Journal of Molecular Liquids 251 (2018) 70–76

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Interactions of glycine with aqueous solutions of sodium phosphate buffer at T = (288.15, 293.15, 298.15, 303.15, 308.15, 310.15, 313.15, 318.15, 323.15 and 328.15) K: Volumetric and UV absorption studies

Poonam Patyar [a], Kuldeep Kaur [a], Gagandeep Singh [b,*]

[a] Department of Chemistry, Punjabi University, Patiala, Punjab 147 002, India
[b] University College, Ghudha, Bathinda, Punjab 151 401, India

ARTICLE INFO

Article history:
Received 1 July 2017
Received in revised form 28 September 2017
Accepted 7 November 2017
Available online 8 December 2017

Keywords:
Glycine
Density
Partial molar volume
Partial molar expansibilities
Hydration number
Buffers
Absorption spectra

ABSTRACT

Interactions of glycine with sodium phosphate buffer have been investigated by volumetric and UV absorption studies. Densities have been measured for glycine in water of pH = (1.00, 7.40 and 13.40) and in 0.1 M, 0.5 M and 1 M aqueous sodium phosphate buffer (NaPB) solutions as a function of concentration at T = (288.15 to 328.15) K and at pH = (1.00, 7.40 and 13.40) by using digital density meter. Apparent molar volumes ($V_{\varnothing}$) and partial molar volumes (V_2^o) obtained from these density data have been used to calculate partial molar volumes of transfer ($\Delta_{tr}V_2^o$) from water to aqueous sodium phosphate buffer solutions, which are positive for zwitterionic and deprotonated form of glycine. Interaction coefficients have been obtained from McMillan-Mayer's approach. Effect of temperature on these thermodynamic properties have been studied by determining the partial molar expansibilities $(\partial V_2^o/\partial T)_P$ at infinite dilution and their second order derivative $(\partial^2 V_2^o/\partial T^2)_P$ at different temperatures and at pH = (1.00, 7.40 and 13.40). Hydration number (n_H) of glycine at pH 7.40 have been determined from the V_2^o data. The results have been rationalized in terms of various interactions taking place in these systems. Further, absorption spectra have also been recorded for the present system with the help of UV–visible spectrophotometer at 298.15 K which is helpful in interpreting the possible molecular interactions between glycine and NaPB.

1. Introduction

Various biomolecules e.g. proteins, nucleic acids, lipids and complex carbohydrates, function as a result of their interactions with their aqueous environment [1]. These interactions are affected by the presence of surrounding solute and solvent molecules. Hence, the physicochemical properties of proteins are strongly affected by the presence of these solutes. The direct interactions between solute and solvent molecules may lead to change in environment around protein molecules and thus these solutes can change various properties of globular proteins, such as their hydration, solubility, stability and the activity of enzymes [2]. Amino acids as fundamental units of peptides and proteins play an important role in biological systems by affecting solubility, denaturation, and activity of biomolecules [3–5]. Therefore, the study of the effects of buffer solutions on thermodynamic properties of these model compounds can provide important information about solute-solvent and solute-solute interactions in biomolecules [6–7].

Buffer solutions contain the salts that undergo reversible protonation and thus, aid in maintenance of the pH of solution. This is particularly important in biological reactions that are often sensitive to small change in pH [8]. The intracellular and extracellular fluids of all organisms tend to have a characteristic and constant pH, which is regulated by various biological activities [9]. Sodium dihydrogen phosphate and disodium hydrogen phosphate (NaH_2PO_4 – Na_2HPO_4) constitute the phosphate buffer. It is mostly an intracellular buffer and is of less importance in plasma due to its low concentration with pK of 6.8 (close to pH of blood i.e. 7.4) [10]. Phosphate and its protonated forms hydrogen phosphate, dihydrogen phosphate and phosphoric acid are of great relevance for numerous physiological reactions as well as for a large number of industrial and agricultural applications. Phosphates play a crucial role as main structural components in the backbone of nucleic acids [11]. Remarkable experimental work has been reported on thermodynamic properties of amino acids in aqueous salt solutions [12–32]. However, these studies were not focused on physiological conditions or biological environment i.e. at controlled pH and physiological temperature which is prerequisite to understand the complex biological phenomena like protein folding/unfolding, protein dynamics, energetics, stability etc. Moreover, no systematic studies are available on

* Corresponding author.
E-mail address: gdeepchem@yahoo.co.in (G. Singh).

https://doi.org/10.1016/j.molliq.2017.11.055
0167-7322/

thermodynamic properties of amino acids in the presence of buffer solutions at controlled pH.

