



Application of Prigogine–Flory–Patterson theory to volumetric, ultrasonic, and compressibility parameters of (glycylglycine + CuCl₂) in aqueous ethanol mixtures

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ARTICLE INFO

Article history:

Received 23 February 2011

Received in revised form 15 March 2011

Accepted 2 April 2011

Available online 12 April 2011

Keywords:

PFPP theory

Glycylglycine

CuCl₂

Compressibility

ABSTRACT

The molar volume and compressibility of (glycylglycine + CuCl₂) in aqueous ethanol mixtures have been obtained at four different temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$ from ultrasonic velocity and density measurements. Excess molar volumes were found to be negative throughout the composition range indicating notable changes in hydrogen bonding and electrostatic interactions. Using the Prigogine–Flory–Patterson theory, quantitative estimation of different contributions, *i.e.* interactional, free volume, and P^* effect to V^E have been obtained. The molar isentropic compressibility has been computed using the ultrasonic velocity and excess volume data. The trends in κ_s^E are affected by the size of the molecule leading to negative contributions. In order to compare the theoretical values of ultrasonic velocity, the equations of Nomoto and Junjie were used and found to predict the experimental data very well.

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1. Introduction

For the last 100 years, the study of protein molecular stability has engaged the attention of chemists because of its fundamental importance [1,2]. Thermal stability of proteins is highly affected by the presence of concentrated aqueous solutions of some solutes, such as metal salts and alcohols [3], which have different effects upon the structure of water. It is difficult to interpret a large amount of denaturant associated with denaturation process because of the large number of interactions which contribute to the overall thermodynamic properties of the protein in each state. Studies on simple compounds that model some specific aspects of a protein can provide estimates of the contributions from particular functional groups on the protein to the thermodynamics of unfolding [4–8]. It is a well known fact that electrolytes affect the structure and stability of biomolecules. A reasonably interesting aspect is to study the behaviour of biomolecules like peptides and proteins in presence of metal salts. Solvent mixtures play an important role in chemical industries and in research laboratories. The physicochemical properties of solvent mixtures often show large deviations from ideal behaviour. A survey of the literature revealed that studies on excess thermodynamic functions of solvent mixtures are very few [9–13]. However, there are results of the measurements of partial molar volumes \bar{V}_2 and molar isentropic compressibility $\bar{\kappa}^0$ of various organic solvents at different temperatures and compositions [14,15]. The Prigogine–Flory–Patterson theory has been used to study various binary mixtures by earlier

worker [16–18]. Taghi *et al.* [19] have carried out volumetric studies of (CuCl₂ + ethanol) at 25 °C but a mixture of (glycylglycine + CuCl₂) in aqueous ethanol system at different temperatures and concentrations would be much more interesting and may serve as an extension in similar lines. Hence, as a contribution towards a more comprehensive molecular interaction and in continuation of our earlier studies [20–24] on aqueous and aqueous ethanol systems of dipeptide and metal salts, this paper presents a detailed thermodynamic description on how alcohols and metal salts affect the behaviour of glycylglycine under diverse conditions.

2. Experimental

2.1. Materials

Glycylglycine (CAS 556-50-3) and copper (II) chloride dihydrate (CAS 10125-13-0) of mass fraction purity 0.99 were purchased from Sigma–Aldrich, Germany. Commercially available glycylglycine of the highest purity was used without further purification. Copper (II) chloride dihydrate was used after drying for 72 h in a vacuum desiccator at room temperature. Deionised, 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. Ethanol (CAS 64-17-5) was purchased from Changshu Yangyuan Chemicals, China and had mass fraction purity 0.999. Ethanol was further distilled and used in our experiments to ensure maximum purity. The solutions were prepared on a mass basis by using a Mettler balance having a precision of $\pm 0.01 \text{ mg}$. Care was taken to avoid evaporation and contamination during mixing.

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In our studies, glycyglycine and CuCl_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 ethanol was varied in terms of mole fraction (x). 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°C above the measurement temperature before filling the ultrasonic and densimetric cells.

