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Effect of hydrophilic additives on volumetric and viscosity properties of amino acids in aqueous solutions at T = (283.15 to 333.15) K

Nandhibatla V. Sastry *, Pinakin H. Valand, Pradip M. Macwan

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388120, Gujarat, India

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ABSTRACT

Apparent molar volumes and partial molar volumes at infinite dilution, $\overline{V}_2^\circ$ for amino acids (glycine, L-valine, L-leucine, L-phenylalanine, and L-aspargine) aqueous solutions in sucrose (0.05 to 0.2 (w/w)), urea (0.05), 2,3-butane diol (0.05) and 2-butoxyethanol (0.05) as additives have been calculated from the experimental densities at T = (283.15 to 233.15) K. Limiting partial molar expansibilities, E_2°, side chain partial molar volumes, $\overline{V}_{2,\mathrm{tr}}^\circ$ and transfer volumes (from water to aqueous additive environment), $\Delta V_{\mathrm{tr}}^\circ$ for both the amino acids and their side chains have also been calculated. Relative viscosities for same systems were also calculated over the same temperature range and were analyzed in terms of Jones–Dole equation to calculate *B*-coefficients. The analysis of volumetric functions and *B*-coefficients suggests that the solute–co-solute interactions are more favored at elevated temperatures and in presence of high concentration of sucrose. Otherwise the hydrophobic side chains facilitate the solute–solute interactions and also time induced hydrophobic hydration in the bulk water.

1. Introduction

The volumetric and thermodynamic properties of simple organic compounds of several types that model the protein structure have been extensively investigated for their thermo-physical behavior in aqueous media. For example, there is a great deal of literature on the aqueous solutions of either amino acids, or N-acetyl amino acid amides, or tripeptides of type gly-X-gly, or cyclic dipeptides and or diketopiperizines. Amino acids are the model compounds with structures that mimic the peptide back bone chains of biological macromolecules such as globular proteins. A review of literature shows that the integral enthalpies [1,2], ultrasonic velocity and absorption [3], apparent molar volumes [1,4–14], heat capacities [1,6,12–15] and viscosities [4,5,9] of either some amino acids, or di- and tri-peptide aqueous solutions in absence or presence of additives such as t-butanol [1], urea [2,13–15], glycerol [4], 1,2-propane diol [5], and sugars [6–9] have been measured and the respective transfer functions corresponding to change from water to aqueous additive environment were derived. These studies concluded that interesting interactions are possible in these systems depending on the nature of the amino acid side chain and co-solute. The relative predominance of hydrophilic and hydrophobic interactions between amino acids in aqueous alcohol (TBA) solutions was found to be highly dependent on the mole fraction of the additive. For example it was suggested that in the lower alcohol mole fraction, the overlapping of the co-spheres of respective solute molecules occurs and the same would squeeze out the water molecules usually from the hydrophobic hydration sphere of alcohol, while on the other hand, at higher alcohol concentrations, hydrogen bonding between zwitterions of amino acid molecules and hydroxyl group of alcohol dominates. Similarly, the side chains in amino acids facilitate the hydrophobic hydration around alkyl chains of alcohols. Urea, which has a typical carbamide structure and its interaction with the amino acids (with longer alkyl side chains) may lead to both exothermic (due to the direct interaction between the zwitterion ($-\mathrm{CHCOO}^-\!-\mathrm{NH}_3^+$) structures of amino acid and polar groups of urea) or endothermic effects (caused by the partial dehydration of hydration shells around amino acid and urea co-spheres). Simple sugar molecules such as glucose is a polyhydroxy compound and its addition to amino acid (with short alkyl chains) aqueous solutions were found to enhance the zwitterions ($-\mathrm{CHCOO}^-$ and NH_3^+) – hydrophilic –OH group interactions and almost eliminate the effects of hydrophilic–hydrophobic interactions between the –OH group of glucose or water and non-polar alkyl chain of amino acids, at higher concentrations. Sucrose molecules have a ring structure and have several –OH groups and therefore are reported to interact weakly with L-glycine and L-alanine as compared to glucose, at room temperature. However, in aqueous solutions of amino acids (with long alkyl chains), the same additive especially at its high concentration interact with the water molecules probably via the hydrogen bonding. The above observations are based on data mostly collected at temperatures ranging from (288.15 to 308.15) K. The hydration (either of the hydrophilic or

* Corresponding author. Tel.: +91 2692 226856x227; fax: +91 2692 237258.
E-mail address: nvsastry_17@rediffmail.com (N.V. Sastry).

