



# Investigation on molecular interaction of amino acids in aqueous disodium hydrogen phosphate solutions with reference to volumetric and compressibility measurements



Harsh Kumar\*, Meenu Singla, Rajeev Jindal

Department of Chemistry, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar 144 011, Punjab, India

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## ABSTRACT

The interactions of amino acids glycine (Gly), L-alanine (Ala), and L-valine (Val) with disodium hydrogen phosphate (DSHP) as a function of temperature have been investigated by combination of volumetric and acoustic measurements. Densities ( $\rho$ ) and speeds of sound ( $u$ ) of amino acids in aqueous solutions of disodium hydrogen phosphate have been measured at  $T = (288.15, 293.15, 298.15, 303.15$  and  $308.15)$  K and atmospheric pressure. The apparent molar volume ( $V_\phi$ ), the partial molar volume ( $V_\phi^0$ ) and standard partial molar volumes of transfer ( $\Delta V_\phi^0$ ) for amino acids from water to aqueous disodium hydrogen phosphate solutions have been calculated from density data. Partial molar adiabatic compressibility ( $\kappa_{\phi,s}$ ) and partial molar adiabatic compressibility of transfer ( $\Delta \kappa_{\phi,s}^0$ ) have been calculated from speed of sound data. The pair ( $V_{AB}, \kappa_{AB}$ ) and triplet ( $V_{ABB}, \kappa_{ABB}$ ) interaction coefficient have been calculated from both the properties. The results have been explained based on competing patterns of interactions of co-solvents and the solute.

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## 1. Introduction

Binary solvents, representing a concentrated mixture of a co-solvent and water as the principal solvent, are of special interest from both the biological and the physico-chemical viewpoints [1–3]. The added co-solvent may exert a stabilizing or destabilising influence on the native confirmation of a protein or may be neutral [4]. Due to complex conformational and configurational three dimensional structures of proteins, a direct study of proteins interaction with other components is quite difficult. Amino acids, the model compounds for proteins are important biological active and basic structural units of proteins and are useful to investigate the solvation behaviour [5,6]. Extensive work [7–14] has been done on thermodynamic properties of amino acids in aqueous electrolyte solutions, carbohydrates, surfactants etc. but the biologically and industrially important phosphate salts which found, pharmaceutical and cosmetic industries and also in many biochemical processes [15–17] have been included in few studies [18–20]. Our main aim is to study the interactional behaviour of amino acids with these salts of biological and industrial importance, which will further help in better understanding of these classes of compounds. In earlier study [21], we have reported the density and speeds of sound of glycine and L-alanine in aqueous solutions of

dipotassium hydrogen phosphate (DKHP) at different temperatures. In order to have better understanding of the interactions of amino acids with phosphate salts, in the present work we report densities and speeds of sound of glycine, L-alanine and L-valine in aqueous disodium hydrogen phosphate solutions at different temperatures (288.15, 293.15, 298.15, 303.15 and 308.15) K and atmospheric pressure. Disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) (DSHP) is a sodium salt of phosphoric acid which is highly hygroscopic and water-soluble. It is therefore used commercially as an anti-caking additive in powdered products. It is also known as disodium hydrogen orthophosphate, sodium hydrogen phosphate or sodium phosphate dibasic. DSHP is also used as emulsifier, texturizer and buffer. As per our knowledge, no data on densities and speeds of sound of amino acids with disodium hydrogen phosphate mixtures has been reported, so far.

## 2. Experimental

### 2.1. Materials

Disodium hydrogen phosphate (DSHP) with mass fraction purity > 0.98, glycine (Gly), L-alanine (Ala), and L-valine (Val) with mass fraction purities > 0.99 were obtained from Merck, Germany. All the chemicals were dried in vacuum and stored in desiccators over  $\text{P}_2\text{O}_5$  for at least two days before their use. The specifications

\* Corresponding author. Tel.: +91 9876498660.

E-mail addresses: [h.786.man@gmail.com](mailto:h.786.man@gmail.com), [manchandah@nitj.ac.in](mailto:manchandah@nitj.ac.in) (H. Kumar).

**TABLE 1**  
Specification of chemical samples.

Chemical name	Provenance	Mass fraction purity	Structure
Disodium hydrogen phosphate	Merck, Germany	>0.99	
Glycine	Merck, Germany	>0.99	
L-Alanine	Merck, Germany	>0.99	
L-Valine	Merck, Germany	>0.99	

and structures of the chemicals used in this study are given in [table 1](#).

