Physicochemical study of solute–solute and solute–solvent interactions of glycine, L-alanine, L-valine and L-isoleucine in aqueous-D-mannose solutions at temperatures from 293.15 K to 318.15 K

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A B S T R A C T

Densities, ρ, ultrasonic speeds, u, and viscosities, η of aqueous-D-mannose (2.5% and 5% of D-mannose, w/w in water) and of solutions of glycine, L-alanine, L-valine and L-isoleucine in aqueous-D-mannose solvents were measured at temperatures (293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K and at atmospheric pressure. These experimental values have been used to calculate the apparent molar volume, V_ϕ, limiting apparent molar volume, V_ϕ° and the slope, S_v, apparent molar compressibility, $K_{s,\phi}$, limiting apparent molar compressibility, $K_{s,\phi}^\circ$ and the slope, S_k, transfer limiting apparent molar volume, $V_{\phi,tr}^\circ$, transfer limiting apparent molar compressibility, $K_{s,\phi,tr}^\circ$, hydration number, n_H, Falkenhagen coefficient, A, Jones–Dole coefficient, B, and temperature derivative of B-coefficient, dB/dT. The Gibbs free energies of activation of viscous flow per mole of solvent, $\Delta\mu_1^{\circ\#}$ and per mole of solute, $\Delta\mu_2^{\circ\#}$ were also calculated. The results are interpreted in terms of solute–solvent and solute–solute interactions in these systems. The structure-making/breaking ability of the amino acids has also been discussed in terms of the sign of dB/dT. Furthermore, the values of V_ϕ°, $K_{s,\phi}^\circ$, $V_{\phi,tr}^\circ$, $K_{s,\phi,tr}^\circ$, B and $\Delta\mu_2^{\circ\#}$ have been split into groups' contributions of the amino acids using linear correlation with number of carbon atoms in the alkyl chain of the amino acids.

1. Introduction

Studies in the stability of proteins have generated a great interest for a long time, but because of complications due to their complex structures and large molar mass, their low molar mass model compounds are generally taken for investigations [1,2]. Physicochemical properties of amino acids in mixed aqueous media are important in investigating the solute–solvent and solute–solute interactions, which help in understanding the complex mechanism of molecular interactions occurring in various biochemical processes in the human body [3–7]. But due to complicated structure of proteins the study of their interactions are somewhat difficult, therefore, the physicochemical properties of amino acids, peptides and their derivatives in aqueous solutions have been extensively studied to gain a better understanding of solute–solvent interactions and their role in the conformational stability of proteins [8–12].

It is well known [13,14] that various substances cause changes in the conformation of proteins when present in aqueous-protein solutions. The additives, like sugars, alcohols, polyhydroxy alcohols, *etc.* decrease the denaturation of proteins [13], in particular, sugars help in stabilizing the native conformation of globular proteins [14]. This stabilizing ability of different sugars depends on the number of hydroxyl groups present in them. Back et al. [15] and Fujita et al. [16] studied the effect of a variety of sugars on the thermal transition of lysozyme and other proteins and enzymes and tried to correlate the stabilizing effect of sugars and polyols to the number and configuration of the OH groups present in them. Several physicochemical properties of constituent amino acids in aqueous and mixed aqueous solutions have been used by various researchers to investigate solute–solute and solute–solvent interactions [3–12,17,18].

In continuation to our earlier studies [19–25] on amino acids in aqueous-carbohydrate solutions, we report here the densities, ρ, ultrasonic speeds, u, and viscosities, η of aqueous-D-mannose (2.5% and 5% of D-mannose, w/w in water) and of solutions of glycine, L-alanine, L-valine and L-isoleucine in aqueous-D-mannose solvents were measured at 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K and at atmospheric pressure. These experimental data have been used to calculate the values of various parameters, *viz.*, V_ϕ, V_ϕ°, S_v, $K_{s,\phi}$, $K_{s,\phi}^\circ$, S_k, $V_{\phi,tr}^\circ$, $K_{s,\phi,tr}^\circ$, n_H, Coefficient A, Coefficient B and dB/dT. These parameters have been used to discuss the

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solute–solute and solute–solvent interactions in these systems. The Gibbs free energies of activation of viscous flow per mole of solvent, $\Delta\mu_1^{\circ\#}$ and per mole of solute, $\Delta\mu_2^{\circ\#}$ were also calculated are discussed in terms of transition state theory. Furthermore, the values of V_ϕ°, $K_{s,\phi}^\circ$, $V_{\phi,tr}^\circ$, $K_{s,\phi,tr}^\circ$, B and $\Delta\mu_2^{\circ\#}$ have been split into groups' contributions of the amino acids using linear correlation with number of carbon atoms in the alkyl chain of the amino acids.