2.2. Methods

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 are made at a fixed frequency of 2 MHz. The volume of the measuring cell was 7 cm^3 . The calibration of ultrasonic interferometer was made by measuring the velocity in AR grade benzene and carbon tetrachloride. The estimated uncertainty in ultrasonic velocity measurements was $\pm 0.08\%$. The temperature was controlled by circulating water around the liquid cell from a thermostatically controlled adequately stirred water bath with an uncertainty of $\pm 0.01 \text{ K}$. Densities were measured using the (Mettler Toledo) Density 30PX digital densitometer with an uncertainty of $\pm 0.001 \text{ g} \cdot \text{cm}^{-3}$. The densitometer was calibrated using double distilled water. The sample and reference resonator cells with minimum volumes of 0.5 cm^3 were thermostated with an uncertainty of $\pm 0.01 \text{ K}$, and a previously described differential technique was employed for all measurements [25]. The ultrasonic velocity and density for aqueous ethanol solutions of glycyglycine– CuCl_2 were measured at four different temperatures $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$. Each measurement was repeated thrice and the reported values are an average of all three measurements.

3. Results and discussion

The experimental values of ultrasonic velocity (u) and density (ρ) along with isobaric thermal expansion (α_p) and molar heat capacity (C_p) for (glycyglycine + CuCl_2) in aqueous ethanol system are given in table 1.

3.1. Excess volume

The excess volume (V^E) and excess molar volume (V_m^E) for (glycyglycine + CuCl_2) in aqueous ethanol mixtures at different temperatures have been calculated using the experimentally determined density values. The results have been fitted into Redlich–Kister equation of the form:

$$V^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = x(1-x) \sum_i A_i (2x-1)^i, \quad (1)$$

$$V_m^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_m} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right). \quad (2)$$

The values of the coefficient A_i and the standard deviation of the fit are given in table 2. The ρ_m is the density of mixture; x_1 and x_2 are the mole fraction of solution and solvent; M_1 and M_2 are the molar masses; ρ_1 and ρ_2 are the densities of solution and solvent respectively. Figure 1 presents the variation of V^E as a function of mole fraction of ethanol at four different temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$. The V^E values are negative throughout the composition range indicating significant changes in the hydrogen bonding (water + ethanol + glycyglycine) equilibria and electrostatic interactions (CuCl_2). Contributions to the value of V^E

may arbitrarily be divided into three important effects namely, physical, chemical, and structural contributions. Physical contributions comprise of non-specific physical interactions between $\text{C}=\text{O}$ (carbonyl) of glycyglycine peptide bond and a hydrogen atom in the added ethanol that contribute to the negative values of V^E . The chemical effects lead to the making up of water–ethanol liquid order giving rise to negative contribution of V^E . The structural effects also contribute to the negativity of V^E arising from geometrical fitting of (glycyglycine + water + ethanol) molecules into each other and possible complexation of (glycyglycine + CuCl_2) with the Cu atoms being attached to the more feasible carboxylic end. In the present system, one may conclude that, all three effects contribute to V^E . On the other hand, CuCl_2 reduces the electrostriction of neighbouring water molecules around the charged centres of glycyglycine. As ethanol is less compressible compared to water, the electrostricted water enters the hydrated sphere of Cu ions making a negative contribution. Hence, the negative contributions clearly indicate the participation of peptide groups in hydrogen bonding with water and ethanol.

In order to gain insight into the behaviour of mixtures, the generation of plots of partial excess molar volumes of the respective components, \bar{V}_1^E and \bar{V}_2^E is an important strategy. These parameters have been calculated using the equations:

$$\bar{V}_1^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = V_1 - \bar{V}_1 = \frac{V^E}{x} + x(1-x) \left[\frac{\partial(V^E/x)}{\partial x} \right]_{p,T}, \quad (3)$$

$$\bar{V}_2^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = V_2 - \bar{V}_2 = \frac{V^E}{(1-x)} + x(1-x) \left[\frac{\partial \left\{ \frac{V^E}{(1-x)} \right\}}{\partial(1-x)} \right]_{p,T}, \quad (4)$$

