



Volumetric Investigations on Molecular Interactions of Glycine/L-alanine in Aqueous Citric Acid Solutions at Different Temperatures

Poonam Patyar¹ · Gurpreet Kaur¹ · Tarnveer Kaur¹

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Abstract

Apparent molar volumes (ϕ_V) of glycine/L-alanine in water and in aqueous citric acid (CA) solutions of varying concentrations, *i.e.* (0.05, 0.10, 0.20, 0.30, 0.40 and 0.50) mol·kg⁻¹ were determined from density measurements at temperatures $T = (288.15, 298.15, 308.15, 310.15$ and $318.15)$ K and at atmospheric pressure. Limiting partial molar volumes (ϕ_V°) and their corresponding partial molar volumes of transfer ($\Delta_{tr}\phi_V$) have been calculated from the ϕ_V data. The negative $\Delta_{tr}\phi_V$ values obtained for glycine/L-alanine from water to aqueous CA solutions indicate the dominance of hydrophilic–hydrophobic/hydrophobic–hydrophilic and hydrophobic–hydrophobic interactions over ion/hydrophilic–dipolar interactions. Further, pair and triplet interaction coefficients, *i.e.* (V_{AB}) and (V_{ABB}) along with hydration number (n_H) have also been calculated. The effect of temperature on the volumetric properties of glycine/L-alanine in water and in aqueous CA solutions has been determined from the limiting partial molar expansibilities ($\partial\phi_V^\circ/\partial T$)_p and their second-order derivative ($\partial^2\phi_V^\circ/\partial T^2$)_p. The apparent specific volumes (v_ϕ) for glycine and L-alanine tend to approach sweet taste behavior both in the presence of water and in aqueous CA solutions. The v_ϕ values for glycine/L-alanine increase with increase in concentration of CA at all temperatures studied. This reveals that CA helps in enhancing the sweet taste behavior of glycine/L-alanine which also supports the dominance of hydrophobic–hydrophobic interactions.

Keywords Hydration number · Interaction coefficients · Partial molar expansibilities · Partial molar volumes · Partial molar volumes of transfer · Apparent specific volumes

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✉ Poonam Patyar
poonam_chem@yahoo.co.in

¹ Department of Chemistry, Punjabi University, Patiala, Punjab 147 002, India

1 Introduction

Amino acids are the building blocks of proteins, thus they are regarded as an ideal model for the study of protein functioning and their complex structure [1, 2]. The functional properties of protein molecules depend upon their three dimensional structure which arises due to a particular sequence of amino acids (hereafter written as AA) in a polypeptide chain. All AAs exist as zwitterionic species in aqueous solutions [3], thus their thermodynamic properties in a variety of media can provide valuable information about the stability and denaturation of proteins [4–16]. Recently, Lomesh and Kumar [17, 18] have reported the volumetric and acoustic properties of glycine, diglycine, L-alanine and L-phenylalanine in water and in $0.1 \text{ mol}\cdot\text{kg}^{-1}$ aqueous citric acid at different temperatures. Further, a literature survey reveals that not much systematic data is available regarding the thermodynamic and transport properties of AA as a function of concentration in citric acid solutions at different temperatures.

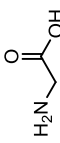
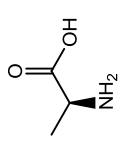
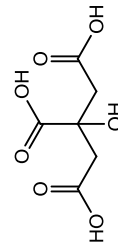
Citric acid (CA) (2-hydroxy-1,2,3-propanetricarboxylic acid) is a tri-basic acid and common metabolite of plants and animals. It is an environmentally acceptable organic acid, used in food, beverages, pH adjustment in buffers, and pharmaceuticals (as an acidifier) [19, 20], and is known to increase the stability of proteins [13]. The presence of one hydroxyl and three carboxyl groups in CA provides effective chemical properties so that it can act as an important metabolite in the citric acid cycle (CAC) of all aerobic organisms [21]. It also acts as a precursor for the bio-synthesis of many compounds in CAC including AA [22]. Therefore, it is of great interest to investigate the molecular interactions of AA with CA which can influence the behavior and conformational stability of proteins. In light of the above facts, presently we report the apparent molar volumes (ϕ_V) of glycine/L-alanine (both are non-essential amino acids) in water and in aqueous CA solutions, m_c (molality of aqueous CA) $\approx (0.05, 0.10, 0.20, 0.30, 0.40$ and $0.50) \text{ mol}\cdot\text{kg}^{-1}$ at temperatures, $T = (288.15, 298.15, 308.15, 310.15$ and $318.15) \text{ K}$ and at atmospheric pressure, obtained from experimental densities. Partial molar volumes (ϕ_V^0) calculated from ϕ_V data have been used to calculate partial molar volumes of transfer ($\Delta_{tr}\phi_V$), apparent specific volumes (v_ϕ), pair (V_{AB}) and triplet (V_{ABB}) interaction coefficients, partial molar expansibilities ($\partial\phi_V^0/\partial T$)_p, their second order derivatives ($\partial^2\phi_V^0/\partial T^2$)_p and hydration number (n_H). The volumetric behavior of glycine in aqueous CA solutions (present work) are compared with glycine in aqueous succinic acid (SA) solutions, reported earlier from our laboratory [23].

2 Experimental Section

2.1 Chemicals Used

Glycine ($\text{C}_2\text{H}_5\text{NO}_2$), L-alanine ($\text{C}_3\text{H}_7\text{NO}_2$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) of analytical grade with mass fraction purity $\geq 99\%$ were procured from S. D. Fine Chemical Ltd. (SDFCL), India. Specifications of the chemicals used are given in Table 1. All the chemicals were used without any further purification; however, they were dried in a vacuum oven for 24 h at $T = 318.15 \text{ K}$, and then kept in a vacuum desiccator over anhydrous CaCl_2 prior to their use.

Table 1 Specifications of the chemicals used in present work

Chemical name	Molecular formula	Structure	Molecular weight (10^{-3} , $\text{kg}\cdot\text{mol}^{-1}$)	CAS no.	Source	Mass fraction purity (%)
Glycine	$\text{C}_2\text{H}_5\text{NO}_2$		75.07	56-40-6	SDFCL	≥ 99
L-Alanine	$\text{C}_3\text{H}_7\text{NO}_2$		89.09	56-41-7	SDFCL	≥ 99
Citric acid, anhydrous	$\text{C}_6\text{H}_8\text{O}_7$		192.13	77-92-9	SDFCL	≥ 99

Deionized, double distilled and degassed water with specific conductance $< 1 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$ was used to prepare all the solutions. The pHs of the experimental solutions were checked using a pH meter (Systronics digital pH meter-335, India). The standard deviation obtained for the whole set of experimental data is ± 0.02 pH unit. Accuracy in pH measurements was checked by calibrating the pH meter using standard buffer solutions of pH 7.00 and pH 9.20. The pHs of the stock solutions, *i.e.* at all concentrations of aqueous citric acid solutions, lie between 2.08 and 2.44, in the case of glycine in aqueous citric acid solutions the pHs lie from 1.96 to 3.61 and for L-alanine in aqueous citric acid solutions it varies from 1.99 to 3.94. Solutions were prepared on the molality basis using a Citizen CY-204 balance having a precision of ± 0.1 mg. The overall uncertainty in molality was estimated to be $< 5 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$. Solution densities were measured using a vibrating-tube digital density meter (DMA 4500 M from Anton Paar, Austria). The sensitivity of the instrument corresponds to a precision in density measurements of $\pm 1 \times 10^{-2} \text{ kg}\cdot\text{m}^{-3}$ and accuracy of $\pm 5 \times 10^{-2} \text{ kg}\cdot\text{m}^{-3}$, respectively. The density meter has a built in thermostat to maintain the desired temperatures within ± 0.01 K and was calibrated with double distilled and degassed water before each series of experiments. The performance of the density meter was checked by measuring the densities of aqueous sodium chloride (NaCl) solutions, which agree well with the literature values [24] as shown in Fig. 1.