2. Experimental

Glycine, L-alanine and L-valine (SRL, India, purity > 99%) and L-isoleucine (Thomas Baker, India, mass fraction purity > 0.99) were used after recrystallization from ethanol–water mixture and dried in vacuum over P_2O_5 at room temperature for 72 h. The purity of the purified amino acids was checked by performing gas chromatography analysis using Shimadzu Gas Chromatograph (Model: GC-2010 Plus). The D-mannose (SRL, India, mass fraction purity > 0.99) was used as received without further purification, except drying in oven for 24 h. The final purities and other specifications of the chemicals used are given in Table 1. The aqueous-D-mannose solvents (2.5% and 5% of D-mannose, w/w in water) were prepared using triple distilled water (conductivity less than 1×10^{-6} S·cm^{-1}) and these were used as solvents to prepare amino acid solutions of six different molal concentrations (ranging from 0 to 0.15) m. The weighing was done on an electronic balance (Model: GR-202R, AND, Japan) with a precision of ±0.01 mg. The solutions were prepared with care and stored in special airtight bottles to avoid contamination and evaporation. The uncertainty in the molality of the solutions was estimated within ±1 × 10^{-4} mol·kg^{-1}.

The densities of the solutions were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ~10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The densities of pure water used in the calibration at required temperatures were taken from the literature [26]. The uncertainty in density measurements was within ±0.60 kg·m^{-3}. The ultrasonic speeds in the solutions were measured using a single-crystal variable-path multifrequency ultrasonic interferometer (Model: M-81DS, Mittal Enterprises, India) having stainless steel sample cell (with digital micrometer) operating at 3 MHz. The uncertainty in ultrasonic speed measurements was within ±1.5 m·s^{-1}. The viscosities of the solutions were measured by using Ubbelohde type suspended level viscometer. The viscometer was calibrated by using triple distilled water. The viscosities of pure water for calculations of viscosity at required temperatures were taken from the literature [27]. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The times of flow were recorded in triplicate with a digital stopwatch with an accuracy of ±0.01 s and the results were averaged. The uncertainty in viscosity measurements was within ±1.1%. The temperature of the test

solutions during the measurements was maintained to an accuracy of ±0.01 K in an electronically controlled thermostatic water bath (JULABO, Model: ME-31A, Germany).

3. Results

The experimental values of density, ρ, ultrasonic speed, u, and viscosity, η of aqueous-D-mannose solvents and of solutions of amino acids in aqueous-D-mannose as functions of amino acid/D-mannose concentration and temperature are listed in Tables 2–4. The experimental data of ρ and η have been compared with the available values in the literature at (298.15, 308.15 and 318.15) K. The comparison has been given graphically as Figs. S1 and S2 in the Supplementary Material along with the citations. The comparison is found good in general, except few data points. However, the deviations were found within the stated uncertainty limits.

3.1. Apparent molar volume and compressibility

The ultrasonic speed may be considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed; in which case, the ultrasonic absorption of the acoustic waves is negligible [28]. The apparent molar volume, V_ϕ and apparent molar compressibility, $K_{s,\phi}$ of these solutions were calculated by using the relations

$$V_\phi = \frac{1000(\rho_o - \rho)}{m\rho\rho_o} + \frac{M}{\rho} \tag{1}$$

$$K_{s,\phi} = \frac{1000(\kappa_s\rho_o - \kappa_s^o\rho)}{m\rho\rho_o} + \frac{\kappa_s M}{\rho} \tag{2}$$

where m is the molal concentration of the amino acid (glycine/L-alanine/L-valine/L-isoleucine), ρ and ρ_o are the densities of the solution and the solvent (aqueous-D-mannose), respectively; M is the molar mass of the amino acid, and κ_s and κ_s° are the isentropic compressibility of the solution and the solvent (aqueous-D-mannose), respectively, calculated using the relation

$$\kappa_s = 1/u^2\rho \tag{3}$$

The values of V_ϕ and $K_{s,\phi}$, as functions of amino acid concentration and temperature, are shown graphically as Figs. S4—S7 in the Supplementary Material. It is observed that, for these amino acids in aqueous-D-mannose solvents, the curves of V_ϕ and $K_{s,\phi}$ vs. m (Figs. S4—S7) are found to be almost linear in the studied concentration range and at each investigated temperature.

3.2. Limiting apparent molar volume and compressibility

The values of limiting apparent molar volume, V_ϕ° and the slope, S_v, limiting apparent molar compressibility, $K_{s,\phi}^\circ$ and the slope, S_k have been obtained using method of linear regression of V_ϕ and $K_{s,\phi}$ vs. m from the following relations [29]

Table 1
Specification of chemical samples.

Chemical name (CAS number)	Provenance	Purification method	Final mass fraction purity	Analysis method
Glycine (50-40-6)	SRL, India	Re-crystallization	>0.998	GC[a]
L-Alanine (56-41-7)	SRL, India	Re-crystallization	>0.996	GC
L-Valine (72-18-4)	SRL, India	Re-crystallization	>0.996	GC
L-Isoleucine (72-32-5)	Thomas Baker, India	Re-crystallization	>0.994	GC
D-Mannose (3458-28-4)	SRL, India	Used as received	>0.99	–

[a] GC = Gas chromatography.