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Effect of potassium phosphate buffer on volumetric behavior of glycine in aqueous solutions at different temperatures

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ABSTRACT

The apparent molar volume ($V_{\varnothing}$) of glycine in water and in 100, 500 and 1000 mM aqueous potassium phosphate buffer (KPB) solutions have been obtained from density measurements at different temperatures (288.15 to 328.15 K, including physiological temperature) and at different pH values (1.00, 7.40 and 14.00) by using vibrating-tube digital density meter. The estimated partial molar volumes at infinite dilution (V_2^o) have been used to obtain the corresponding transfer volume ($\Delta_{tr}V_2^o$) from water to aqueous potassium phosphate buffer solutions. Interaction parameters have been calculated from $\Delta_{tr}V_2^o$ data. The partial molar expansibilities $(\partial V_2^o|\partial T)_P$ at infinite dilution and $(\partial^2 V_2^o|\partial T^2)_P$ values have also been determined from the V_2^o data at different temperatures. The hydration numbers (n_H) of glycine at pH 7.4 have been determined from the V_2^o data in the presence of KPB at different temperatures. The results have been discussed in terms of various interactions operating in these systems.

1. Introduction

The study of interactions between salts and proteins is useful to understand the physiological systems [1–5]. However, proteins are complex molecules and their behavior in solutions is governed by a variety of interactions. Therefore the direct study of solute–solvent interactions of these systems is difficult [6]. One useful approach that reduces the degree of complexity in the study of these interactions is to study the interactions in systems containing smaller biomolecules such as amino acids. Amino acids are the building blocks of the proteins; their study provides important information which can be related to the behavior of larger biomolecules such as proteins [7].

The physical and chemical characteristics of virtually all biologically relevant molecules depend strongly upon the pH of their aqueous environment. In order to maintain the biological function and catalytic activity, it is desirous that proteins maintain their native structure under physiological conditions. However, most proteins are sensitive to slightest change in cellular and environmental conditions like temperature, pH, pressure and the presence of salts. Moderate change in solution pH and/or strength often results in drastic change in the conformational state of the protein and/or dissociation of protein complex.

Buffer solutions contain the salts that undergo reversible protonation and thus, aid in maintaining 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. Moreover, the first line of defense of living organisms against change in their internal pH is provided by buffer systems [9]. The phosphate buffer system, important in intracellular fluid, consists of conjugate acid–base pair $H_2PO_4^-$, as proton donor, and HPO_4^{2-}, as proton acceptor tends to resist change in pH in the range of (6.1 to 7.7) and would therefore be effective in providing buffering power in intracellular fluid whose pH is in the range of (6.9 to 7.4). Extensive work has been done on thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solutions of various additives which provide information about solute-solvent and solute-solute interactions operating in these systems [10–24]. However, these studies were not focused on physiological conditions or biological environment, i.e. at controlled pH and physiological temperature which is a prerequisite to understand the complex biological phenomena like protein folding/unfolding, protein dynamics, energetics, and stability. Literature survey reveals that no study on thermodynamic properties of amino acids in the presence of buffer solutions at controlled pH is available. Our aim in the present study is to determine the interactions of glycine in the presence of buffer solutions. So, we are the first to report, the partial molar volume of glycine in the presence of potassium phosphate buffer (KPB) solutions at different temperatures (288.15 to 328.15 K, including physiological temperature) and at specific pH values i.e. 7.40, 1.00 and 14.00, where amino acids exist predominantly in zwitter ionic, protonated and deprotonated form, respectively.

