

Short communication

Excess molar volumes, viscosity deviations and isentropic compressibility changes in glycylglycine–NiCl₂ aqueous ethanol mixtures

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ABSTRACT

The densities, viscosities and ultrasonic velocities for glycylglycine–NiCl₂ in aqueous ethanol mixtures have been studied in the temperature range 288.15–318.15 K. The excess molar volumes, viscosity deviations and changes in isentropic compressibility for the binary mixtures have been calculated and discussed in terms of hydrogen bonding and structure-breaking effect. The computed results are fitted to the Redlich–Kister polynomial. The results clearly indicate that there is a strong association in the mixtures studied.

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1. Introduction

Electrolyte solutions are of fundamental importance to chemistry and biology as they form a basic matrix for technological fluids and the evolution and function of life. The transition metal salts in particular play an important role in the specific regulation of biomolecular processes. The interaction of polypeptides and proteins with metal salts has been the subject of considerable interest since Hofmeister's pioneering study of the preparation of hen lysozyme using different salts [1]. Earlier studies focused largely on the effect of ionic strength on the pH dependent denaturation of proteins [2–4], and on theoretical models of the metal ion–protein interactions [5]. In recent years, interest in the study of the interaction of metal salts with peptides has increased especially with the advent of de novo protein engineering. Since the discovery of metal-ion-induced α -helix formation using natural [6] and synthetic amino acids [7] as ligands, a wide variety of interactions of metals with polypeptides and proteins have been designed and explored [8–10]. There have been considerable upsurge in the theoretical and experimental investigations of excess thermodynamic properties of binary liquid mixtures [11,12]. Mixed aqueous solvents are used extensively in chemistry and other fields to control factors such as reactivity and stability of systems. Since volumetric, compressibility and viscosity studies are still scant, an attempt has been made here to understand the behavior of glycylglycine and NiCl₂ in aqueous ethanol mixtures at different temperatures

and compositions. Our interests in nickel chloride results from the role they play in many industrial processes. The simple salts of nickel are often considered to be very useful subjects for testing experimental rules and theoretical hypotheses. Nickel, with a coordination number six, combines with two moles of glycylglycine and displaces two hydrogen ions from each. Therefore the peptide linkage acts as an acidic group in coordination with a metal ion. Hence, we believe that a systematic study of the structural and energetic consequences of the interactions between water and ethanol will enable us to understand how water exercises thermodynamic and kinetic control over the chemical activities of peptide with metal salts in aqueous media. Therefore, it is of interest to study the dynamics of dipeptide-transition metal salt solution systems which would provide new insights and better understanding of this field of science. In continuation of our previous studies [13,14], we have measured the densities, viscosities and ultrasonic velocities for glycylglycine–NiCl₂ in aqueous ethanol mixture over a range of compositions in the temperature range 288.15–318.15 K. The excess molar volumes (V^E), viscosity deviations ($\Delta\eta$) and isentropic compressibility changes ($\Delta\kappa_S$) are reported. Through this paper, an attempt has been made to present variations occurring under diverse conditions.

2. Experimental

2.1. Materials

Glycylglycine and nickel(II) chloride hexahydrate of 99% purity were purchased from Sigma–Aldrich, Germany and Loba Chemi, Mumbai respectively. Commercially available glycylglycine of the

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highest purity purchased was used without further purification. Nickel(II) chloride hexahydrate 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 $1.29 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ was used for the preparation of solutions. Ethanol of analytical grade purity 99.9% used after distillation was purchased from Changshu Yanguan Chemicals, China. The solutions were prepared on a weight basis by using a Mettler balance having a precision of ± 0.01 mg. Care was taken to avoid evaporation and contamination during mixing. The temperature of water was controlled within ± 0.01 K using a thermostat. In our studies, glycyglycine and NiCl_2 were kept constant at $0.020 \text{ mol kg}^{-1}$ and 0.25 mol 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 $< 1 \times 10^{-4}$. 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