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hydrophobic type) properties of solutes in general are known to be strongly temperature dependent for polar solutes [16–20], and tripeptides [21–23]. Moreover the increase in temperature can cause a dramatic effect on solvent mediated solute–co-solute interactions, which in turn have a considerable impact on either isothermal unfolding of oligo-peptides in varying concentrations of additive in aqueous solutions or thermal induced unfolding for a fixed additive concentration. Therefore the data on volumetric and transport properties of protein model compounds such as amino acids in aqueous solutions in presence or absence of hydrophilic additives at wide temperature range are expected to throw some light on temperature induced effects on the net balance of solute–solvent, solute–co-solute, solute–solute and co-solute–solvent interactions. The knowledge of side chain partial volumes and their transfer functions at different temperatures are also of fundamental value and may help understand the temperature induced conformational transitions of protein molecules in aqueous media. Therefore it is thought worthwhile to measure new experimental data on densities and dynamic viscosities of aqueous solutions of typical amino acids in presence of four different types of non-electrolyte additives namely sucrose, urea, 2-butoxyethanol, and 2,3-butanediol. We have chosen five amino acids namely glycine, L-valine, L-leucine, L-phenylalanine and L-aspargine for the sake of structural simplicity. Glycine has the simplest of the structure and is often taken as a reference for estimating the aliphatic side chain properties. The amino acids L-valine and L-leucine have isopropyl and isobutyl chains, while L-phenylalanine has an aromatic methylphenyl side chain and L-aspargine has a carboxylamide moiety. The selected additives are also typical, as sucrose is a sugar and is highly hydrophilic, urea has three potential sites for hydrogen bonding, 2-butoxyethanol has a terminal –OH group but intramolecularly hydrogen bonded to etheric oxygen in the same molecule and lastly 2,3-butanediol, a di-hydroxy molecule with terminal hanging hydrophobic methyl groups. So we hope to scrutinize the role of both hydrophobic and hydrophilic parts of solute amino acids, co-solute additives on solute–co-solute, solute–solvent and co-solute–solvent interactions. The measurements over a wide temperature range have been carried out to ascertain the temperature dependence of the side chain volumes and their transfer functions and such information would be of fundamental utility in understanding the contributions of possible conformational changes in the side chains to the overall stability of oligo-peptides in aqueous media. The partial molar volumes at infinite dilution, transfer volumes, ΔV° from water to aqueous additive solution at infinite dilution were calculated. The viscosity data were treated in terms of Jones–Dole equation to estimate the *B*-coefficient values for different systems.

2. Experimental

2.1. Materials

Reagent grade glycine (with 0.99 mass fraction purity was twice re-crystallized from (ethanol + water) mixtures. The L-valine, L-leucine, L-phenylalanine of highest mass fraction purity 0.99 were procured from Lancaster Co.; L-aspargine mass fraction purity 0.99 was purchased from UBICHEM, UK; sucrose of extra pure grade (mass fraction purity > 0.99) was purchased from Himedia, India. Analytical reagent grade 2-butoxyethanol with a purity of 0.99 was obtained locally while 2,3 butanediol and urea each with mass fraction purity 0.99 were obtained from Fluka. All the substances were dried over P_2O_5 in a vacuum desiccator for 72 h at room temperature. The stock solutions were prepared in four times distilled and degassed water by mass (accurate to ±0.01 mg) using a Dhona balance. Measurements on the fresh solutions were made on the same day to avoid any aging effects. Amino acids were considered as solutes while the additives (sucrose, urea, 2,3-butanediol, and 2-butoxy ethanol) were considered as co-solutes.

2.2. Methods

Densities measurements were done using a vibrating tube digital densimeter (Model DMA 5000, Anton Paar, Austria). The instrument was calibrated with air, four times distilled and degassed

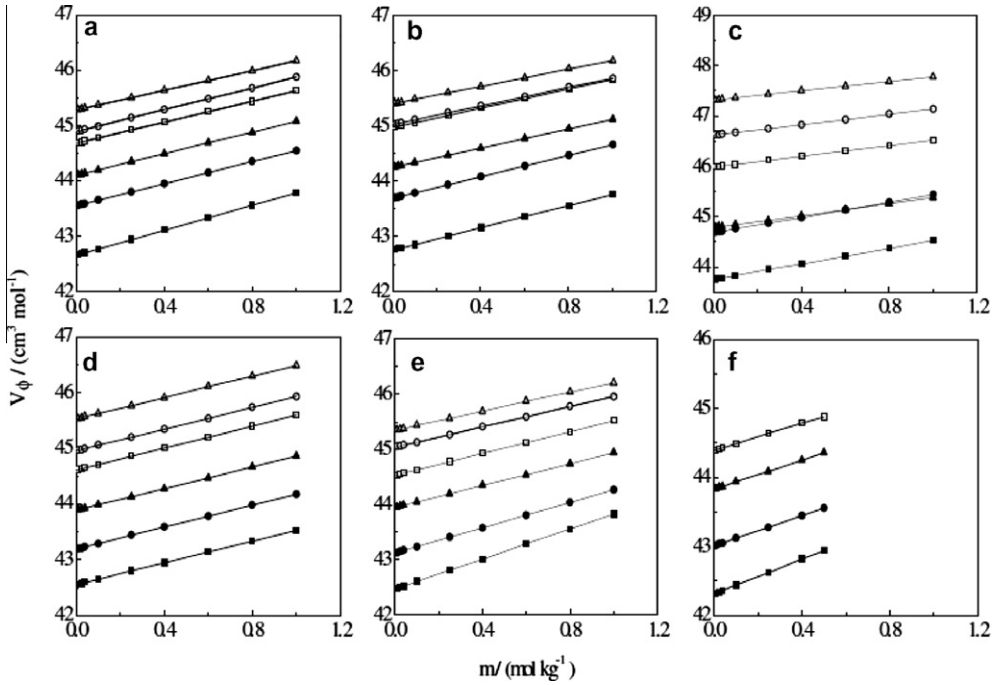

FIGURE 1. Plots of apparent molar volumes (V_ϕ) *versus* molality (m) for glycine aqueous solutions in presence of various additive solutions: (a) 0.05 (w/w) sucrose, (b) 0.1 (w/w) sucrose, (c) 0.2 (w/w) sucrose, (d) 0.05 (w/w) urea, (e) 0.05 (w/w) 2-butoxyethanol, (f) 0.05 (w/w) 2,3-butanediol at different temperatures (■) 10 °C, (•) 20 °C, (▲) 30 °C, (▼) 40 °C, (►) 50 °C, and (□) 60 °C (— fitted values from equation (3)).