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Volumetric, ultrasonic, and viscometric behaviour of glycine, DL-alanine, and L-valine in aqueous 1,4-butanediol solutions at different temperatures

Anil Kumar Nain [a,*], Dinesh Chand [b]

[a] Department of Chemistry, Dyal Singh College, University of Delhi, New Delhi 110 003, India
[b] Department of Chemistry, Amity School of Engineering, Amity University, Sector 125, Noida 201303, U.P., India

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ABSTRACT

Densities, ρ, ultrasonic speeds, u, and viscosities, η, of aqueous-1,4-butanediol (20% and 40% w/w of 1,4-butanediol) and of solutions of glycine (Gly), DL-alanine (Ala), and L-valine (Val) in aqueous-1,4-butanediol were measured at $T = (298.15, 303.15, 308.15, 313.15,$ and $318.15)$ K. From these experimental results, apparent molar volume, V_ϕ, limiting apparent molar volume, V_ϕ° and the slope, S_v, apparent molar compressibility, κ_ϕ, limiting apparent molar compressibility, κ_ϕ°, and the slope, S_k, transfer volume, $V_{\phi,\mathrm{tr}}^\circ$, Falkenhagen coefficient, A, Jones–Dole coefficient, B, 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 calculated. The results are interpreted from the point of view of solute–solvent and solute–solute interactions in these systems. It has been observed that there exist strong solute–solvent interactions in these systems, which increase with rise in temperature. For the amino acids studied, the values of V_ϕ° follow the order: Gly < Ala < Val, indicating that the increased hydrophobic/non-polar character of the side chain of these amino acids causes a reduction in electrostriction at the terminal charged groups. These amino acids act as structure-breakers in aqueous-1,4-butanediol solvents. The thermodynamics of viscous flow has also been discussed.

1. Introduction

Hydration of proteins plays a significant role in the stability, dynamics, structural characteristics, and functional activity of these biopolymers. Since proteins are large complex molecules, the direct study of protein–water interactions is difficult. Therefore, one useful approach is to investigate interactions of the model compounds of proteins, *i.e.*, amino acids in aqueous and mixed-aqueous solutions [1–4]. Since amino acids are the building blocks of all living organisms and incorporate structural features of proteins, their physicochemical and thermodynamic properties in aqueous solutions are found to provide valuable information on solute–solute and solute–solvent interactions that are important in understanding the stability of proteins. Some of these interactions are found implicated in several biochemical and physiological processes in a living cell [5]. The choice of water for preparing mixed solvent stems from its important and unique role in determining the structure and stability of protein since its presence is known to give rise to hydrophobic forces [6], which are of prime importance in stabilizing the native globular structure of protein [7].

It is known [8,9] that polyhydric alcohols increase the thermal stability of proteins or reduce the extent of their denaturation by other substances. The alkanediols have wide range of applications in pharmacology and cosmetic industry; however, they are not components of living organisms, but they act as a vehicle for pharmaceuticals or cosmetics when introduced into living organisms [10]. Thus, the properties of amino acids in aqueous-polyols solutions are essential for understanding the chemistry of biological systems [11–13] in the presence of these media.

In continuation to our earlier studies [14–17], we report here the densities, ρ, ultrasonic speeds, u, and viscosities, η of (0.025, 0.05, 0.075, 0.1, 0.125, 0.15, 0.2, and 0.25) m glycine (Gly), DL-alanine (Ala), and L-valine (Val) in aqueous-1,4-butanediol (20% and 40% 1,4-butanediol, w/w) at $T = (298.15, 303.15, 308.15, 313.15,$ and $318.15)$ K. These experimental results 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, κ_ϕ, limiting apparent molar compressibility, κ_ϕ° and the slope, S_k, transfer volume, $V_{\phi,\mathrm{tr}}^\circ$, Falkenhagen coefficient, A, Jones–Dole coefficient, B, temperature derivative of B-coefficient, $\mathrm{d}B/\mathrm{d}T$ and hydration number, H_n. These parameters have been used to discuss the solute–solvent/co-solvent and solute–solute interactions in the aforementioned systems. Furthermore, the free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{\circ\#}$ per mole of solute, and $\Delta\mu_2^{\circ\#}$ for these amino acids in aqueous-1,4-butanediol solvents were also calculated. The thermodynamics of viscous flow has also been discussed.

* Corresponding author. Tel.: +91 11 24365948; fax: +91 11 24365606.
E-mail address: ak_nain@yahoo.co.in (A.K. Nain).

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2. Experimental

Glycine (E. Merck, mass fraction purity 0.997), DL-alanine (E. Merck, 0.99), and L-valine (Loba Chemie, 0.99) were used after recrystallization from ethanol–water mixture and dried in vacuum over P_2O_5 at room temperature for 72 h. 1,4-Buatnediol (E. Merck, Germany, mass fraction purity >0.990) was used as such without further purification, except drying over 0.4 nm molecular sieves. The mixed solvents aqueous-1,4-butanediol (20% and 40% 1,4-butanediol, w/w) were prepared using triply distilled water (conductivity less than $1 \cdot 10^{-6}$ S · cm^{-1}) and were used as solvents to prepare amino acid solutions of different molal concentrations (0.025, 0.05, 0.075, 0.1, 0.125, 0.15, 0.2, and 0.25) *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 utmost care and stored in special airtight bottles to avoid contamination and evaporation.