where \bar{V}_1 and \bar{V}_2 represent the partial molar volumes of components 1 and 2. The excess partial molar volumes, \bar{V}_i^E , of glycyglycine and CuCl_2 in aqueous ethanol mixtures are shown in figure 2. The limiting values, \bar{V}_2^0 and $\bar{V}_2^{E,0}$ for the systems studied are listed in table 3 together with the values of molar volumes of respective components. A strong interaction through hydrogen bonding accompanied by minor destruction of ethanol structure leads to negative partial excess molar volumes. In the dilute aqueous region, structural effects dominate indicating the negative $\bar{V}_1^{E,0}$ and positive $\bar{V}_2^{E,0}$ whereas destruction of associated structures is important in the dilute alcohol region.

Using the well known Prigogine–Flory–Patterson theory [26,27], a quantitative estimation of different contributions to V^E can be obtained. In terms of three contributions, their approximate expression for V^E is:

$$\frac{V^E}{x_1 V_1^* + x_2 V_2^*} = \frac{(\tilde{v}^{1/3} - 1) \tilde{v}^{2/3} \psi_1 \theta_2 X_{1,2}}{(4/3 \tilde{v}^{-1/3} - 1) P_1^*} \underset{\text{(interactional)}}{} - \frac{(\tilde{v}_1 - \tilde{v}_2)^2 (14/9 \tilde{v}^{-1/3} - 1) \psi_1 \psi_2}{(4/3 \tilde{v}^{-1/3} - 1) \tilde{v}} \underset{\text{(\tilde{v} curvature)}}{} + \frac{(\tilde{v}_1 - \tilde{v}_2) (P_1^* + P_2^*) \psi_1 \psi_2}{P_2^* \psi_1 + P_1^* \psi_2} \underset{\text{(P* effect)}}{} \quad (5)$$

where P_i^* and V_i^* are the characteristic pressure and volume of the pure components. The θ_2 represents the site fraction, \tilde{v} the reduced volume and ψ the contact energy fraction as given in previous work [27].

The parameters of various component mixtures obtained from Flory theory [28] are listed in table 4. The values of the interaction parameter X_{12} for the mixture studied have been calculated using the equimolar V^E values and are listed in table 5 together with equimolar values for each of the three contributions to V^E . An

TABLE 1
 Ultrasonic velocity (u), density (ρ), isentropic compressibility (κ_S), isobaric thermal expansion (α_p), and molar heat capacities (C_p) for (glycylglycine (0.020 mol · kg⁻¹) + CuCl₂ (0.25 mol · kg⁻¹)) in aqueous ethanol mixture at $T = (288.15 \text{ to } 318.15) \text{ K}$.