## 2.2. Methods

Freshly prepared triply distilled and degassed water (specific conductance  $< 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ ) was used for the preparation of solutions. The solutions were prepared by weighing on a balance having precision of  $\pm 0.00001 \text{ g}$ . The uncertainties in the molality of solutions are within  $\pm 2 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$ . The densities,  $\rho$  and speed of sound,  $u$  of the solutions were simultaneously, and automatically measured, using an Anton Paar DSA 5000 M densimeter. A density check or an air/water adjustment was performed at  $20^\circ \text{C}$  with triply distilled, degassed water, and with dry air at atmospheric pressure. Before each series of measurements, the densimeter was calibrated with triple distilled and degassed water, in the experimental temperature range. Both the density and speed of sound are extremely sensitive to temperature, so it was controlled to  $\pm 1 \cdot 10^{-3} \text{ K}$  by built-in Peltier device. The sensitivity of the instrument corresponds to a precision in density and speed of sound measurements of  $1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $1 \cdot 10^{-2} \text{ m} \cdot \text{s}^{-1}$ . The uncertainty of the density and speeds of sound estimates was found to be within  $\pm 5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $\pm 5 \cdot 10^{-2} \text{ m} \cdot \text{s}^{-1}$ , respectively.

## 3. Results and discussion

### 3.1. Apparent molar volume

The experimental values of solution densities,  $\rho$  of glycine, L-alanine and L-valine in (0.2, 0.4 and 0.6)  $\text{mol} \cdot \text{kg}^{-1}$  aqueous solutions of disodium hydrogen phosphate were measured at temperatures (288.15, 293.15, 298.15, 303.15 and 308.15) K. These values of densities were used to calculate apparent molar volumes ( $V_\phi$ ) using following equation:

$$V_\phi = M/\rho - (\rho - \rho_0)/m\rho\rho_0, \quad (1)$$

where  $m$  is the molality ( $\text{mol} \cdot \text{kg}^{-1}$ ) of the solution,  $M$  is the molar mass of the solute ( $\text{kg} \cdot \text{mol}^{-1}$ ) and  $\rho_0$  and  $\rho$  are the densities ( $\text{kg} \cdot \text{m}^{-3}$ ) of the solvent and solution, respectively. The values of

apparent molar volumes along with densities are reported in [table 2](#).

The data reported in [table 2](#) reveals that the apparent molar volume for glycine, L-alanine and L-valine increases with increase in DSHP concentration and temperature. The positive values of  $V_\phi$  are indicative of greater solute–solvent interactions, which increase from glycine to L-alanine to L-valine at all temperatures as shown in [scheme 1](#). Further, we have compared the densities and apparent molar volume for amino acids in aqueous solutions of DSHP reported in the present study with densities and apparent molar volume for amino acids in aqueous solutions of dipotassium hydrogen phosphate (DKHP) reported earlier [21]. The densities values of glycine in  $0.2 \text{ mol} \cdot \text{kg}^{-1}$  DKHP and DSHP have been plotted in [figure 1](#) at different temperatures. In addition, the apparent molar volumes have been compared graphically for glycine and alanine in  $0.2 \text{ mol} \cdot \text{kg}^{-1}$  DKHP and DSHP at different temperatures as shown in [figure 2](#). The comparison of the results shows that values of  $V_\phi$  in both cases increases with increase in the molar mass of amino acid *i.e.* with increase in the alkyl part. The values of  $V_\phi$  are higher for DKHP [21] as compared to DSHP for all amino acids. The higher values in the case of DKHP are attributed to the fact that potassium is placed above sodium in the Hofmeister series. As we move from sodium to potassium in the Hofmeister series, the kosmotropic nature or structure making ability of the cation increases so, solute–solvent interaction increases which is further responsible for the higher values of apparent molar volume in case of DKHP as compared to DSHP.

### 3.2. Partial molar volume

The partial molar volume  $V_\phi^0$ , which is the limiting value of apparent molar volume, is calculated by least square fitting of apparent molar volume  $V_\phi$  by following equation:

$$V_\phi = V_\phi^0 + S_V^* m, \quad (2)$$

where  $S_V^*$  the experimental slope is the volumetric pair wise interaction coefficient and  $m$  is the molality of the salt. The values of  $V_\phi^0$  and  $S_V^*$  together with standard errors derived by least squares fitting of the  $V_\phi$  values to equation (2) are reported in [table 3](#). The positive  $V_\phi^0$  values, which indicate the presence of solute–solvent interactions, increase with increase in the DSHP concentration

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