3 Results and Discussion

3.1 Volumetric Properties

The apparent molar volumes (ϕ_V) of glycine and L-alanine in water and in varying concentrations of aqueous CA solutions were calculated from experimental solution densities (ρ) at temperatures $T = (288.15, 298.15, 308.15, 310.15 \text{ and } 318.15) \text{ K}$ and at atmospheric pressure, by employing the following equation:

$$\phi_V = M/\rho - [1000(\rho - \rho_0)]/m_A\rho\rho_0 \quad (1)$$

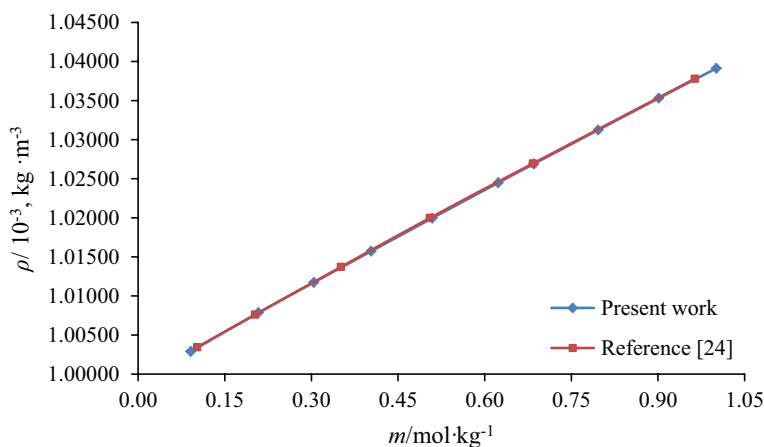


Fig. 1 Representative plots of densities (ρ) versus molality (m): (blue filled square, present work; red filled square, literature values [24]) of NaCl solutions at 288.15 K (Color figure online)

where M ($\text{kg}\cdot\text{mol}^{-1}$) is the molar mass of the glycine/L-alanine, m_A ($\text{mol}\cdot\text{kg}^{-1}$) is the molality of glycine/L-alanine, ρ_0 and ρ are the densities of the solvent (water or water + CA) and solution (water + CA + glycine/L-alanine), respectively. The ϕ_V values of glycine/L-alanine along with ρ_0 and ρ as a function of molality, in water and in aqueous CA solutions at different temperatures, are summarized in Table 2. The standard uncertainty in the apparent molar volume due to molality $u(m)$ and density $u(\rho)$ has been calculated and is (≤ 0.0960 and $\leq 1.611 \times 10^{-6} \text{ m}^3\cdot\text{mol}^{-1}$), respectively. Representative plots of ϕ_V values for the presently studied systems (*i.e.* glycine, L-alanine and citric acid in water) at $T=288.15$ K agree well with earlier reported data [25–34] and are shown in Figs. 2, 3 and 4. The values reported by the authors [25, 33] are higher (at lower concentrations) than to our present results as well as with the other literature data. (The standard uncertainty in molality, $u(m)$ and apparent molar volume, $u(\phi_V)$ of (succinic acid + glycine) system are $\leq 2.21 \times 10^{-4} \text{ mol}\cdot\text{kg}^{-1}$ and $(0.03\text{--}0.65) \times 10^{-6} \text{ m}^3\cdot\text{mol}^{-1}$, respectively).

The variation of ϕ_V versus m_A for glycine/L-alanine in water and in different concentrations of aqueous CA solutions at 288.15 K are shown in Figs. 5 and 6, respectively (representative plots only). It is observed from Figs. 5 and 6 that the ϕ_V values of glycine/L-alanine in aqueous CA solutions vary almost linearly with increases in AA concentration as well as with temperature, whereas these values decrease with increases in the concentration of aqueous CA in these solutions. The higher ϕ_V values obtained for glycine/L-alanine in water indicate that strong solute–solvent interactions exist between glycine/L-alanine and water. In fact, strong interactions of the three carboxyl groups and one hydroxyl group of CA with water via hydrogen bonds leads to the higher ϕ_V values, however the hydrophobic group in SA [23] reduces its ability to form strong hydrogen bonds with water, thus resulting in smaller ϕ_V values (Fig. 7a). The basic structures of citric acid (CA), succinic acid (SA), glycine and L-alanine are given in Scheme 1.

Solute–solute interactions are eliminated at infinite dilution and hence the apparent molar volume (ϕ_V) becomes equal to the limiting partial molar volume (ϕ_V^0). The ϕ_V^0 values have been evaluated by least-squares fitting of the following equation to the corresponding data:

$$\phi_V = \phi_V^0 + S_V m_A \quad (2)$$

where ϕ_V^0 provides a measure of solute–solvent interactions, and the experimental slope S_V provides information regarding solute–solute interactions [28]. ϕ_V^0 and S_V values of glycine/L-alanine in water and in aqueous CA solutions at different temperatures are listed in Table 3. The standard uncertainty of the limiting partial molar volumes has been found to be $\leq 0.07 \times 10^{-6} \text{ m}^3\cdot\text{mol}^{-1}$. The ϕ_V^0 values of glycine/L-alanine in water agree well with the literature values at different temperatures and are shown in Figs. 8 and 9 [8, 23, 26–28, 30, 35, 36]. Table 3 shows that the ϕ_V^0 values are higher for L-alanine in water and in aqueous CA solutions compared to glycine, as expected, which is due to the increase in the molar mass of L-alanine. The magnitude of the ϕ_V^0 values is higher than the S_V values, which suggests that the extent of solute–solvent interactions is greater compared to solute–solute interactions. Moreover, the ϕ_V^0 values decrease with increase in aqueous CA concentration whereas they increase with increasing temperature. The decrease in ϕ_V^0 values with increasing concentration of CA may be attributed to the disruption of side group hydration by that of the charged end groups (a similar explanation has been given by Wang et al. [37], which supports our results for the ϕ_V^0 values), whereas the increase in ϕ_V^0 values of glycine/L-alanine in CA solutions with increase in temperature may lead to reduction of the electrostriction around the zwitterions [38]. Also, at higher temperatures, solvent from the secondary solvation layer of glycine/L-alanine is released into the bulk of solvent which results in the expansion of the solution and leads to higher ϕ_V^0 values [39].

