

Partial molar volumes, expansibilities and compressibilities of glyglyglycine in aqueous sucrose and fructose solutions between 288.15 and 308.15 K

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ABSTRACT

Apparent molar volumes (V_{ϕ}) and apparent molar adiabatic compressibilities ($K_{\phi,s}$) of triglycine (glyglyglycine) in aqueous and mixed aqueous solutions of fructose and sucrose (2, 4, and 6 mass%) have been determined at 288.15, 293.15, 298.15, 303.15, and 308.15 K. From these data, limiting partial molar volumes (V_{ϕ}^0) and limiting partial molar adiabatic compressibilities ($K_{\phi,s}^0$) for glyglyglycine in aqueous sucrose and fructose solutions have been evaluated, together with the standard partial molar properties of transfer $\Delta_{tr}Y$ of the glyglyglycine from water to aqueous saccharides solutions. Transfer parameters have been interpreted in terms of solute–cosolute interactions on the basis of a cosphere overlap model. Pair and triplet interaction coefficients have also been calculated from transfer parameter data. The partial molar volume at infinite dilution (V_{ϕ}^0) were used to obtain the partial molar expansion at infinite dilution, E_2^0 , for glyglyglycine to examine the temperature dependence of such interactions.

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1. Introduction

The stabilization of native conformations of biological macromolecules is commonly related to several interactions including hydrogen bonding, electrostatic and hydrophobic interactions. These interactions are affected by the surrounding solutes and solvent of macromolecules; for this reason, the physico-chemical behaviours of proteins are strongly influenced by the presence of solutes. Volume and compressibility are fundamental thermodynamic observables that have been proven sensitive to solute hydration [1–4]. Volumetric measurements have been applied to characterizing conformational states of proteins, including the native, compact intermediate, fully and partially unfolded states [5–9]. Peptides are also among the building units of complex biomolecules such as proteins. Therefore the determination of various thermodynamic properties for aqueous and mixed aqueous solutions of peptides has occupied our attention [10–13]. The partial molar volume (V_{ϕ}^0) data at infinite dilution for the peptides are of particular interest because of their use in group additivity schemes to characterize the fully unfolded proteins [11,14].

Despite the significance of partial molar volume measurements, a complete understanding of such hydration phenomenon requires determination of the partial molar expansibility and compressibility. Such measurements are scarce [15–18]. In a recent paper [18],

we described the partial molar volumes (V_{ϕ}^0) and partial molar adiabatic compressibilities ($K_{\phi,s}^0$) of glyglyglycine at infinite dilution in aqueous and mixed aqueous solutions of glucose from high precision density and sound speed measurements. In continuation of the previous study, the present paper reports partial molar volume (V_{ϕ}^0) and partial molar adiabatic compressibility ($K_{\phi,s}^0$) at infinite dilution of glyglyglycine (0.03–0.10 mol kg⁻¹) in pure water to 6 mass% of sucrose and fructose at temperatures: 288.15, 293.15, 298.15 K, 303.15 and 308.15 K. The corresponding transfer functions and partial molar expansions are also reported. These results were combined with the results of our previous work [18] to obtain a better understanding of the hydration of biological systems. The results have been discussed in terms of various solute–solvent and solute–solute interactions.

2. Experimental

The peptide triglycine (glyglyglycine) (G1377) (minimum assay 98.0%) of highest purity was obtained from Sigma Chemicals Co., and was used as such without further purification. However, before use this was dried over P₂O₅ under vacuum at room temperature. Analytical reagent grade saccharides: sucrose (minimum assay 98.0%) from Hi Media, Mumbai and fructose (minimum assay 98.0%) from Loba Chemie Pvt. Ltd., were used after drying at 333.15 K in a vacuum oven for a minimum of 48 h. All solutions were prepared by using deionized doubly glass-distilled water (having specific conductance less than 10⁻⁶ S) that had been freshly degassed by vacuum pump. Solutions of saccharides were pre-

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pared by mass in the range 2–6% and used on the day they were prepared. Solutions of glyglyglycine in the concentration range 0.03–0.10 mol kg⁻¹ were made by mass on the molality concentration scale with an accuracy of $\pm 1 \times 10^{-5}$. The weighings were done on an A&D Company, Limited electronic balance (Japan, Model GR-202) with a precision of ± 0.01 mg. The uncertainties in the solution molalities were in the range $\pm 2 \times 10^{-5}$ mol kg⁻¹. Densities (ρ) and speeds of sound (u) of glyglyglycine in aqueous sucrose and fructose solutions at different temperatures were measured simultaneously and automatically, using an Anton Paar DSA 5000 instrument. Both speed of sound and density are extremely sensitive to temperature, so it is controlled to $\pm 1 \times 10^{-2}$ K by built-in-solid state thermostat. Before each series of measurements, the instrument was calibrated at temperatures: 288.15, 293.15, 298.15, 303.15, and 308.15 K with doubly distilled water and dry air. The sensitivity of instrument corresponded to a precision in density and speed of sound measurements of $\pm 1 \times 10^{-6}$ g cm⁻³ and $\pm 1 \times 10^{-2}$ m s⁻¹, respectively. The reproducibility of density and speed of sound was found to be better than $\pm 5 \times 10^{-6}$ g cm⁻³ and $\pm 5 \times 10^{-2}$ m s⁻¹, respectively.

