening of the local solvent structure in close neighborhood of the solute molecules.

5. Conclusions

The physical parameters such as viscosity, ultrasonic velocity, density and refractive index have been reported for glycylglycine–$MnCl_2$ aqueous ethanol mixtures at temperatures $T = (288.15$ to $318.15)$ K. Excess molar volumes, viscosity deviations, ultrasonic velocity deviations, refractive index deviations, excess isentropic compressibilities, and molar refractivity deviations, have been deduced. The mixtures showed positive ultrasonic velocity, refractive index deviation whereas excess volume, molar refraction deviation, and excess isentropic compressibility were negative. The deviation and excess property data were successfully fitted with a Redlich–Kister equation. The variations in refractive index deviations were due to the formation of a close ion pair indicating interactions between solute and solvent molecules.

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