Table 2 Densities (ρ) and apparent molar volumes (ϕ_v) of glycine and L-alanine in water and in aqueous CA solutions at $T=(288.15, 298.15, 308.15, 310.15, 318.15)$ K and $p=101.3$ kPa

m_A (mol·kg ⁻¹)	$T(K) \rightarrow 288.15$		308.15		310.15		318.15	
	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_v \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_v \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_v \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_v \times 10^6$ (m ³ ·mol ⁻¹)
Glycine in water								
0.0000	0.99909	0.99704	0.99403	0.99332	0.99332	0.99332	0.99021	0.99021
0.1078	1.00259	1.00046	0.99738	0.99667	0.99667	0.99667	0.99353	0.99353
0.1991	1.00551	1.00331	1.00018	1.00018	1.00018	1.00018	0.99631	0.99631
0.2911	1.00841	1.00614	1.00296	1.00296	1.00296	1.00296	0.99907	0.99907
0.4034	1.01189	1.00954	1.00632	1.00632	1.00632	1.00632	1.00239	1.00239
0.5282	1.01569	1.01326	1.01000	1.01000	1.01000	1.01000	1.00602	1.00602
0.6791	1.02022	1.01769	1.01437	1.01437	1.01437	1.01437	1.01035	1.01035
0.8244	1.02448	1.02186	1.01849	1.01849	1.01849	1.01849	1.01443	1.01443
0.9504	1.02807	1.02539	1.02199	1.02199	1.02199	1.02199	1.01756	1.01756
Glycine in 0.05 (mol·kg ⁻¹) CA								
0.0000	1.00237	1.00023	0.99715	0.99643	0.99643	0.99643	0.99328	0.99328
0.1981	1.00876	1.00647	1.00330	1.00330	1.00330	1.00330	0.99935	0.99935
0.3022	1.01205	1.00967	1.00646	1.00646	1.00646	1.00646	1.00247	1.00247
0.4196	1.01570	1.01322	1.00997	1.00997	1.00997	1.00997	1.00593	1.00593
0.5062	1.01835	1.01581	1.01248	1.01248	1.01248	1.01248	1.00844	1.00844
0.6103	1.02149	1.01886	1.01550	1.01550	1.01550	1.01550	1.01142	1.01142
0.7179	1.02470	1.02200	1.01859	1.01859	1.01859	1.01859	1.01448	1.01448
0.7599	1.02591	1.02319	1.01976	1.01976	1.01976	1.01976	1.01566	1.01566
0.8538	1.02956	1.02677	1.02330	1.02330	1.02330	1.02330	1.01912	1.01912
Glycine in 0.10 (mol·kg ⁻¹) CA								
0.0000	1.00729	1.00503	1.00186	1.00186	1.00186	1.00186	0.99790	0.99790
0.2258	1.01458	1.01217	1.00886	1.00886	1.00886	1.00886	1.00484	1.00484

Table 2 (continued)

m_A (mol·kg ⁻¹)	298.15		308.15		310.15		318.15	
	T (K) → 288.15	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)
0.3080	1.01719	42.43	1.01465	43.36	1.01136	43.82	1.01058	43.89
0.4154	1.02053	42.56	1.01791	43.44	1.01454	43.94	1.01378	44.00
0.5221	1.02380	42.66	1.02110	43.53	1.01769	44.03	1.01689	44.13
0.6159	1.02665	42.73	1.02383	43.66	1.02038	44.16	1.01960	44.22
0.7295	1.03005	42.81	1.02715	43.71	1.02362	44.25	1.02283	44.32
0.8388	1.03324	42.93	1.03027	43.81	1.02669	44.34	1.02591	44.39
0.9371	1.03609	43.01	1.03303	43.89	1.02994	44.39	1.02860	44.49
Glycine in 0.20 (mol·kg ⁻¹) CA								
0.0000	1.01523		1.01277		1.00943		1.00866	
0.0859	1.01803	42.19	1.01552	42.78	1.01214	43.28	1.01137	43.29
0.1891	1.02136	42.24	1.01878	42.89	1.01535	43.40	1.01457	43.46
0.3102	1.02520	42.34	1.02251	43.10	1.01903	43.58	1.01825	43.62
0.4066	1.02819	42.48	1.02540	43.30	1.02191	43.70	1.02112	43.81
0.5207	1.03169	42.58	1.02880	43.42	1.02522	43.92	1.02441	44.01
0.5506	1.03256	42.68	1.02968	43.46	1.02608	43.97	1.02527	44.05
0.6985	1.03700	42.78	1.03393	43.67	1.03026	44.18	1.02945	44.25
0.8041	1.04011	42.87	1.03695	43.76	1.03322	44.29	1.03240	44.36
0.9182	1.04342	42.96	1.04016	43.85	1.03639	44.37	1.03559	44.44
Glycine in 0.30 (mol·kg ⁻¹) CA								
0.0000	1.02329		1.02064		1.01710		1.01631	
0.1008	1.02658	42.06	1.02388	42.57	1.02030	42.99	1.01949	43.19
0.1934	1.02956	42.15	1.02676	42.72	1.02317	43.22	1.02235	43.38
0.2606	1.03169	42.23	1.02882	42.89	1.02521	43.38	1.02438	43.54
0.3647	1.03495	42.34	1.03196	43.06	1.02835	43.51	1.02749	43.70

Table 2 (continued)

m_A (mol·kg ⁻¹)	$T(K) \rightarrow 288.15$		308.15		310.15		318.15	
	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)
0.5281	1.03999	42.47	1.03680	43.21	1.03316	43.72	1.03232	43.82
0.5944	1.04199	42.54	1.03866	43.32	1.03503	43.88	1.03419	43.97
0.6569	1.04386	42.60	1.04042	43.46	1.03677	44.01	1.03592	44.11
0.7337	1.04614	42.67	1.04260	43.58	1.03887	44.18	1.03805	44.23
0.8901	1.05073	42.77	1.04723	43.74	1.04322	44.30	1.04238	44.37
Glycine in 0.40 (mol·kg ⁻¹) CA								
0.0000	1.03179		1.02894		1.02525		1.02443	
0.3118	1.04192	41.83	1.03898	42.14	1.03519	42.48	1.03424	42.89
0.4341	1.04574	42.01	1.04279	42.26	1.03898	42.56	1.03798	42.97
0.5122	1.04814	42.11	1.04518	42.34	1.04138	42.59	1.04032	43.05
0.5820	1.05023	42.24	1.04727	42.45	1.04350	42.63	1.04239	43.12
0.6992	1.05373	42.38	1.05079	42.54	1.04703	42.68	1.04584	43.20
0.7254	1.05447	42.45	1.05155	42.58	1.04779	42.72	1.04659	43.24
0.9271	1.06035	42.64	1.05741	42.77	1.05372	42.82	1.05541	43.34
Glycine in 0.50 (mol·kg ⁻¹) CA								
0.0000	1.04293		1.03988		1.03601		1.03516	
0.0981	1.04617	41.50	1.04309	41.81	1.03918	42.33	1.03830	42.53
0.2034	1.04959	41.61	1.04647	41.96	1.04251	42.42	1.04160	42.61
0.2978	1.05261	41.71	1.04945	42.12	1.04547	42.48	1.04456	42.68
0.4130	1.05622	41.86	1.05297	42.35	1.04909	42.53	1.04810	42.75
0.4988	1.05887	41.96	1.05554	42.52	1.05164	42.62	1.05070	42.80
0.6104	1.06225	42.10	1.05885	42.67	1.05499	42.71	1.05402	42.90
0.6678	1.06397	42.16	1.06052	42.76	1.05669	42.76	1.05571	42.95