x	$u/(\text{m} \cdot \text{s}^{-1})$	$\rho \cdot 10^{-3}/(\text{kg} \cdot \text{m}^{-3})$	$\kappa_S/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})$	$\alpha_p \cdot 10^{-4}/(\text{K}^{-1})$	$C_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
$T/K = 288.15$					
0.00000	1790.16	1.4816	4.62325	10.214	223.195
0.08572	1795.42	1.4389	4.46374	11.346	217.807
0.17156	1802.34	1.3962	4.29808	12.478	212.419
0.25724	1808.57	1.3535	4.13797	13.610	207.031
0.34301	1815.49	1.3108	3.97694	14.742	201.643
0.42887	1821.73	1.2681	3.82107	15.874	196.255
0.51459	1829.64	1.2254	3.66055	17.006	190.867
0.60033	1838.85	1.1823	3.49651	18.142	185.476
$T/K = 298.15$					
0.00000	1823.42	1.4193	4.26875	14.217	210.528
0.08572	1831.38	1.3797	4.11365	15.531	204.352
0.17156	1839.24	1.3401	3.96151	16.845	198.176
0.25724	1847.10	1.3005	3.81180	18.159	192.000
0.34301	1854.96	1.2609	3.66447	19.473	185.824
0.42887	1860.82	1.2213	3.52707	20.787	179.648
0.51459	1870.68	1.1817	3.37682	22.101	173.472
0.60033	1878.59	1.1416	3.23482	23.416	167.294
$T/K = 308.15$					
0.00000	1859.68	1.3536	3.91394	17.362	198.736
0.08572	1865.49	1.3192	3.79075	18.601	191.384
0.17156	1872.46	1.2848	3.66446	19.840	184.032
0.25724	1880.63	1.2504	3.53543	21.079	176.680
0.34301	1888.30	1.2160	3.41029	22.318	169.328
0.42887	1896.28	1.1814	3.28543	23.557	161.976
0.51459	1905.82	1.1450	3.15240	24.796	154.624
0.60033	1916.34	1.1012	2.99862	26.036	147.284
$T/K = 318.15$					
0.00000	1895.06	1.2984	3.61545	21.298	185.347
0.08572	1902.38	1.2648	3.49484	22.562	177.860
0.17156	1907.56	1.2312	3.38355	23.826	170.373
0.25724	1915.74	1.1976	3.26316	25.090	162.886
0.34301	1921.92	1.1640	3.15125	26.354	155.399
0.42887	1931.10	1.1307	3.03206	27.618	147.912
0.51459	1942.28	1.0968	2.90739	28.882	140.425
0.60033	1950.47	1.0616	2.79050	30.146	132.936

TABLE 2
 Least square coefficients of equation (1) and standard deviation, σ , for glycylglycine ((0.020 mol · kg⁻¹) + CuCl₂ (0.25 mol · kg⁻¹)) in aqueous ethanol mixture at $T = (288.15 \text{ to } 318.15) \text{ K}$.

Parameter	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	σ^a
$T/K = 288.15$									
$V^m/(\text{cm}^3 \cdot \text{mol}^{-1})$	-0.4224	1.1143	-0.5326	0.4562	-0.3118	-3.3248	-0.8221	4.3187	0.003
$\kappa_S^E/(\text{m}^{-3} \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})$	-9.35	6.71	-2.21	2.83	-2.56	-3.48	0.09	4.28	0.004
$T/K = 298.15$									
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-0.1892	1.4554	0.0738	1.7847	0.6221	-3.4263	0.0856	2.5532	0.003
$\kappa_S^E/(\text{m}^{-3} \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})$	-31.27	6.23	3.14	0.95	-4.28	2.20	4.36	-3.38	0.004
$T/K = 308.15$									
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	0.3148	4.1214	-4.1762	-2.2342	2.7635	4.1028	-2.0656	-3.6798	0.003
$\kappa_S^E/(\text{m}^{-3} \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})$	-152.65	73.18	-35.47	-6.21	5.82	3.37	6.32	-8.24	0.002
$T/K = 318.15$									
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	0.2564	4.5263	-3.5282	-3.2834	3.4812	4.8746	3.1092	-1.6237	0.004
$\kappa_S^E/(\text{m}^{-3} \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})$	-183.63	71.18	7.87	-4.43	6.26	-1.89	3.36	2.51	0.002

^a σ has the units of V^E and κ_S^E accordingly.

analysis of each of the three contributions to V^E shows that X_{12} and the corresponding interactional contribution term are always positive. Both free volume and P^* contributions are negative with the studied system. From the theoretical results given in table 5 and figure 3, it can be concluded that both the interactional term and P^* are important in magnitude for the (glycylglycine + CuCl₂) aqueous ethanol mixture.

The third contribution, i.e. the free volume term decides the overall magnitude. In comparison to the above two contributions, its effect is less at high temperatures and highly significant at low temperatures. In addition, the negative region of V^E corresponds to a high concentration of the component with higher P^* parameter.