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2. Experimental

Glycine, potassium di-hydrogen orthophosphate (KH_2PO_4) and di-potassium hydrogen orthophosphate (K_2HPO_4) of highest purity ≥99% were obtained from S.D. Fine Chem. Ltd. These were used as such without further purification. However, these were dried in vacuum oven and kept in a desiccator at room temperature before use. Double-distilled, deionized water was used to prepare the solutions. All the solutions were prepared afresh on weight basis in by using electronic balance (CITIZEN CY 204) having precision $\pm 1 \times 10^{-4}$ g. The required pH for water was attained by using 1 M KOH and 1 M Phosphoric acid (H_3PO_4). Potassium phosphate buffer was prepared by adding KH_2PO_4 and K_2HPO_4. The desired pH value 14.00 and 1.00 was maintained by using KOH and H_3PO_4. We were not able to attain pH 14.00 in KPB, 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 measuring the densities of aqueous sodium chloride solutions, which agreed well with the literature values [25].

Table 1
Densities (ρ) and apparent molar volumes ($V_\varnothing$) of glycine in water of pH = 1.00, 7.40 and 14.00 at different temperatures, T = (288.15 to 328.15) K.[a]

[a]m/ (mol·kg^{-1})	ρ/ (g·cm^{-3})	$V_\varnothing$/ (cm^3·mol^{-1})	ρ/ (g·cm^{-3})	$V_\varnothing$/ (cm^3·mol^{-1})	ρ/ (g·cm^{-3})	$V_\varnothing$/ (cm^3·mol^{-1})	ρ/ (g·cm^{-3})	$V_\varnothing$/ (cm^3·mol^{-1})	ρ/ (g·cm^{-3})	$V_\varnothing$/ (cm^3·mol^{-1})
pH = 1.00										
	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
0.04107	1.00748	50.98	1.00650	51.49	1.00527	51.76	1.00382	52.05	1.00217	52.58
0.07041	1.00820	50.67	1.00722	50.97	1.00598	51.29	1.00452	51.61	1.00287	51.94
0.09973	1.00894	50.31	1.00794	50.73	1.00670	50.97	1.00523	51.31	1.00357	51.65
0.19859	1.01145	49.74	1.01042	50.11	1.00915	50.39	1.00766	50.68	1.00598	50.98
0.29918	1.01393	49.70	1.01287	50.06	1.01157	50.36	1.01006	50.63	1.00835	50.94
0.40370	1.01673	49.07	1.01564	49.42	1.01430	49.74	1.01277	50.00	1.01103	50.32
0.49965	1.01948	48.32	1.01835	48.68	1.01699	48.99	1.01543	49.26	1.01368	49.55
0.84967	1.02966	46.61	1.02842	46.96	1.02697	47.25	1.02533	47.52	1.02352	47.77
1.00473	1.03405	46.25	1.03277	46.59	1.03128	46.89	1.02961	47.15	1.02777	47.39
	310.15 K		313.15 K		318.15 K		323.15 K		328.15 K	
0.04107	1.00146	52.60	1.00034	52.64	0.99833	52.94	0.99615	53.25	0.99382	53.33
0.07041	1.00215	52.10	1.00102	52.28	0.99900	52.63	0.99682	52.83	0.99449	52.91
0.09973	1.00285	51.77	1.00172	51.90	0.99970	52.16	0.99751	52.43	0.99517	52.60
0.19859	1.00525	51.10	1.00411	51.23	1.00205	51.59	0.99751	63.79	0.99750	51.97
0.29918	1.00761	51.06	1.00646	51.19	1.00440	51.45	1.00218	51.68	0.99980	51.92
0.40370	1.01027	50.46	1.00909	50.64	1.00702	50.87	1.00480	51.06	1.00241	51.27
0.49965	1.01293	49.64	1.01175	49.79	1.00966	50.03	1.00742	50.22	1.00502	50.43