Table 2 (continued)

m_A (mol·kg ⁻¹)	298.15		308.15		310.15		318.15	
	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)
L-Alanine in water								
0.0000	0.99909	59.71	0.99704	0.99403	0.99332	0.99332	0.99021	
0.1078	1.00224	59.71	1.00012	0.99707	0.99635	0.99635	0.99323	61.22
0.1818	1.00436	59.81	1.00220	0.99912	0.99840	0.99840	0.99527	61.27
0.3114	1.00802	59.91	1.00580	1.00267	1.00194	1.00194	0.99877	61.41
0.4077	1.01069	59.97	1.00841	1.00525	1.00452	1.00452	1.00132	61.49
0.7149	1.01892	60.19	1.01649	1.01323	1.01247	1.01247	1.00924	61.64
0.8130	1.02144	60.28	1.01896	1.01567	1.01491	1.01491	1.01166	61.73
0.8986	1.02363	60.33	1.02112	1.01779	1.01704	1.01704	1.01369	61.85
L-Alanine in 0.05 (mol·kg ⁻¹) CA								
0.0000	1.00484		1.00268	0.99958	0.99885	0.99885	0.99569	
0.1330	1.00871	59.61	1.00654	1.00344	1.00270	1.00270	0.99953	60.12
0.1973	1.01054	59.71	1.00837	1.00527	1.00453	1.00453	1.00135	60.20
0.2631	1.01239	59.80	1.01021	1.00711	1.00637	1.00637	1.00318	60.31
0.4041	1.01628	59.94	1.01407	1.01098	1.01023	1.01023	1.00705	60.43
0.4940	1.01871	60.02	1.01648	1.01339	1.01263	1.01263	1.00945	60.54
0.5800	1.02100	60.10	1.01874	1.01566	1.01489	1.01489	1.01173	60.60
0.6971	1.02406	60.20	1.02177	1.01867	1.01791	1.01791	1.01476	60.72
0.7833	1.02626	60.29	1.02396	1.02088	1.02011	1.02011	1.01693	60.83
0.9042	1.02933	60.37	1.02696	1.02387	1.02255	1.02255	1.01994	60.94
L-Alanine in 0.10 (mol·kg ⁻¹) CA								
0.0000	1.00978		1.00752	1.00433	1.00358	1.00358	1.00036	
0.1073	1.01290	59.53	1.01064	1.00745	1.00669	1.00669	1.00347	59.91

Table 2 (continued)

m_A (mol·kg ⁻¹)	298.15		308.15		310.15		318.15		
	T (K) → 288.15	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)
0.1924	1.01533	1.01307	59.68	1.00987	59.83	1.00911	59.91	1.00588	60.06
0.2994	1.01833	1.01606	59.72	1.01288	59.89	1.01210	60.02	1.00886	60.19
0.3970	1.02101	1.01875	59.82	1.01555	60.02	1.01478	60.09	1.01151	60.32
0.4955	1.02366	1.02139	59.93	1.01820	60.13	1.01742	60.21	1.01414	60.44
0.6009	1.02645	1.02418	60.03	1.02096	60.27	1.02020	60.31	1.01692	60.52
0.7062	1.02920	1.02692	60.10	1.02371	60.34	1.02293	60.40	1.01965	60.60
0.8129	1.03190	1.02963	60.22	1.02643	60.42	1.02562	60.52	1.02234	60.70
0.9539	1.03542	1.03315	60.33	1.02993	60.56	1.02915	60.61	1.02577	60.89
L-Alanine in 0.20 (mol·kg ⁻¹) CA									
0.0000	1.01781	1.01535		1.01197		1.01120		1.00789	
0.0990	1.02068	1.01821	59.39	1.01483	59.56	1.01406	59.69	1.01075	59.80
0.1844	1.02310	1.02063	59.53	1.01725	59.76	1.01648	59.79	1.01316	59.94
0.3128	1.02669	1.02420	59.61	1.02083	59.85	1.02005	59.91	1.01670	60.14
0.3873	1.02872	1.02623	59.70	1.02286	59.93	1.02207	60.01	1.01871	60.24
0.4935	1.03157	1.02909	59.81	1.02571	59.93	1.02491	60.12	1.02155	60.33
0.5962	1.03428	1.03177	59.90	1.02841	60.06	1.02758	60.26	1.02424	60.42
0.7044	1.03708	1.03458	59.99	1.03121	60.12	1.03037	60.34	1.02699	60.55
0.7844	1.03906	1.03660	60.12	1.03321	60.21	1.03239	60.42	1.02900	60.63
0.8932	1.04177	1.03929	60.22	1.03591	60.32	1.03506	60.55	1.03169	60.73
L-Alanine in 0.30 (mol·kg ⁻¹) CA									
0.0000	1.02690	1.02424		1.02072		1.01991		1.01647	
0.0858	1.02937	1.02671	59.30	1.02319	59.49	1.02237	59.63	1.01893	59.74
0.1864	1.03222	1.02955	59.39	1.02603	59.63	1.02521	59.71	1.02177	59.82

Table 2 (continued)

m_A (mol·kg ⁻¹)	298.15		308.15		310.15		318.15		
	T (K) → 288.15	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)
0.2857	1.03498	1.03230	59.47	1.02879	59.70	1.02795	59.82	1.02452	59.90
0.4147	1.03849	1.03580	59.58	1.03230	59.80	1.03146	59.90	1.02802	60.01
0.5290	1.04153	1.03883	59.68	1.03534	59.90	1.03449	60.00	1.03104	60.13
0.6150	1.04377	1.04106	59.76	1.03758	59.98	1.03671	60.10	1.03325	60.25
0.7023	1.04600	1.04328	59.85	1.03980	60.08	1.03892	60.21	1.03546	60.35
0.7884	1.04817	1.04544	59.93	1.04195	60.18	1.04107	60.30	1.03759	60.46
0.8430	1.04952	1.04676	59.99	1.04329	60.25	1.04239	60.38	1.03892	60.53
L-Alanine in 0.40 (mol·kg ⁻¹) CA									
0.0000	1.03479	1.03193		1.02825		1.02741		1.02385	
0.1711	1.03965	1.03679	59.29	1.03311	59.55	1.03226	59.64	1.02870	59.75
0.2959	1.04310	1.04022	59.39	1.03655	59.66	1.03569	59.76	1.03213	59.84
0.3711	1.04513	1.04225	59.48	1.03857	59.77	1.03771	59.85	1.03416	59.91
0.4846	1.04815	1.04526	59.58	1.04157	59.87	1.04071	59.94	1.03716	60.03
0.5712	1.05039	1.04751	59.69	1.04382	59.95	1.04294	60.05	1.03937	60.18
0.7049	1.05381	1.05093	59.80	1.04724	60.05	1.04635	60.15	1.04276	60.31
0.9162	1.05905	1.05615	59.93	1.05246	60.23	1.05157	60.31	1.04797	60.48
L-Alanine in 0.50 (mol·kg ⁻¹) CA									
0.0000	1.04164	1.03860		1.03475		1.03389		1.03024	
0.0825	1.04399	1.04095	59.14	1.03710	59.36	1.03624	59.38	1.03259	59.50
0.1808	1.04674	1.04370	59.24	1.03985	59.46	1.03898	59.54	1.03533	59.66
0.2848	1.04959	1.04656	59.34	1.04270	59.56	1.04183	59.62	1.03818	59.74
0.3801	1.05215	1.04911	59.44	1.04527	59.64	1.04439	59.72	1.04074	59.84
0.4973	1.05525	1.05221	59.53	1.04837	59.73	1.04748	59.82	1.04384	59.92

Table 2 (continued)

m_A (mol·kg ⁻¹)	T (K) → 288.15		298.15		308.15		310.15		318.15	
	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\rho \times 10^{-3}$ (kg·m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)
0.6030	1.05797	59.64	1.05493	59.74	1.05110	59.83	1.05021	59.91	1.04657	60.01
0.7018	1.06045	59.75	1.05738	59.89	1.05359	59.93	1.05269	60.02	1.04905	60.13
0.7889	1.06259	59.85	1.05952	59.99	1.05574	60.03	1.05484	60.11	1.05117	60.25
0.8216	1.06337	59.90	1.06031	60.03	1.05652	60.09	1.05559	60.20	1.05197	60.28