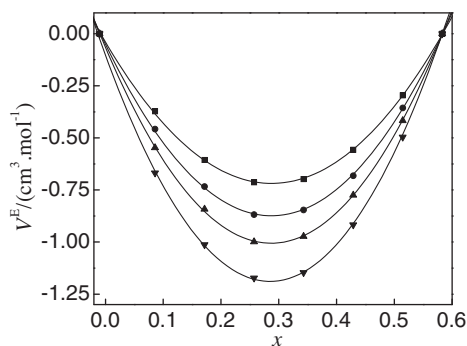


FIGURE 1. Composition dependence of excess molar volume, V^E , for (glycylglycine + CuCl_2) in aqueous ethanol mixtures at different temperatures: (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; and (▼) 318.15 K.

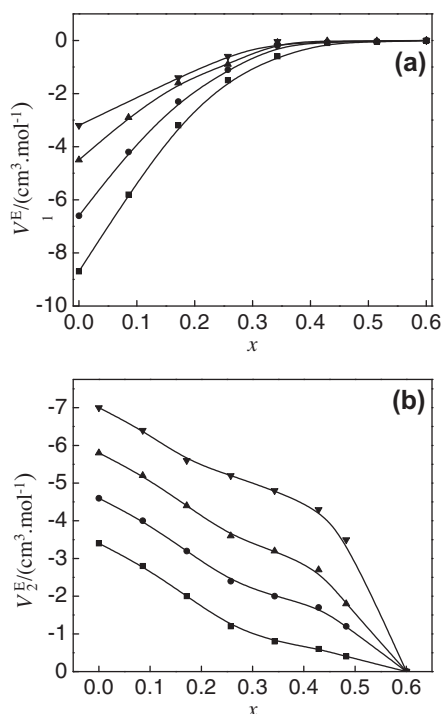


FIGURE 2. Partial molar excess volumes (a) \bar{V}_1^E and (b) \bar{V}_2^E for (glycylglycine ($0.020 \text{ mol} \cdot \text{kg}^{-1}$) + CuCl_2 ($0.25 \text{ mol} \cdot \text{kg}^{-1}$)) in aqueous ethanol mixtures at different temperatures: (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; and (▼) 318.15 K.

3.2. Ultrasonic velocity and compressibility

A combination of ultrasonic velocity and density enables us to determine [29] the molar isentropic compressibility coefficient and its apparent value, which provides information on the nature of interaction operating in mixtures. In order to calculate the isentropic compressibility, the values of c and V^E have been combined using the relation:

$$\kappa_S / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}) = \frac{[\sum x_i V_i + V^E]}{(u^2 \sum x_i M_i)} = \frac{V}{Mu^2}, \quad (6)$$

where M is the molar mass of the mixture. Further, the corresponding molar quantity is given by:

$$K_S / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}) = V\kappa_S = \frac{V^2}{Mu^2}, \quad (7)$$

which assumes that dissipative effects are negligible and that the hydrodynamic equation of motion can be placed in linear form. Using A_i from equation (1), the V^E data were extrapolated to the mole fractions of the ultrasonic velocity experiments. By subtracting from κ_S the isentropic compressibility κ_S^{id} for the corresponding ideal mixture, excess molar isentropic compressibility (κ_S^E) was obtained.

$$\kappa_S^E / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}) = \kappa_S - \kappa_S^{id}. \quad (8)$$

It can be shown [14,30] that

$$\kappa_S^{id} / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}) = \sum x_i \left[\kappa_{S,i} + \frac{T(V_i \alpha_{p,i})^2}{C_{p,i}} \right] - \left\{ \frac{T(\sum x_i V_i)^2 (\sum x_i \alpha_{p,i})^2}{(\sum x_i C_{p,i})} \right\}. \quad (9)$$

Equation (2) was again utilized to fit κ_S^E data. Also listed in table 2, there are the coefficient and standard errors. Figure 4 shows the variation of κ_S^E as a function of x at four different temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$. Negative deviations are observed for κ_S^E at all temperatures.