3. Results and discussion

3.1. Apparent molar volume and apparent molar adiabatic compressibility

Densities (ρ) and speeds of sound (u) of solutions are listed in Table 1. Apparent molar volumes (V_ϕ) and apparent molar adiabatic compressibilities ($K_{\phi,s}$) of glyglyglycine were calculated using accurate density and speed of sound data through the following equations:

$$V_\phi = \left\{ \frac{M}{\rho} \right\} - \left\{ \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \right\} \quad (1)$$

$$K_{\phi,s} = \left\{ \frac{M\beta_s}{\rho} \right\} - \left\{ \frac{1000(\beta_{s,0}\rho - \beta_s\rho_0)}{m\rho\rho_0} \right\} \quad (2)$$

where M is the molar mass of the solute (glyglyglycine), ρ_0 , ρ , $\beta_{s,0}$ and β_s are the densities and coefficient of adiabatic compressibilities of saccharide + water and glyglyglycine + saccharide + water, respectively, and m is the molality of glyglyglycine in glyglyglycine + saccharide + water.

The coefficient of adiabatic compressibility (β_s) was determined from the sound speed (u) and density (ρ) data by using the equation:

$$\beta_s = \frac{1}{u^2\rho} \quad (3)$$

The results obtained using Eqs. (1) and (2) are listed in Table 2. Infinite dilution apparent molar volumes (V_ϕ^0) and apparent molar adiabatic compressibilities ($K_{\phi,s}^0$), which are equal to standard partial molar volumes and standard partial molar adiabatic compressibilities, were obtained by least squares fitting of experimental data to the following equation:

$$Y_\phi = Y_\phi^0 + S_Q m \quad (4)$$

where Y_ϕ^0 (denotes V_ϕ^0 or $K_{\phi,s}^0$) is the infinite dilution apparent molar property (equal to standard partial molar property) and S_Q (S_Q denotes S_V or S_K) is the experimental slope. The resulting values of V_ϕ^0 , $K_{\phi,s}^0$, S_V and S_K are summarized in Table 3. At infinite dilution, the solute–solute interaction is negligible; therefore, the standard partial molar property and its temperature dependence provide valuable information of the solute–solvent interactions [19–21]. Table 3 shows that glyglyglycine has positive V_ϕ^0 and negative $K_{\phi,s}^0$ values in aqueous fructose and sucrose solutions as in case of glucose [18], which indicates the presence of strong solute–solvent

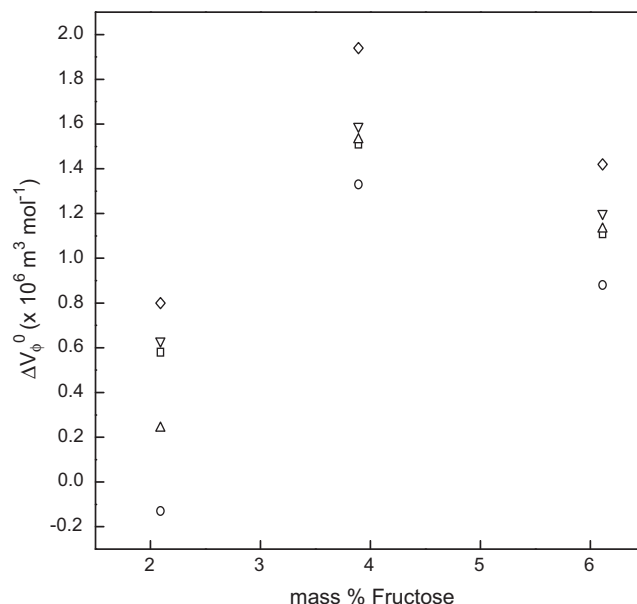


Fig. 1. Variation of partial molar volume of transfer at infinite dilution for glyglyglycine in aqueous fructose solution at: (□) 288.15 K, (○) 293.15 K, (△) 298.15 K, (▽) 303.15 K, and (◇) 308.15 K.

interactions [22]. The V_ϕ^0 and $K_{\phi,s}^0$ values increase with increase in temperature in aqueous saccharide solutions, indicating the presence of strong solute–solvent interactions as the temperature of the solution increases. This may be due to the reduced electrostriction of water as a result of the zwitterionic groups of the glyglyglycine. The V_ϕ^0 values first increase up to 4 mass% of aqueous fructose solution and then decrease at higher mass percentages and reverse trend has been observed in aqueous sucrose solutions. The overall values of V_ϕ^0 in aqueous saccharide solutions follow the order: sucrose > fructose > glucose [18].

It indicates the presence of strong interaction of tripeptide with disaccharide sucrose as compared to monosaccharides glucose [18] and fructose.

The experimental slopes S_V values are influenced by number of effects [23]. The magnitude of the slope is related to the solute–solute interactions. As can be seen from Table 3 that the values of slope are negative in aqueous sucrose solutions and 4 mass% of fructose suggesting weak solute–solute interactions. $K_{\phi,s}^0$ values for glyglyglycine are negative in aqueous fructose and sucrose solutions and their magnitude are less than the corresponding values in water as for glucose solutions [18].

Partial molar properties of transfer at infinite dilution of glyglyglycine from water [18] to aqueous saccharide solutions were calculated from:

$$\Delta_{tr} Y = Y_\phi^0(\text{in aqueous saccharide solutions}) - Y_\phi^0(\text{in water}) \quad (5)$$

The values are given in Table 4 and represented in Figs. 1 and 2.

3.2. Dependence of volumetric properties on saccharides

It can be seen from Figs. 1 and 2 that ΔV_ϕ^0 values are positive for glyglyglycine in aqueous fructose (except at $T=303.15$ K in lower mass percentage) and sucrose solutions at all temperatures. A positive ΔV_ϕ^0 can be explained on the basis that the saccharides interact with the charged centers of tripeptide, thereby leading to a reduction in their electrostriction of the solvent and, hence, a positive volume of transfer. The values of ΔV_ϕ^0 first increase from 2 to 4 mass percentage of fructose and then

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