The densities of the mixed solvent and the amino acid solutions were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ~10 cm^3. 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 uncertainty in density measurements was within ±0.02 kg · m^{-3}. The ultrasonic speeds in the mixed solvent and the amino acid solutions were measured using a single-crystal variable-path multi-frequency ultrasonic interferometer (Model: M-84, Mittal Enterprises, Delhi, India) with stainless steel sample cell operating at 3 MHz. The uncertainty in ultrasonic speed measurements was within ±0.03%. The viscosities of the mixed solvent and the amino acid solutions were measured by using Ubbelohde type suspended level viscometer. 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 time of flow were recorded in triplicate with a digital stopwatch with an accuracy of ±0.01 s. The uncertainty in viscosity measurements was within $\pm 1 \cdot 10^{-6}$ N · s · m^{-2}. 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-31 A, Germany).

3. Results and discussion

The experimental values of density, ρ, ultrasonic speed, *u*, and viscosity, η of glycine (Gly), DL-alanine (Ala), and L-valine (Val) in aqueous-1,4-butanediol (20% and 40% 1,4-butanediol) as functions of amino acid concentration and temperature are listed in tables 1 and 2. The apparent molar volumes, V_ϕ and apparent molar compressibility, κ_ϕ of the amino acids in aqueous-1,4-butanediol were calculated by using the relations

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

$$\kappa_\phi = \frac{1000(\kappa_s\rho_\circ - \kappa_s^\circ\rho)}{m\rho\rho_\circ} + \frac{\kappa_s M}{\rho}, \tag{2}$$

where *m* is the molal concentration of the solute (amino acid), ρ and ρ_o are the densities of the solution and the solvent (aqueous-1,4-butanediol), respectively; *M* is the molar mass of the solute (amino acid), and κ_s and κ_s° are the isentropic compressibility of the solution and the solvent (aqueous-1,4-butanediol), respectively, calculated using the relation,

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

The values of V_ϕ and κ_ϕ as functions of amino acid concentration and temperature are shown graphically in figures 1 to 4. The values of V_ϕ are positive and increase with increase in temperature (figures 1 and 2). For each amino acid in both the solvent systems, V_ϕ and κ_ϕ *vs. m* curves (figures 1 to 4) were found to be almost linear over the concentration range studied and at each temperature investigated. The values of V_ϕ° and κ_ϕ° were obtained using the relations [18]

$$V_\phi = V_\phi^\circ + Sm, \tag{4}$$

$$\kappa_\phi = \kappa_\phi^\circ + S_k m, \tag{5}$$

where the intercepts, V_ϕ° or κ_ϕ°, by definition are free from solute–solute interactions and therefore provide a measure of solute–solvent interactions, whereas the experimental slope, S_v or S_k provides information regarding solute–solute interaction, and were obtained by using linear regression of V_ϕ and κ_ϕ *vs. m* from equations (4) and (5), respectively. The values of V_ϕ°, S_v, κ_ϕ°, and S_k along with the standard deviations of linear regression, σ for all the three amino acids at different temperatures are listed in table 3. The trends observed in V_ϕ° values of amino acids in aqueous-1,4-butanediol may be due to their hydration behaviour, which comprises of following interactions in these systems [11,19–24]:

(a) The terminal groups of zwitterions of amino acids, NH_3^+, and COO^- are hydrated in an electrostatic manner, and the interaction between zwitterions and hydroxyl groups of 1,4-butanediol.
(b) The overlap of hydration co-spheres of terminal NH_3^+ and COO^- groups and of adjacent groups results in volume change. The V_ϕ° values increase due to reduction in the electrostriction at terminals, whereas it decreases due to disruption of side group hydration by that of the charged end.

A perusal of table 3 reveals that the values of V_ϕ° are positive and they increase with the rise in temperature for all three amino acids in aqueous-1,4-butanediol solutions suggesting strong solute–solvent interactions. The observed positive V_ϕ° values indicate that the ion–hydrophilic and hydrophilic–hydrophilic group interactions exist in these systems. Interaction of two –OH groups of 1,4-butanediol with amino acid zwitterions are localized at the head groups, which decreases the electrostriction of water caused by the charged centres of amino acids, resulting in an increase in volume. The V_ϕ° values also increase with the rise in 1,4-butanediol concentrations due to increased 1,4-butanediol–amino acid interactions. Similar trends in V_ϕ° have also been reported by Ali *et al.* [25] for Gly in (water + 1,2-butanediol/1,2-propanediol/1,3-butanediol) solutions and Banipal *et al.* [26] for Gly and Ala in (water + 1,2-propanediol) solutions.

The V_ϕ° values are in the sequence: Gly < Ala < Val, which is also the order of the size of the side chain (hydrophobic group) of these amino acids, *i.e.*, the increase in V_ϕ° may be attributed to the increased hydrophobic/non-polar character of the side chain of these amino acids causing a reduction in electrostriction at the terminal charged groups. Banipal *et al.* [27] reported similar trends in V_ϕ° values with increasing size of the side chain of these amino acids and Ali *et al.* [28] also reported similar trends for these amino acids in aqueous-glycerol solutions. The V_ϕ° values (table 3) increase with rise in temperature for all the three amino acids studied, which can be explained by considering the size of primary and secondary solvation layers around the dipolar ions. At higher temperatures, the solvent from the secondary solvation layer is released into the bulk of the solvent, resulting in the expansion of the solution [28,29], as inferred from larger V_ϕ° values at higher temperatures.

The values of κ_ϕ are negative (figures 3 and 4) for all the three amino acids in aqueous-1,4-butanediol solutions, indicating that the water molecules around ionic charged groups of amino acids are less compressible than the water molecules in the bulk solution [30,31]. This further support the conclusion that the interaction of