In view of the above and in continuation of our previous work [33], we have undertaken a study on the volumetric properties of glycine in aqueous sodium phosphate buffer solutions. Thus, in the present paper we report the volumetric study of glycine in aqueous sodium phosphate buffer (NaPB) at T = (288.15 to 328.15) K and at pH values i.e. 1.00, 7.40 and 13.40, where amino acids exist predominantly in protonated, zwitterionic and deprotonated form, respectively. Further, UV absorption study of glycine in water of pH = (1.00, 7.40 and 13.40) and in NaPB of pH = (1.00, 7.40 and 13.40) at 298.15 K has also been reported.

2. Experimental

Glycine, sodium dihydrogen orthophosphate (NaH_2PO_4) and disodium hydrogen orthophosphate (Na_2HPO_4) of highest purity ≥99% were obtained from S D Fine Chem. Limited. These were used as such without further purification. However, these were dried in vacuum oven and kept in desiccator at room temperature before use. Double-distilled, deionized and degassed water with specific conductance $< 10^{-6}$ S·cm^{-1}was used to prepare the solutions. All the solutions were prepared afresh on weight basis by using electronic balance (CITIZEN CY 204) having precision $\pm 1 \times 10^{-4}$ g. Different concentrations of sodium phosphate buffer were prepared by adding equimolar amount of NaH_2PO_4 and Na_2HPO_4. The desired pH value 14.00 and 1.00 was maintained by using 1 M NaOH and 1 M H_3PO_4. However, we were not able to attain pH 14.00 in NaPB, so the present work has been carried out at pH 13.40. The solution densities were measured using vibrating-tube digital density meter (Anton Paar, DMA 4500 M). Temperature around the cell was controlled to $\pm 1 \times 10^{-2}$ K by built in a solid state thermostat. The accuracy and precision in density measurements was found to be $\pm 5 \times 10^{-5}$ g·cm^{-3} and $\pm 1 \times 10^{-5}$ g·cm^{-3}, respectively. The working of density meter was checked by the method described elsewhere [34]. UV spectra of glycine in water and aqueous sodium phosphate buffer (pH = 1.00, 7.40 and 13.40) were recorded at 298.15 K on Labtronics LT-2900 UV–visible spectrophotometer over a wavelength range 190–250 nm. The concentration of NaPB was 0.1 M, 0.5 M and 1 M, and the molalities of glycine were varied in the range (0.01 to 0.05) mol·kg^{-1}. The pH of the solution was measured using pH meter (Systronics Digital pH meter 335). Accuracy in pH measurements was checked by calibrating pH meter using standard buffer solutions of pH = 7.00 and 9.20 and it was found to be ±0.02 pH unit. Quartz cuvettes of 1 cm path length were used for the measurement.

3. Results and discussion

3.1. Densities and partial molar volumes

The apparent molar volumes ($V_\varnothing$) of glycine in water and in different concentrations of sodium phosphate buffer (0.1, 0.5 and 1) M at T = (288.15 to 328.15) K and at pH = (1.00, 7.40 and 13.40) have been calculated as follows