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 the 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 are 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 carbon tetrachloride. The maximum estimated error in ultrasonic velocity measurements was $\pm 0.08\%$. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled water bath. Densities were measured using the (Mettler Toledo) Density 30PX digital densitometer having a precision of $\pm 1 \times 10^{-3} \text{ kg m}^{-3}$ and an accuracy of $\pm 3 \times 10^{-3} \text{ kg m}^{-3}$. The densitometer was calibrated using double distilled water. The sample and reference resonator cells with minimum volumes of 0.5 cm^3 were thermostated to an accuracy of ± 0.01 K, and a previously described differential technique was employed for all measurements [15]. The physical parameters for aqueous ethanol solutions of glycyglycine– NiCl_2 were measured at four temperatures: 288.15 K, 298.15 K, 308.15 K, and 318.15 K. The measured values of viscosity and density and their uncertainties agreed well with the literature values [16]. Each measurement was repeated thrice and the reported values are an average of all three measurements.

3. Results

The densities, viscosities and ultrasonic velocities for glycyglycine– NiCl_2 in aqueous ethanol mixture as a function of mole fraction of ethanol at $T = 288.15\text{--}318.15$ K are presented in Table 1.

Isentropic compressibility (κ_S) was calculated using the formula,

$$\kappa_S = \frac{1}{u^2 \rho}, \quad (1)$$

where u is the ultrasonic velocity, and ρ is the density of the experimental liquid.

The excess functions have been evaluated using the following equations:

$$V^E = V - (V_1 x_1 + V_2 x_2), \quad (2)$$

Table 1

Density, ρ , viscosity, η , and ultrasonic velocity, u , for glycyglycine– NiCl_2 in aqueous ethanol mixture at $T = 288.15\text{--}318.15$ K, for different mole fractions, x_1 , of ethanol.

| x_1 | ρ ($\times 10^{-3} \text{ kg m}^{-3}$) | η (mPa s) | u (m s^{-1}) |
|---------------------|---|----------------|---------------------------|
| T = 288.15 K | | | |
| 0.00000 | 1.2971 | 1.42 | 1760.39 |
| 0.08572 | 1.2872 | 1.86 | 1768.21 |
| 0.17156 | 1.2699 | 2.37 | 1773.06 |
| 0.25724 | 1.2545 | 3.05 | 1779.54 |
| 0.34301 | 1.2336 | 3.95 | 1785.14 |
| 0.42887 | 1.2195 | 4.71 | 1791.37 |
| 0.51459 | 1.1911 | 4.92 | 1797.62 |
| 0.60033 | 1.1614 | 5.50 | 1806.87 |
| T = 298.15 K | | | |
| 0.00000 | 1.2585 | 1.28 | 1789.56 |
| 0.08572 | 1.2420 | 1.60 | 1796.37 |
| 0.17156 | 1.2224 | 2.14 | 1800.42 |
| 0.25724 | 1.2031 | 2.75 | 1804.65 |
| 0.34301 | 1.1835 | 3.43 | 1809.73 |
| 0.42887 | 1.1642 | 3.99 | 1815.69 |
| 0.51459 | 1.1449 | 4.26 | 1822.22 |
| 0.60033 | 1.1128 | 4.74 | 1829.07 |
| T = 308.15 K | | | |
| 0.00000 | 1.2199 | 1.14 | 1817.05 |
| 0.08572 | 1.1967 | 1.45 | 1822.31 |
| 0.17156 | 1.1735 | 1.85 | 1826.47 |
| 0.25724 | 1.1503 | 2.31 | 1831.54 |
| 0.34301 | 1.1271 | 2.88 | 1837.69 |
| 0.42887 | 1.1039 | 3.37 | 1843.82 |
| 0.51459 | 1.0810 | 3.63 | 1848.08 |
| 0.60033 | 1.0600 | 3.89 | 1855.26 |
| T = 318.15 K | | | |
| 0.00000 | 1.1813 | 1.03 | 1848.47 |
| 0.08572 | 1.1482 | 1.30 | 1855.06 |
| 0.17156 | 1.1151 | 1.60 | 1861.34 |
| 0.25724 | 1.0841 | 1.95 | 1867.81 |
| 0.34301 | 1.0504 | 2.48 | 1873.14 |
| 0.42887 | 1.0173 | 2.75 | 1880.53 |
| 0.51459 | 0.9842 | 2.94 | 1886.72 |
| 0.60033 | 0.9511 | 3.22 | 1894.88 |