The trends in V^E are different from those of κ_S^E as both V^E and κ_S^E are affected by the size of the molecule. The apparent molar compressibility $\kappa_{S,\phi}$ of a solute in a solution is defined by the equations given elsewhere [31–33]. The limiting value $\kappa_{S,\phi}^0$ of the apparent molar isentropic compressibility was calculated by a linear extrapolation using the least squares fit to the below equation:

$$\kappa_{S,\phi} = \kappa_{S,\phi}^0 + S_k x_2, \quad (10)$$

where $\kappa_{S,\phi}^0$ is the infinite dilution molar isentropic compressibility and S_k is the experimental slope, indicative of solute–solvent interactions arising from dilute concentration effects. At infinite dilution, $\kappa_{S,\phi}^0 = \bar{K}^0$, i.e. infinite dilution partial molar isentropic compressibility. The values of \bar{K}^0 and S_k are given in table 3. A close agreement for the aqueous ethanol mixture is seen when limiting \bar{K}_2^0 values of alcohols with the corresponding molar isentropic compressibility $\kappa_{S,\phi,2} = (\kappa_{S,2} V_{S,2})$ where $\kappa_{S,\phi,2}$ can be considered as partial compressibility of the solute when dissolved in itself, i.e. pure liquid was compared. After dissolution, the molecular volume of the solute molecules is practically unaffected and that the molecules are in a force field similar to that in pure liquid state. This statement is implied by a near agreement in the \bar{K}_2^0 and $\kappa_{S,\phi,2}$ values of the solute in solution and pure liquid.

The presence of relatively strong interactions between respective components is indicated by the parameter S_k . In the mixture studied, $S_{k,2}$ shows negative values ruling out the possibility of strong interactions. By calculating the excess apparent isentropic

TABLE 3

Molar volume, V_2 , excess partial molar volumes, $\bar{V}_2^{E,0}$, limiting partial molar volumes, \bar{V}_2^0 , molar isentropic compressibility, $\kappa_{S,2}$, partial molar isentropic compressibilities, \bar{K}_2^0 , and the parameter, S_k , for (glycylglycine ($0.020 \text{ mol} \cdot \text{kg}^{-1}$) + CuCl_2 ($0.25 \text{ mol} \cdot \text{kg}^{-1}$)) in aqueous ethanol mixtures at infinite dilution and temperatures $T = (288.15 \text{ to } 318.15) \text{ K}$.

T (K)	$V_2 / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\bar{V}_2^{E,0} / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\bar{V}_2^0 / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_{S,2} \cdot 10^{-8} / (\text{Pa}^{-1} \cdot \text{cm}^3 \cdot \text{mol}^{-1})$	$\bar{K}_2^0 \cdot 10^{-8} / (\text{Pa}^{-1} \cdot \text{cm}^3 \cdot \text{mol}^{-1})$	S_k
288.15	72.14	-0.48	72.02	5.233	5.113 ± 0.04	-0.712 ± 0.09
298.15	89.28	3.14	89.14	8.459	8.243 ± 0.05	-3.415 ± 0.12
308.15	101.46	1.96	100.98	11.328	11.058 ± 0.08	-5.233 ± 0.14
318.15	117.57	0.10	117.21	19.592	19.316 ± 0.07	-7.745 ± 0.20

TABLE 4
Isothermal compressibility (κ_T), reduced volume (\bar{v}), characteristic volume (V^*), characteristic temperature (T^*), and characteristic pressure (P^*) of various components at $T = 318.15$ K.

Component	$\kappa_T/(\text{TPa}^{-1})$	\bar{v}	$V^*/(\text{cm}^3 \cdot \text{mol}^{-1})$	$T^*/(\text{K})$	$P^*/(\text{J} \cdot \text{cm}^{-3})$
Aq. glycylglycine	512.24	1.3246	73.27	7224	732.38
Aq. CuCl_2	719.37	1.3641	91.30	6345	648.27
Aq. (GG + CuCl_2)	1348.28	1.4373	62.49	5482	551.73
Aq. ethanol (GG + CuCl_2)	2317.64	1.5422	46.36	4598	432.64

TABLE 5
Calculated values of three contributions to the excess volume from PFP theory for various components at $T = 318.15$ K.