Standard uncertainties: $u(m_A) \leq 5.86 \times 10^{-3}$ mol·kg⁻¹, $u(\phi_V) \leq 1.16 \times 10^{-6}$ (m³·mol⁻¹), $u(T) = 0.03$ K, $u(\rho) = 0.5$ kPa

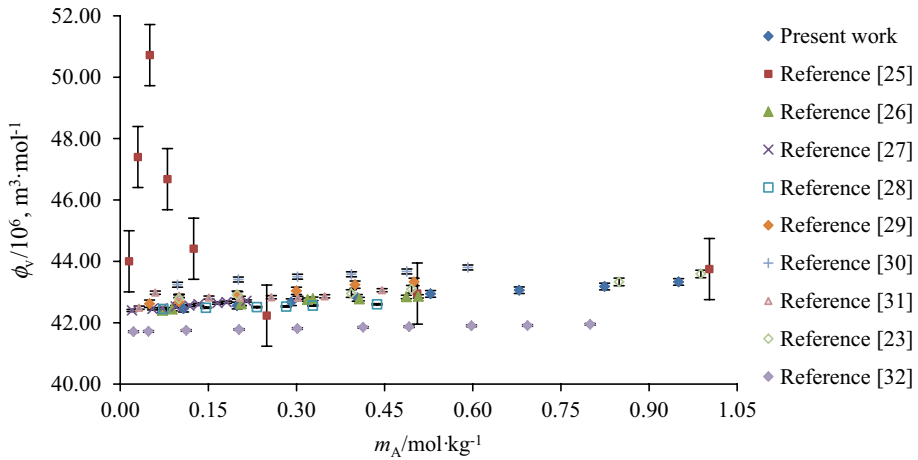


Fig. 2 Representative plots of apparent molar volumes (ϕ_V) versus molality (m_A) of glycine in water at 288.15 K: (red filled square, present work and blue filled square, literature values [23, 25–32]) (Color figure online)

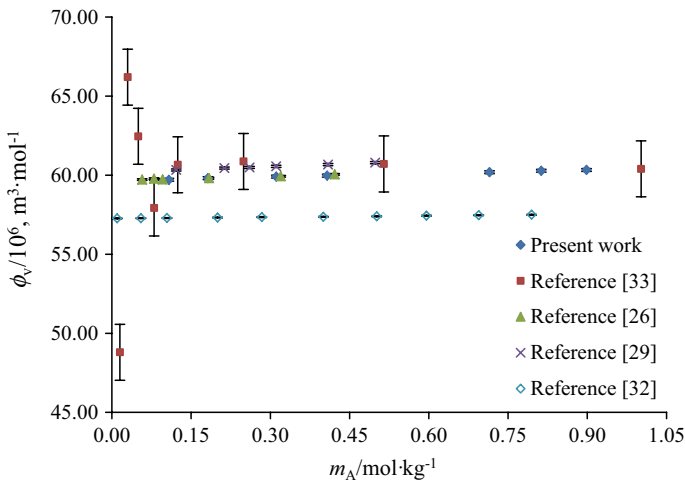


Fig. 3 Representative plots of apparent molar volumes (ϕ_V) versus molality (m_A) of L-alanine in water at 288.15 K: (red filled square, present work and blue filled square, literature values [26, 29, 32, 33]) (Color figure online)

Comparison of ϕ_V and ϕ_V^0 values of glycine in CA (present work) with previously reported data of glycine in SA [23] reveals that the magnitudes of ϕ_V and ϕ_V^0 values for glycine–CA are higher than for glycine–SA (Figs. 7(a), (b), 10). As discussed earlier, the higher magnitudes for glycine in CA solutions are again attributed to the presence of additional hydrophilic groups (–OH and –COOH in CA) which leads to stronger interactions between glycine/L-alanine and CA, *i.e.* it is due to the formation of hydrogen bonds (Scheme 2) [40]. Further, the effect of pH on speciation and charge distribution of these systems involves the stronger interaction among citrate ion and the ionized ammonium group. The amino and carboxyl groups of glycine/L-alanine dissociate

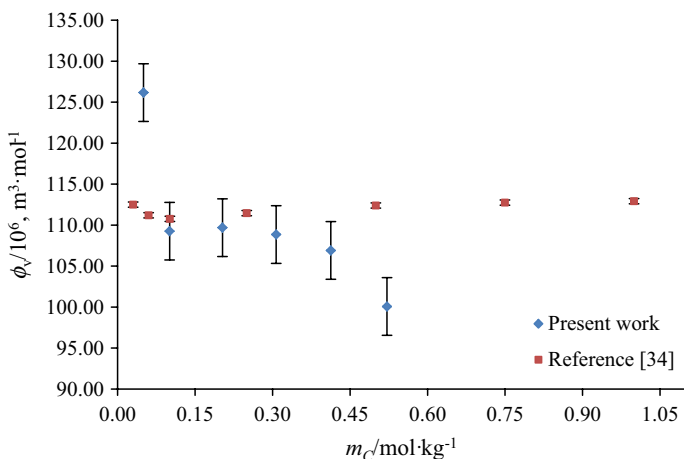


Fig. 4 Representative plots of apparent molar volumes (ϕ_v) versus molality (m_c) of citric acid in water at 288.15 K: red filled square, Present work and blue filled square literature values [34] (Color figure online)

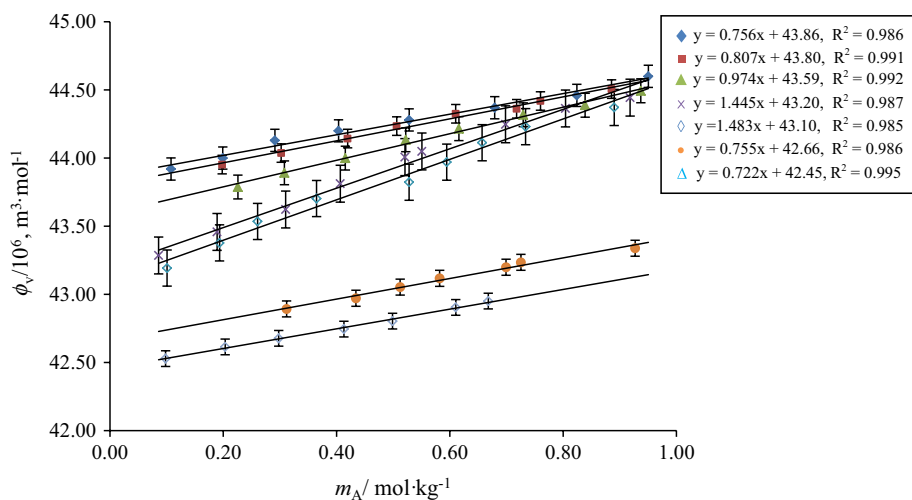
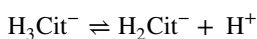


Fig. 5 Representative plots of apparent molar volumes (ϕ_v) versus molality (m_A) of glycine in water and in different concentrations of aqueous CA solutions at 288.15 K: (m_c)=blue filled diamond, water; red filled square, 0.05; Green filled triangle, 0.10; Violet multiply symbol, 0.20; blue open diamond, 0.30; orange filled circle, 0.40; blue open triangle, 0.50 mol.kg⁻¹ (Color figure online)

in aqueous citric acid solutions and form negatively and positively charged ions (*i.e.*, $^+\text{NH}_3\text{-(CH(H/CH}_3\text{)-COO}^-)$). Dissociation of citric acid in aqueous solutions [19], *i.e.* the negatively and positively charged ions, results in the formation of new species in aqueous solutions as:



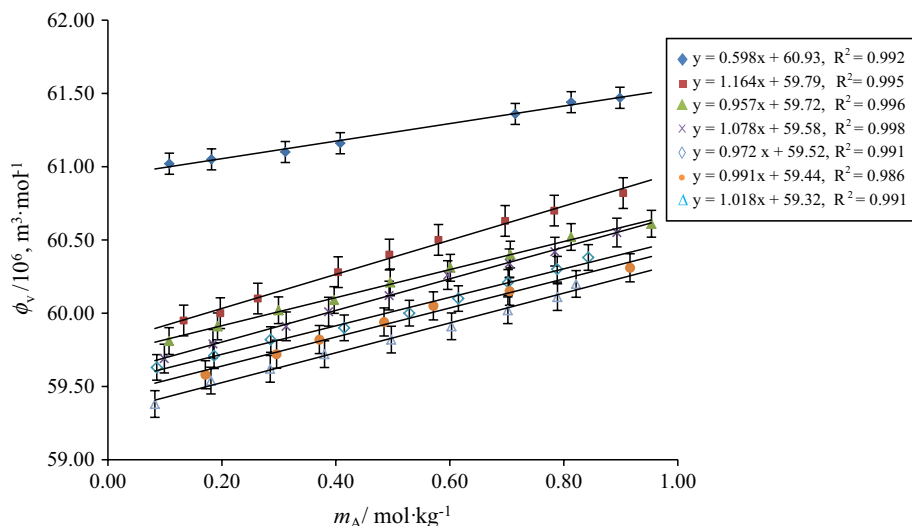
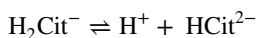


Fig. 6 Representative plots of apparent molar volumes (ϕ_v) versus molality (m_A) of L-alanine in water and in different concentrations of aqueous CA solutions at 288.15 K: (m_c)=blue filled diamond, water; red filled square, 0.05; Green filled triangle, 0.10; Violet multiply symbol, 0.20; blue open diamond, 0.30; orange filled circle, 0.40; blue open triangle, 0.50 mol·kg⁻¹ (Color figure online)



Partial molar volumes of transfer ($\Delta_{tr}\phi_v$) of glycine/L-alanine from water to aqueous CA solutions at infinite dilution have been calculated by using the following equation:

$$\Delta_{tr}\phi_v(\text{water} \rightarrow \text{aqueous CA solutions}) = \phi_v^0(\text{in aqueous CA solutions}) - \phi_v^0(\text{in water}) \quad (3)$$

The $\Delta_{tr}\phi_v$ values reported in Table S1 (supplementary material) are negative and decrease with increase in the concentration of aqueous CA solutions at the studied temperatures (Figs. 11 and 12). The standard uncertainty in $\Delta_{tr}\phi_v$ values has been found to be $\leq 0.07 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$. The possible interactions which may exist between ternary system (*i.e.* glycine/L-alanine + aqueous CA) (Scheme 2) can be categorized as: (1) ion/hydrophilic–dipolar interactions between (3COO⁻, -OH) of CA and (NH₃⁺, COO⁻) zwitterions of glycine/L-alanine, (2) hydrophilic–hydrophobic interactions between the (3COO⁻, -OH) groups of CA with the non-ionic group of glycine/L-alanine, (3) hydrophobic–hydrophilic interactions between the non-ionic group of CA and zwitterionic groups of glycine/L-alanine, and (4) hydrophobic–hydrophobic group interactions between the alkyl chains of glycine/L-alanine and CA. According to the co-sphere overlap model [41], the overlap of the hydration co-spheres of hydrophilic and ionic parts (type 1) results in positive $\Delta_{tr}\phi_v$ values, whereas interactions of type 2, 3 and 4 result in negative transfer volumes. The presently observed negative $\Delta_{tr}\phi_v$ values for glycine/L-alanine in aqueous CA solutions at different temperatures suggest the dominance of hydrophilic–hydrophobic and hydrophobic–hydrophobic interactions over ion/hydrophilic–dipolar interactions. The greater magnitude of $\Delta_{tr}\phi_v$ observed in the case of L-alanine in CA may be attributed to the presence of