0.84967	1.02275	47.86	1.02153	48.00	1.01941	48.19	1.01713	48.37	1.01472	48.52
1.00473	1.02699	47.48	1.02577	47.60	1.02362	47.80	1.02133	47.94	1.01891	48.11
pH = 7.40										
	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
0.07123	1.00178	42.41	1.00088	42.70	0.99971	43.13	0.99830	43.43	0.99667	43.88
0.09934	1.00269	42.42	1.00177	42.84	1.00059	43.25	0.99917	43.57	0.99754	43.90
0.20097	1.00593	42.61	1.00497	43.02	1.00375	43.43	1.00231	43.70	1.00065	44.02
0.29864	1.00899	42.76	1.00800	43.14	1.00675	43.52	1.00528	43.81	1.00360	44.10
0.39725	1.01199	43.00	1.01094	43.44	1.00966	43.81	1.00817	44.08	1.00647	44.36
0.49902	1.01509	43.08	1.01402	43.48	1.01271	43.83	1.01119	44.12	1.00947	44.38
0.84614	1.02535	43.36	1.02416	43.74	1.02275	44.08	1.02115	44.35	1.01937	44.59
0.98545	1.02928	43.52	1.02805	43.89	1.02661	44.22	1.02498	44.49	1.02318	44.72
	310.15 K		313.15 K		318.15 K		323.15 K		328.15 K	
0.07123	0.99596	43.89	0.99485	43.90	0.99284	44.07	0.99065	44.24	0.98830	44.41
0.09934	0.99683	43.91	0.99571	44.02	0.99370	44.15	0.99151	44.28	0.98915	44.52
0.20097	0.99994	44.03	0.99880	44.19	0.99678	44.32	0.99458	44.45	0.99222	44.59
0.29864	1.00288	44.14	1.00174	44.26	0.99970	44.42	0.99749	44.56	0.99512	44.69
0.39725	1.00575	44.39	1.00459	44.53	1.00255	44.67	1.00035	44.75	0.99796	44.91
0.49902	1.00873	44.45	1.00757	44.57	1.00551	44.72	1.00328	44.86	1.00090	44.97
0.84614	1.01862	44.65	1.01742	44.77	1.01532	44.93	1.01306	45.06	1.01066	45.17
0.98545	1.02241	44.79	1.02121	44.90	1.01908	45.07	1.01682	45.18	1.01441	45.29
pH = 14.00										
	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
0.07529	1.03978	66.42	1.03832	66.51	1.03667	66.60	1.03486	66.71	1.03290	66.82
0.10031	1.03996	66.19	1.03850	66.27	1.03685	66.37	1.03503	66.57	1.03308	66.59
0.20067	1.04072	65.64	1.03923	65.86	1.03759	65.91	1.03578	66.01	1.03382	66.12
0.30031	1.04142	65.59	1.03997	65.64	1.03832	65.74	1.03652	65.81	1.03456	65.92
0.40197	1.04220	65.39	1.04074	65.48	1.03910	65.54	1.03729	65.65	1.03533	65.76
0.49365	1.04298	65.12	1.04153	65.18	1.03990	65.23	1.03809	65.34	1.03624	65.23
0.97762	1.04822	63.25	1.04675	63.34	1.04509	63.43	1.04327	63.54	1.04130	63.65
	310.15 K		313.15 K		318.15 K		323.15 K		328.15 K	
0.07529	1.03208	66.87	1.03080	66.95	1.02856	67.08	1.02618	67.48	1.02370	67.63
0.10031	1.03227	66.54	1.03098	66.71	1.02874	66.85	1.02635	67.27	1.02387	67.42
0.20067	1.03299	66.22	1.03171	66.29	1.02947	66.42	1.02710	66.61	1.02458	66.95
0.30031	1.03374	65.97	1.03246	66.04	1.03022	66.17	1.02785	66.34	1.02525	66.87
0.40197	1.03451	65.81	1.03317	66.02	1.03093	66.15	1.02853	66.39	1.02594	66.80
0.49365	1.03532	65.47	1.03394	65.74	1.03170	65.87	1.02933	66.02	1.02663	66.60
0.97762	1.04047	63.71	1.03918	63.78	1.03692	63.92	1.03452	64.09	1.03200	64.27

[a] m is the molality of glycine in water; standard uncertainties u in molality, u(m) = 1.3 · 10^{-4} mol·kg^{-1} and apparent molar volume, u($V_\varnothing$) = 0.08 to 0.001 cm^3·mol^{-1}.