Component	$X_{12}/(\text{J} \cdot \text{cm}^{-3})$	Interaction	Free volume	P^* effect
Aq. glycylglycine	10.22	0.0747	-0.0521	-0.2341
Aq. CuCl_2	28.35	0.8243	-0.3567	-0.6284
Aq. (GG + CuCl_2)	97.49	1.8729	-0.9215	-1.2463
Aq. ethanol (GG + CuCl_2)	192.43	3.4152	-2.1843	-3.2518

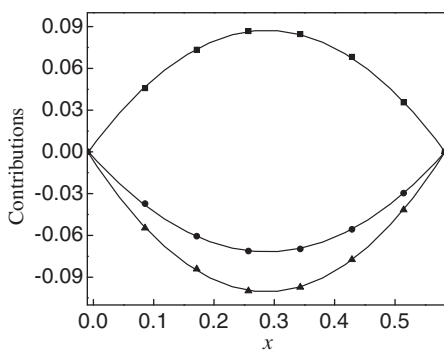


FIGURE 3. Values of the three contributions to the excess volume from the PFP theory for {glycylglycine ($0.020 \text{ mol} \cdot \text{kg}^{-1}$) + CuCl_2 ($0.25 \text{ mol} \cdot \text{kg}^{-1}$)} in aqueous ethanol mixture: (■) interaction; (●) free volume; and (▲) P^* effect.

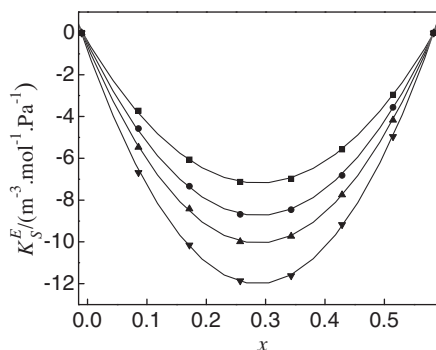


FIGURE 4. Composition dependence of excess isentropic compressibility, κ_S^E , for {glycylglycine ($0.020 \text{ mol} \cdot \text{kg}^{-1}$) + CuCl_2 ($0.25 \text{ mol} \cdot \text{kg}^{-1}$)} in aqueous ethanol mixtures at different temperatures: (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; and (▼) 318.15 K.

compressibility of water and ethanol, the deviations from ideal behaviour may be estimated as:

$$\kappa_{S\phi,1}^E \cdot 10^{-8}/(\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}) = \kappa_{S\phi,1} - \kappa_{S\phi,1}^0, \quad (11)$$

$$\kappa_{S\phi,2}^E \cdot 10^{-8}/(\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}) = \kappa_{S\phi,2} - \kappa_{S\phi,2}^0, \quad (12)$$

where $\kappa_{S\phi,1}$ and $\kappa_{S\phi,2}$ represent the apparent isentropic compressibility at a particular mole fraction and $\kappa_{S\phi,1}^0$ and $\kappa_{S\phi,2}^0$ are values of the apparent molar isentropic compressibility at infinite dilution.

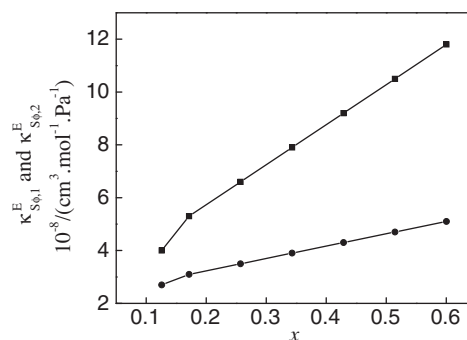


FIGURE 5. Plot of experimental ((■) 288.15 K; (●) 298.15 K; and (▲) 308.15 K) and calculated ((PFP) (▼), interaction; (◆) free volume; and (▲) P^* effect) values of excess volume.