$$V_\varnothing = M/\rho - [(\rho - \rho_o)1000/m\rho\rho_o] \quad (1)$$

where M is the molecular mass of glycine, m is the molality of glycine, and ρ_o and ρ are the densities of solvent and solution, respectively. The $V_\varnothing$ values along with densities are summarized in Tables S(1–3) and given in supplementary file. The overall uncertainty in molality u(m) lies within $\pm 1.3 \times 10^{-4}$ mol·kg^{-1} and in apparent molar volume due to molality and density, u($V_\varnothing$) lies in the range of (0.2303 to 0.0086) cm^3·mol^{-1} for the studied system. The representative plots of $V_\varnothing$ values versus m for glycine in the presence of aqueous NaPB solutions at pH 1.00, 7.40 and 13.40 are shown in Figs. 1–3. At pH 1.00, the $V_\varnothing$ values first decrease with concentration of glycine and then increase slowly in all the concentrations of NaPB studied i.e. 0.1 M, 0.5 M and 1 M (Figs. 1–3). At pH 7.40 linear increase of $V_\varnothing$ values versus concentration has been observed. At pH 13.40, in 0.1 M buffer solution the $V_\varnothing$ values first increase with concentration then decrease, whereas in 0.5 M the $V_\varnothing$ values decrease linearly. The $V_\varnothing$ values of glycine in the presence of NaPB solutions increase with increasing temperature irrespective of their pH values. It has been observed that the $V_\varnothing$ values of glycine are dependent on both the pH and concentration of the buffer solutions. Due to solubility reason at pH 13.40,$V_\varnothing$ values of glycine in 1 M NaPB have not been measured.

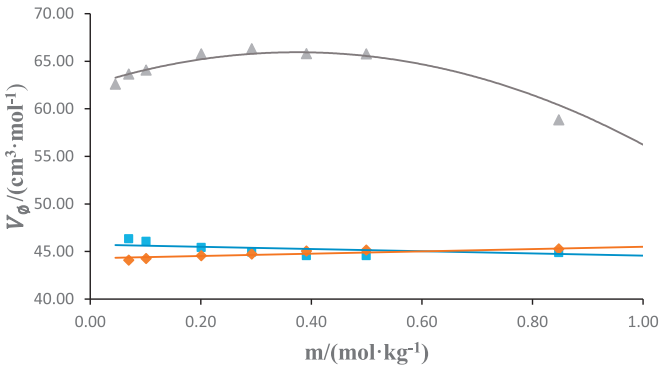

Fig. 1. Representative plots of apparent molar volume ($V_\varnothing$) versus molality (m) of glycine in 0.1 M aqueous NaPB of pH = 1.00 (■), 7.40 (◆), 13.40 (▲) at 310.15 K.

Further we have compared the $V_\varnothing$ values of glycine in aqueous solutions of NaPB reported in the present study with $V_\varnothing$ values of glycine in aqueous solutions of potassium phosphate buffer (KPB) reported earlier [33]. The $V_\varnothing$ values of glycine in 0.1 M KPB and 0.1 M NaPB at 310.15 K (pH 7.40) are plotted in Fig. 4. A comparison of the values shows that glycine has higher $V_\varnothing$ values in KPB as compared to NaPB. The higher values in case of KPB are attributed to the fact that potassium is placed above sodium in the Hofmeister series [35]. The order of effectiveness of ions in stabilizing protein is

$$F^- > SO_4^{2-} > HPO_4^{2-} > Acetate^- > Citrate^- > Cl^- > NO_3^- > Br^- > I^- > SCN^- > NH_4^+ > K^+ > Na^+ > Cs^+ > Li^+ > Mg^{2+} > Ca^{2+} > Ba^{2+} > Gdm^+$$

According to Hofmeister series as we move from right to left, the kosmotropic nature or structure making ability of cation increase so, solute-solvent interaction increase which is further responsible for the higher$V_\varnothing$ values in case of KPB as compared to NaPB. Further, increase

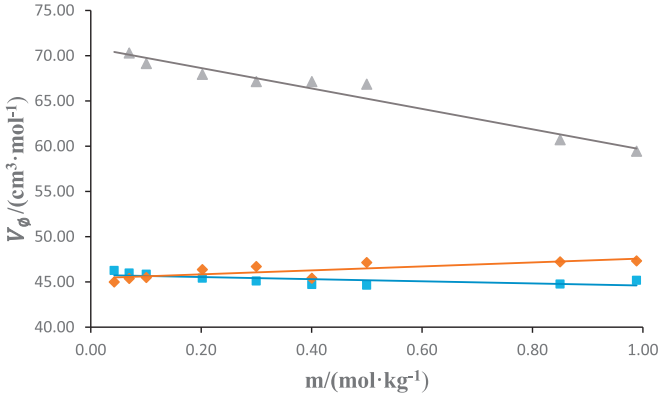

Fig. 2. Representative plots of apparent molar volume ($V_\varnothing$) versus molality (m) of glycine in 0.5 M aqueous NaPB of pH = 1.00 (■), 7.40 (◆), 13.40 (▲) at 310.15 K.