$$\Delta\eta = \eta - (\eta_1 x_1 + \eta_2 x_2), \quad (3)$$

$$\Delta\kappa_S = \kappa_S - (\kappa_{S1} x_1 + \kappa_{S2} x_2), \quad (4)$$

where V , η and κ_S are the respective solution properties and V_1 , V_2 , η_1 , η_2 and κ_{S1} , κ_{S2} are the molar volumes, viscosities and isentropic compressibilities of the pure components, respectively.

The molar volume V is defined by the relation,

$$V = \frac{M_1 x_1 + M_2 x_2}{\rho}, \quad (5)$$

where M_1 and M_2 are the molecular masses of the pure substances and ρ is the density of the mixture.

Graphical representations of V^E , $\Delta\eta$, and $\Delta\kappa_S$ as a function of mole fraction of ethanol are given in Figs. 1–3.

The excess properties Y^E were fitted to the Redlich–Kister equation [17],

$$Y^E = x_1(1 - x_1) \sum A_j(1 - 2x_1)^j, \quad (6)$$

where A_0 , A_1 , A_2 ($j = 0, 1, 2$), are adjustable parameters. These parameters were evaluated by fitting $Y^E/x_1(1 - x_1)$ to Eq. (6) by the method of least squares. The values of these parameters along with the standard deviation $\sigma(Y^E)$ or Y^E as defined by the equation

$$\sigma(Y^E) = \left[\sum \frac{(Y_{\text{obs}}^E - Y_{\text{calc}}^E)^2}{N - M} \right]^{0.5}, \quad (7)$$

are recorded in Table 2 for glycyglycine– NiCl_2 in aqueous ethanol mixtures.

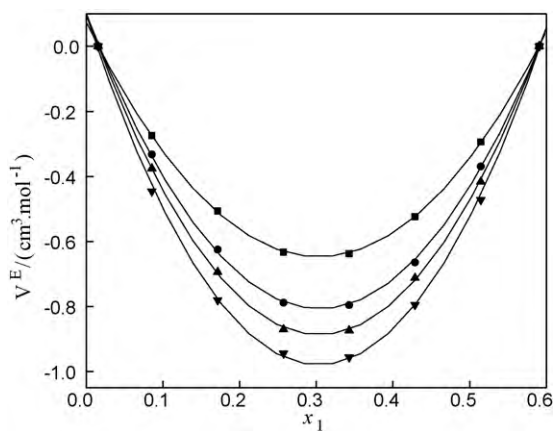


Fig. 1. Variation of V^E for glycylglycine–NiCl₂ in aqueous ethanol mixtures at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

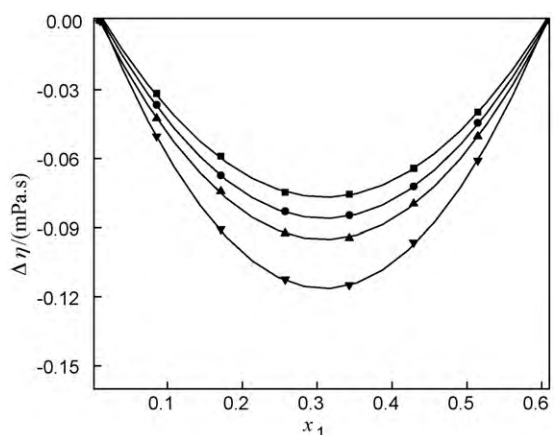


Fig. 2. Variation of $\Delta\eta$ for glycylglycine–NiCl₂ in aqueous ethanol mixtures at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