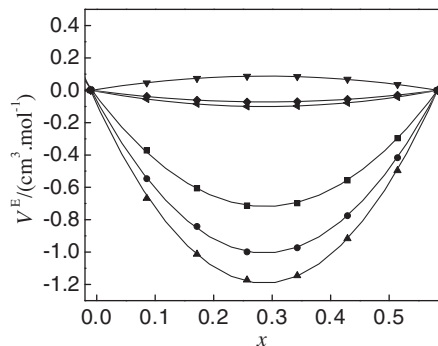


FIGURE 6. $\kappa_{S\phi,1}^E$ and $\kappa_{S\phi,2}^E$ for (glycylglycine + CuCl_2) in aqueous ethanol mixtures at two extreme temperatures: (■) 288.15 K and (●) 318.15 K.

An estimate of the deviations from ideal behaviour is given by the difference between $\kappa_{S\phi,1}^E$ and $\kappa_{S\phi,2}^E$. Figure 5 shows the variation of $\kappa_{S\phi,1}^E$ and $\kappa_{S\phi,2}^E$ at two extreme temperatures of (288.15 and 318.15) K. A plot of experimental values of excess volume and calculated values from PFP theory at temperatures (288.15, 298.15, and 308.15) K is shown in figure 6. This provides clear evidence of the difference between experimental and theoretical methods in determining excess volume. For comparison, the theoretical values of ultrasonic velocity (c) are computed using the equations of Junjie [34] and Nomoto [35], viz. for Junjie

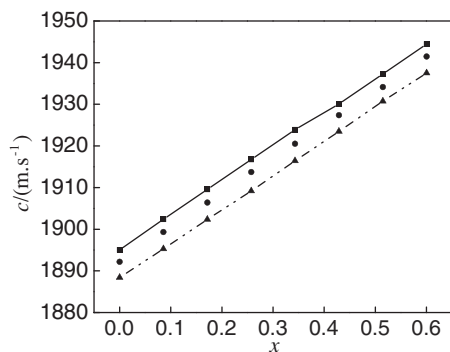


FIGURE 7. Experimental and calculated ultrasonic velocities: (■) c ; (●) c_j ; and (▲) c_N for (glycylglycine + CuCl_2) in aqueous ethanol mixture at $T = 318.15$ K. The error % being 0.12 for c_j and 0.15 for c_N , respectively.

$$c_j / (\text{m} \cdot \text{s}^{-1}) = [(x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_2)] / \{ (x_1 M_1 + x_2 M_2)^{1/2} [(x_1 M_1 / \rho_1^2 c_1^2) + (x_2 M_2 / \rho_2^2 c_2^2)]^{1/2} \} \quad (13)$$

and Nomoto

$$c_N / (\text{m} \cdot \text{s}^{-1}) = [(x_1 R_1 + x_2 R_2) / (x_1 V_1 + x_2 V_2)]^3, \quad (14)$$

where R is Rao's constant given by $R_i = V_i c_i^{1/3}$.

It should be noted that earlier, purely empirical equations, including equations using Rao's and Wada's constants were extended to mixtures by Nomoto. Such empirical equations for predicting the speed of sound in liquid mixtures have been tested and compared by other authors [36,37] in a variety of organic and aqueous organic mixtures. Natta and Baccaredda [38] developed an intuitive model that describes the speed of sound in ideal mixtures by summing distances and propagation times in layers of the unmixed pure liquid components. Later on, using faulty thermodynamic arguments, Junjie [3] arrived at equivalent equations. The computed values of c_j and c_N values in comparison with the experimental values for the studied mixture are shown in figure 7. The results clearly indicate that the two expressions predict the experimental data extremely well.

4. Conclusions

Experimental ultrasonic velocity and density have been used successfully to compute molar volumes and compressibilities. The Redlich–Kister equation was used to fit the excess molar volumes. Hydrogen bonding and interstitial accommodation lead to negative partial excess molar volumes. It is clear from the PFP theory that both free volume and P^* contributions are negative with the studied system and only the interactional contribution is positive. A near agreement in the \bar{K}_2^0 and $\kappa_{S\phi,2}$ values of the solute in solution and pure liquid implies that the molecular volume of

the solute molecules is practically unaffected. Both equations of Nomoto and Junjie provide good support for a comparison between experimental and theoretical predictions of ultrasonic velocity values.

Acknowledgment

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

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