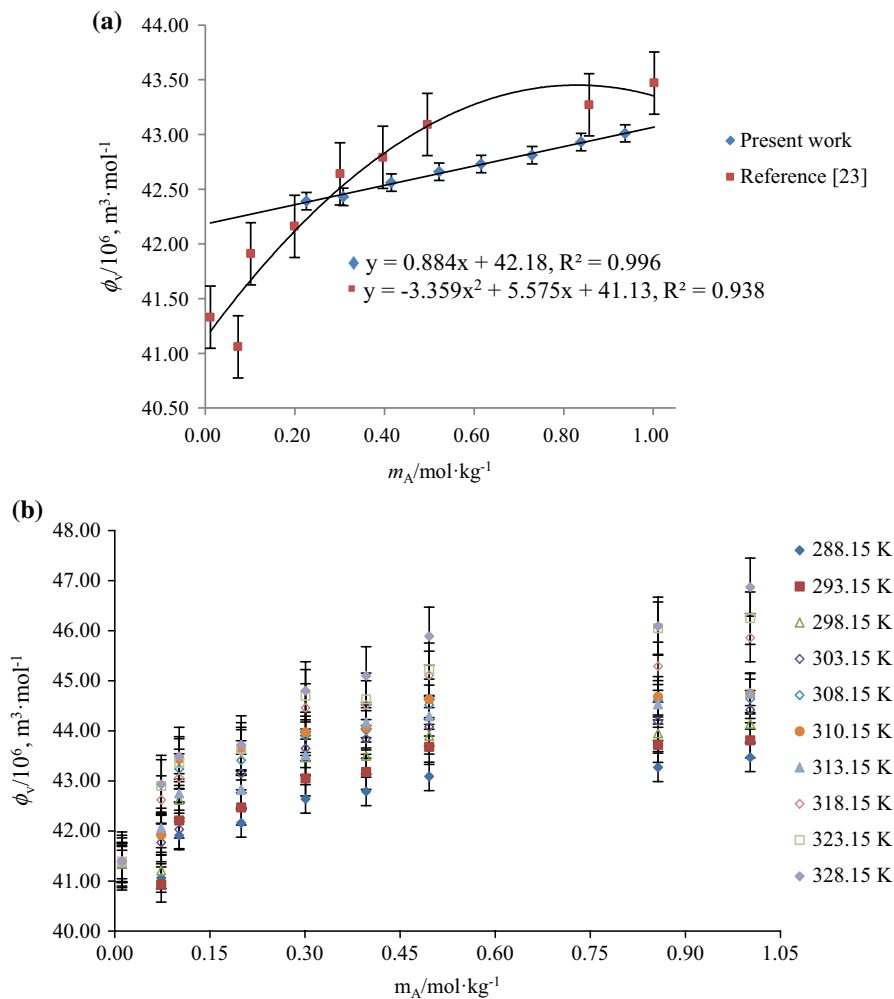


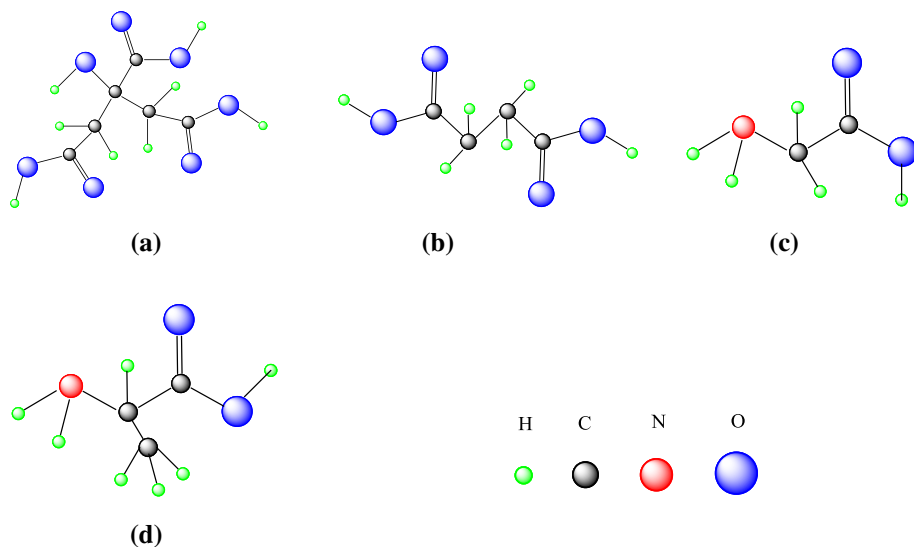
Fig. 7 (a) Representative plots of apparent molar volumes (ϕ_V) versus molality (m_A) of glycine in: blue filled diamond, $0.10 \text{ mol}\cdot\text{kg}^{-1}$ aqueous CA solutions and red filled square, $0.10 \text{ mol}\cdot\text{kg}^{-1}$ in aqueous succinic acid (abbreviated as SA) solutions at 288.15 K. **(b)** Plots of apparent molar volumes (ϕ_V) of glycine versus molality (m_A) in $0.10 \text{ mol}\cdot\text{kg}^{-1}$ aqueous succinic acid solutions (abbreviated as SA) at different temperatures, $T=(288.15\text{--}328.15) \text{ K}$ (Color figure online)

an alkyl group in L-alanine which further strengthens the view that hydrophobic–hydrophobic interactions are dominating in the case of L-alanine–CA (*i.e.* type 4 interactions).

The magnitude of ϕ_V^0 values of glycine/L-alanine in CA can also be explained by considering the modified equation of Shahidi and Farrell [42],

$$\phi_V^0 = V_{v,w} + V_{\text{void}} - V_{\text{shrinkage}} \quad (4)$$

where $V_{v,w}$ is the van der Waal's volume, V_{void} is the volume associated with voids, and $V_{\text{shrinkage}}$ is the volume due to shrinkage that arises from electrostriction of solvent molecules caused by hydrophilic groups present in the solute. Assuming that $V_{v,w}$ and V_{void} are not significantly affected by the presence of CA, then the negative $\Delta_{\text{tr}}\phi_V$ values may



Scheme 1 Basic structures of (a) citric acid, (b) succinic acid, (c) glycine and (d) L-alanine

be attributed to enhanced electrostriction in the vicinity of charged centers of zwitterions which results in an increase of $V_{\text{shrinkage}}$. Further, it is observed from Table S1 that the $\Delta_{\text{tr}}\phi_V$ values for glycine in CA are higher in contrast to glycine in SA solutions [23], which is attributed to the presence of additional hydrophilic groups in CA that leads to the formation of strong hydrogen bonding with glycine (Scheme 2).

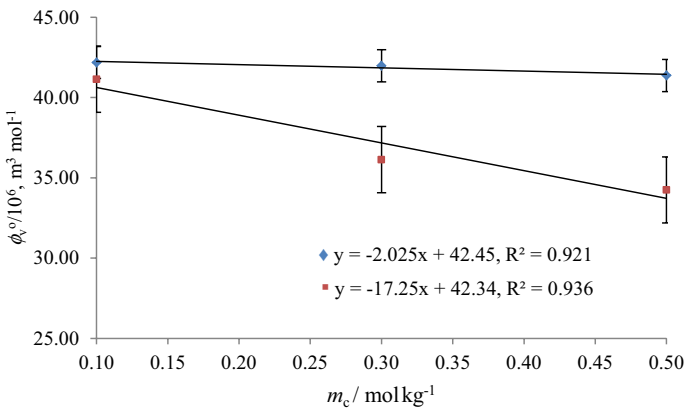
The McMillan–Mayer theory of solutions [43, 44] permits the formal separation of the effects due to the interactions between two or more solutes. According to this theory, the pair and triplet interaction coefficients (V_{AB}) and (V_{ABB}) can be calculated from the partial molar volumes of transfer ($\Delta_{\text{tr}}\phi_V$) by using the following equation:

$$\Delta_{\text{tr}}\phi_V = 2V_{\text{AB}}m_c + 3V_{\text{ABB}}m_c^2 + \dots \quad (5)$$

where A denotes glycine/L-alanine, B denotes CA and m_c is the molality of CA. The V_{AB} and V_{ABB} values of glycine/L-alanine in aqueous CA solutions are given in Table 4. The V_{AB} values for glycine (except at 298.15 K) and L-alanine in aqueous CA solutions are found to be negative at different temperatures. On the other hand, the V_{ABB} values are negative for glycine and positive for L-alanine over the entire temperature range. From Table 4 it is also observed that the magnitude of V_{AB} and V_{ABB} values for L-alanine are greater than for glycine in CA, which suggest that L-alanine interacts more strongly with CA. Overall, the higher magnitude of V_{ABB} values for L-alanine in CA at the studied temperatures indicates the dominance of triplet interactions. Pair interactions dominate for glycine in the presence of CA at lower temperatures (*i.e.* 288.15 and 298.15 K) whereas at higher temperatures (*i.e.* 308.15, 310.15 and 318.15 K) triplet interactions dominate. The reverse trend of V_{AB} and V_{ABB} values has been observed for glycine in SA, *i.e.* V_{AB} dominates at high temperature whereas V_{ABB} dominates at low temperature (no specific reason mentioned). The observed behavior of V_{AB} and V_{ABB} values for glycine in CA may be attributed to the presence of some cooperativity in the interaction of the alkyl group (hydrocarbon part), *i.e.* when two hydrocarbon groups come in contact with each other then it is easier for the third group to join the other two [45].

Table 3 Limiting partial molar volumes (ϕ_V^0) of glycine/L-alanine in water and in aqueous CA solutions at $T=(288.15, 298.15, 308.15, 310.15$ and $318.15)$ K