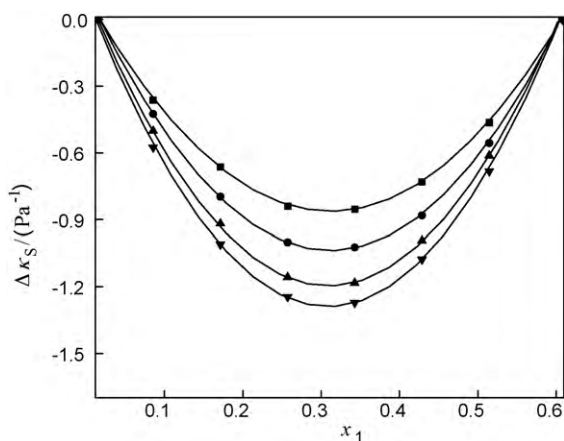


Fig. 3. Variation of $\Delta\kappa_S$ for glycylglycine–NiCl₂ in aqueous ethanol mixtures at different temperatures. (■) 288.15 K; (●) 298.15 K; (▲) 308.15 K; (▼) 318.15 K.

4. Discussion

4.1. Excess molar volume

The studied system shows negative V^E values over the entire range of mole fraction and temperatures (Fig. 1). Volume changes for a mixed system result from changes in the free volume of the liquid, since the bond lengths and bond angles of the molecules

Table 2

Coefficients of least-squares fit by Eq. (6) for excess molar volumes, viscosity deviations, and isentropic compressibility changes for glycylglycine–NiCl₂ in aqueous ethanol mixture at $T=288.15\text{--}318.15\text{ K}$.

| Property | T (K) | A ₀ | A ₁ | A ₂ | σ (Y ^E) |
|--|--------|----------------|----------------|----------------|---------------------|
| V^E (cm ³ mol ⁻¹) | 288.15 | -1.5672 | 0.7348 | -0.2134 | 0.004 |
| | 298.15 | -1.6237 | 0.8026 | -0.3263 | 0.004 |
| | 308.15 | -1.6683 | 0.8657 | -0.4372 | 0.004 |
| | 318.15 | -1.7129 | 0.9214 | -0.5594 | 0.005 |
| $\Delta\eta$ (mPa.s) | 288.15 | -0.8739 | -0.6856 | -0.0567 | 0.002 |
| | 298.15 | -0.7245 | -0.6417 | -0.0826 | 0.002 |
| | 308.15 | -0.5681 | -0.6025 | -0.1108 | 0.002 |
| | 318.15 | -0.4130 | -0.5658 | 0.0184 | 0.002 |
| $\Delta\kappa_S$ (Pa ⁻¹) | 288.15 | -0.7548 | 0.2247 | 0.1347 | 0.003 |
| | 298.15 | -0.7916 | 0.2465 | 0.0825 | 0.003 |
| | 308.15 | -0.8354 | 0.2712 | 0.0693 | 0.003 |
| | 318.15 | -0.8827 | 0.2977 | 0.0426 | 0.003 |

themselves do not vary. The mixing of ethanol with aqueous glycylglycine–NiCl₂ solution is expected to induce changes in hydrogen bonding equilibrium and electrostatic interactions with different contributions to the resultant volume of the mixture. The optimum packing in a system is directly related to the differences in molecular sizes and intermolecular interactions, in particular when hydrogen bonding occurs between unlike molecules creating associated complexes, as well as being affected by the breaking of interactions between like molecules. The investigated system contains all polar molecules and exhibit strong self and cross-associative behavior. Alcohols in mixtures may exhibit amphoteric behavior due to the homo-molecular and hetero-molecular hydrogen bonds, and the molecular interactions in their aqueous systems are complex and show some competition between like and unlike molecules. Moreover, the cell structure (H-bonded structure as in ice) of water weakens the dipole-induced dipole of O–H group on ethanol making the molecule more flexible around water and results in negative values of molar volumes [18]. One can reasonably assume from the observed minima in the curve that these negative values also indicate association through multiple hydrogen bonding between polar groups of ethanol and water. Although pure liquids are presumed to be highly structured, both are protic and ethanol is less protic than water. Hence, there is interaction among them, reducing the molar volume of the mixture considerably [19]. Strengthening of interactions between molecules of aqueous ethanol tend to result in a decrease in volume. Similarly, negative contribution to V^E can be attributed to formation of hydrogen bonds upon interaction of ethanol molecules with aqueous solution of glycylglycine and NiCl₂.

