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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 $T = (288.15 \text{ to } 318.15)$ 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 $T = (288.15 \text{ to } 318.15)$ 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 $1.29 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ 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 $\pm 1 \times 10^{-3}\ \mathrm{kg\,m^{-3}}$. 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 $0.5\ \mathrm{cm}^3$ 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 $\mathrm{MnCl_2}$ were kept constant at $0.020\ \mathrm{mol\,kg^{-1}}$ and $0.25\ \mathrm{mol\,kg^{-1}}$, respectively. The physical parameters for glycylglycine–$\mathrm{MnCl_2}$ 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–$\mathrm{MnCl_2}$ in aqueous ethanol mixtures at $T = (298.15\ \text{to}\ 318.15)$ 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

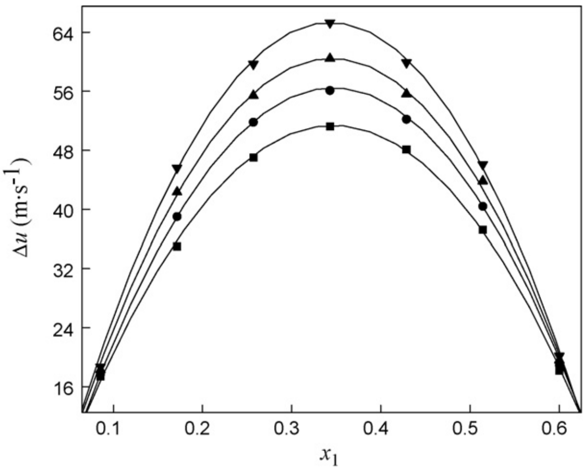

Fig. 1. Ultrasonic velocity deviation, Δu, for ($0.020\ \mathrm{mol\,kg^{-1}}$ glycylglycine + $0.25\ \mathrm{mol\,kg^{-1}}$ $\mathrm{MnCl_2}$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

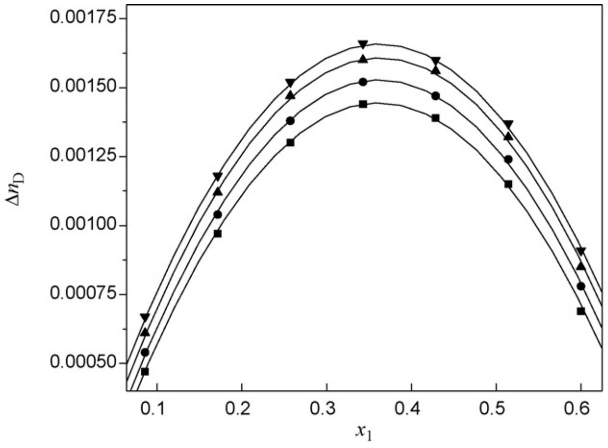

Fig. 2. Refractive index deviation, Δn_D, for ($0.020\ \mathrm{mol\,kg^{-1}}$ glycylglycine + $0.25\ \mathrm{mol\,kg^{-1}}$ $\mathrm{MnCl_2}$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.

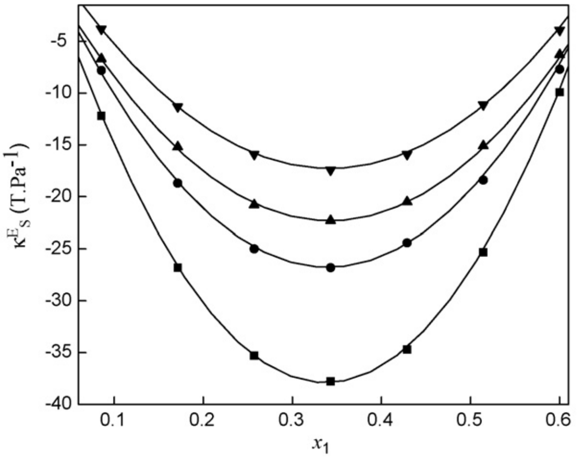

Fig. 3. Excess isentropic compressibility, κ_S^E, for ($0.020\ \mathrm{mol\,kg^{-1}}$ glycylglycine + $0.25\ \mathrm{mol\,kg^{-1}}$ $\mathrm{MnCl_2}$) in aqueous ethanol mixture at different temperatures: 288.15 K, ■; 298.15 K, ●; 308.15 K, ▲; 318.15 K, ▼.