4.2. Viscosity deviations

Glycylglycine–NiCl₂ aqueous ethanol mixtures display negative deviation from ideality over the entire range of mole fraction and temperatures studied (Fig. 2). As the temperature increases the $\Delta\eta$ values become more negative and show greater deviation from ideality. The viscosity behavior corresponds to systems in which there is an associated component; a solute–solute complex is formed due to high stability and the solute–solvent interaction weakens this effect. The negative $\Delta\eta$ values can be interpreted qualitatively by considering the strengths of intermolecular hydrogen bonding, molecular size and shapes of the components. The highly associated aqueous glycylglycine–NiCl₂ mixture seems to undergo a structure-breaking effect when mixed with ethanol. However, ethanol and water molecules can hydrogen bond to one another. Mixing, in this case, involves breaking hydrogen bonds between water molecules, breaking hydrogen bonds between ethanol molecules, and making hydrogen bonds between water and

ethanol molecules. In a similar way, the glycylglycine molecule has H-bonding groups on the N-terminal and on the C-terminal. Together with these, the carbonyl oxygen has tendencies of forming partial hydrogen bonds with the solvents, i.e. water and ethanol. The negative contributions clearly indicate the participation of peptide groups in hydrogen bonding with water and ethanol. The electrostriction of neighboring water molecules around the charged centres of glycylglycine will be reduced in the presence of NiCl_2 . The electrostricted water enters the hydration sphere of these ions and not the bulk due to the presence of ethanol molecules which is less compressible, thus making a negative contribution. Hence, the negative contributions clearly indicate the participation of peptide groups in hydrogen bonding with water and ethanol. Moreover, the dispersion and dipolar forces between the two protic solvents water and ethanol may give rise to negative $\Delta\eta$ values [20].

4.3. Isentropic compressibility changes

The deviations in isentropic compressibility versus mole fraction of ethanol for the systems studied are given in Fig. 3. As observed from Fig. 3, the $\Delta\kappa_S$ values are negative over the entire range of composition and the temperatures. The negative deviations of $\Delta\kappa_S$ are observed in accordance with the packing propensity of the ethanol molecules in water. The compressibility measures the changes in the first two layers of solvent (water) around ethanol molecules [21] and assumes that ethanol molecule itself is compressible. On the other hand, in dilute solutions of ethanol the packing structures are more varied. The solution is predominantly composed of water–water interactions, which form a typical three-dimensional cage-like structure and probably embed both monomers of water or ethanol. The collapse of associated water structure when ethanol molecules are introduced is reflected in the specific compressibility values which rise from $4.54 \times 10^{-5} \text{ cm}^3/\text{g bar}$ (for pure water) to $1.469 \times 10^{-5} \text{ cm}^3/\text{g bar}$ (for ethanol). A more compact hydration layer is formed as strong hydrogen bonds are formed between water and ethanol which explains the minimum observed in the curve. Above this concentration, presumably the energy of the system is concentrated on fitting the ethanol molecules into the cavities formed by the associated water structure around them rather than increased ethanol–water interactions. At concentrations above the minimum compressibility starts to rise. This indicates that the mixtures are more compressible than the corresponding ideal mixture. The cage-like structure of water is increasingly disturbed by the introduction of increasing number of ethanol molecules to the solution. Due to these interactions, the ultrasonic velocity increases and the compressibility of the solution decreases. Moreover, $\Delta\kappa_S$ and V^E values become more negative as temperature increases. All these lead to a possible structural effect in the studied system [22].

From the above discussions, it is clear that there is a strong association in glycylglycine– NiCl_2 aqueous ethanol mixture and this interaction may be accompanied by a disruption of water and/or ethanol associated structures. Further, the viscosity deviations also indicate that the system undergoes structure-breaking effect when mixed with ethanol.

5. Conclusions

The above results clearly suggest that hydrogen bonding is the main cause for the negative values of excess molar volumes because of the weakening of the cell structure of water. The viscosity deviations suggest a structure-breaking effect which is due to the dispersion and dipolar forces between the two protic solvents leading to negative values. The change in isentropic compressibility indicates that the mixture is highly compressible and the cage-like structure of water is disturbed due to the presence of ethanol molecules which explains the negative values.

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