m_c (mol·kg ⁻¹)	$10^6 \times \phi_V^0$ (m ³ ·mol ⁻¹)				
	288.15, T (K)	298.15, T (K)	308.15, T (K)	310.15, T (K)	318.15, T (K)
Glycine					
0.00	42.37 ^a ±0.02 (1.01) ^b [0.99] ^c 42.69 ^d , 42.37 ^e , 42.38 ^f	43.16 ^a ±0.03 (0.93) [0.99] 43.51 ^d , 43.27 ^e , 42.28 ^f 43.16 ^g ,	43.86 ^a ±0.02 (0.66) [0.99] 43.77 ^d , 43.98 ^e , 43.76 ^f 43.87 ^h	43.87 ^a ±0.03 (0.76) [0.99] 44.10 ^d	44.16 ^a ±0.02 (0.75) [0.99] 44.43 ^d , 44.16 ^f 44.17 ^g , 44.14 ^j
0.05	42.32±0.01 (0.92) [0.99]	43.14±0.02 (0.92) [0.99]	43.61±0.03 (0.96) [0.99]	43.80±0.02 (0.81) [0.99]	44.10±0.02 (0.82) [0.99]
0.10	42.18±0.01 (0.82) [0.99]	43.07±0.02 (0.89) [0.99]	43.54±0.02 (0.95) [0.98]	43.60±0.02 (0.97) [0.99]	43.87±0.03 (1.02) [0.99]
0.20	42.08±0.03 [0.99] [0.99]	42.69±0.05 (1.34) [0.99]	43.16±0.04 (1.39) [0.99]	43.20±0.05 (1.44) [0.99]	43.35±0.07 (1.59) [0.99]
0.30	41.98±0.02 (0.92) [0.99]	42.46±0.04 (1.48) [0.99]	42.89±0.05 (1.66) [0.99]	43.10±0.05 (1.48) [0.99]	43.29±0.04 (1.65) [0.99]
0.40	41.43±0.03 (1.35) [0.99]	41.82±0.02 (1.04) [0.99]	42.31±0.01 (0.54) [0.99]	42.66±0.02 (0.77) [0.99]	42.97±0.03 (0.74) [0.99]
0.50	41.37±0.01 (1.18) [0.99]	41.63±0.02 (1.72) [0.99]	42.26±0.02 (0.73) [0.99]	42.46±0.01 (0.72) [0.99]	42.94±0.02 (1.42) [0.99]
L-Alanine					
0.00	59.66 ^a ±0.02 (0.76) [0.99] 59.67 ^e	60.35 ^a ±0.02 (0.64) [0.99] 60.42 ^e	60.84 ^a ±0.02 (0.62) [0.99] 60.88 ^e	60.94 ^a ±0.02 (0.59) [0.99]	61.15 ^a ±0.03 (0.74) [0.99]
0.05	59.53±0.02 (0.97) [0.99]	59.62±0.02 (1.19) [0.99]	59.71±0.02 (1.18) [0.99]	59.80±0.02 (1.16) [0.99]	60.00±0.02 (1.04) [0.99]
0.10	59.44±0.01 (0.96) [0.99]	59.51±0.02 (0.98) [0.99]	59.62±0.03 (1.01) [0.99]	59.72±0.02 (0.96) [0.99]	59.85±0.03 (1.09) [0.99]
0.20	59.31±0.02 (1.01) [0.99]	59.48±0.01 (0.94) [0.99]	59.57±0.01 (0.95) [0.99]	59.59±0.01 (1.08) [0.99]	59.74±0.03 (1.14) [0.99]
0.30	59.21±0.01 (0.90) [0.99]	59.31±0.02 (1.02) [0.99]	59.42±0.02 (0.95) [0.99]	59.52±0.03 (0.97) [0.99]	59.61±0.03 (1.05) [0.99]
0.40	59.13±0.02 (0.92) [0.99]	59.26±0.02 (0.94) [0.99]	59.36±0.03 (0.98) [0.99]	59.44±0.03 (0.99) [0.99]	59.52±0.03 (1.09) [0.99]
0.50	59.05±0.01 (1.00) [0.99]	59.12±0.02 (1.08) [0.99]	59.28±0.02 (0.95) [0.99]	59.32±0.03 (1.02) [0.99]	59.44±0.03 (1.00) [0.99]

Table 3 (continued)^aPresent work^b $S_V \times 10^6$ ($\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$) values in parenthesis ()^cRegression coefficient values in square brackets []^dReference [23]^eReference [26]^fReference [8]^gReference [27]^hReference [35]ⁱReference [36]^jReference [28]The standard uncertainties in molality, $u(m_A)$ is $\leq 5.86 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$ The standard uncertainty in temperature, $u(T)$ is 0.03 KThe standard uncertainty in pressure, $u(p)$ is 0.5 kPaThe standard uncertainty in partial molar volume, $u(\phi_V^0)$ is $\leq 0.07 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ \pm Respective errors in ϕ_V^0 values**Fig. 8** Representative plots of limiting partial molar volumes ϕ_V^0 versus molality (m_c) of glycine in: blue filled diamond, aqueous CA solutions and red filled square, in aqueous SA solutions at 288.15 K (Color figure online)

To study the effect of temperature on ϕ_V^0 , the limiting partial molar expansibilities $(\partial\phi_V^0/\partial T)_p$ and their second-order derivatives $(\partial^2\phi_V^0/\partial T^2)_p$ have been calculated by fitting the following equation to the corresponding data:

$$\phi_V^0 = a + bT + cT^2 \quad (6)$$

where a , b and c are constants and T is the absolute temperature. The $(\partial\phi_V^0/\partial T)_p$ and $(\partial^2\phi_V^0/\partial T^2)_p$ values of glycine/L-alanine in water are $(0.097 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $-0.0023 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$) and $(0.079 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $-0.0019 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$), respectively, which agree well with the literature values [27, 28, 34] and are summarized in Table 5. The $(\partial^2\phi_V^0/\partial T^2)_p$ values of glycine in aqueous CA solutions decrease with increasing temperature except at $m_c = (0.4 \text{ and } 0.5) \text{ mol} \cdot \text{kg}^{-1}$ whereas the $(\partial^2\phi_V^0/\partial T^2)_p$ values for L-alanine increase with increasing temperature.

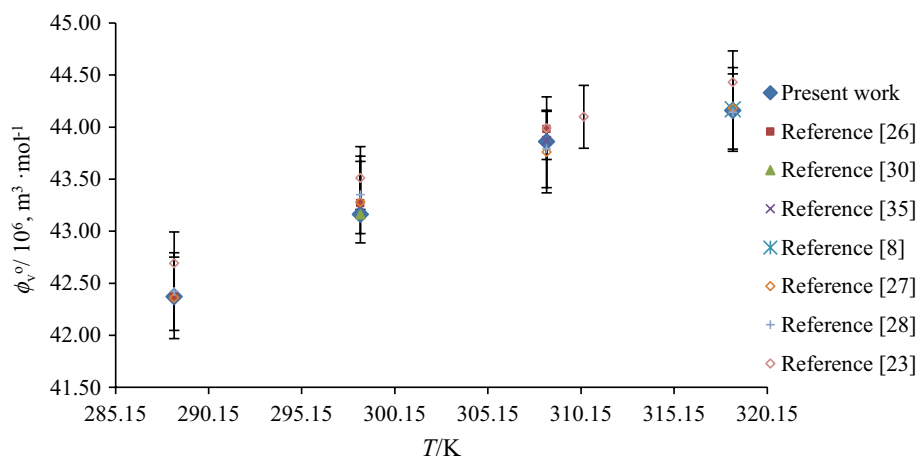


Fig. 9 Comparative plots of limiting partial molar volumes (ϕ_V^o) of glycine in water versus temperature, $T=(288.15\text{--}318.15)$ K

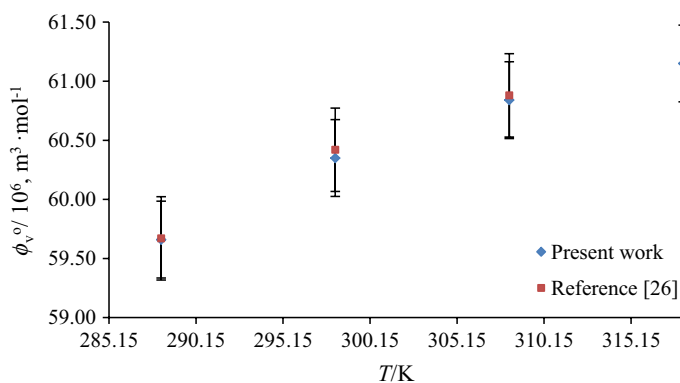
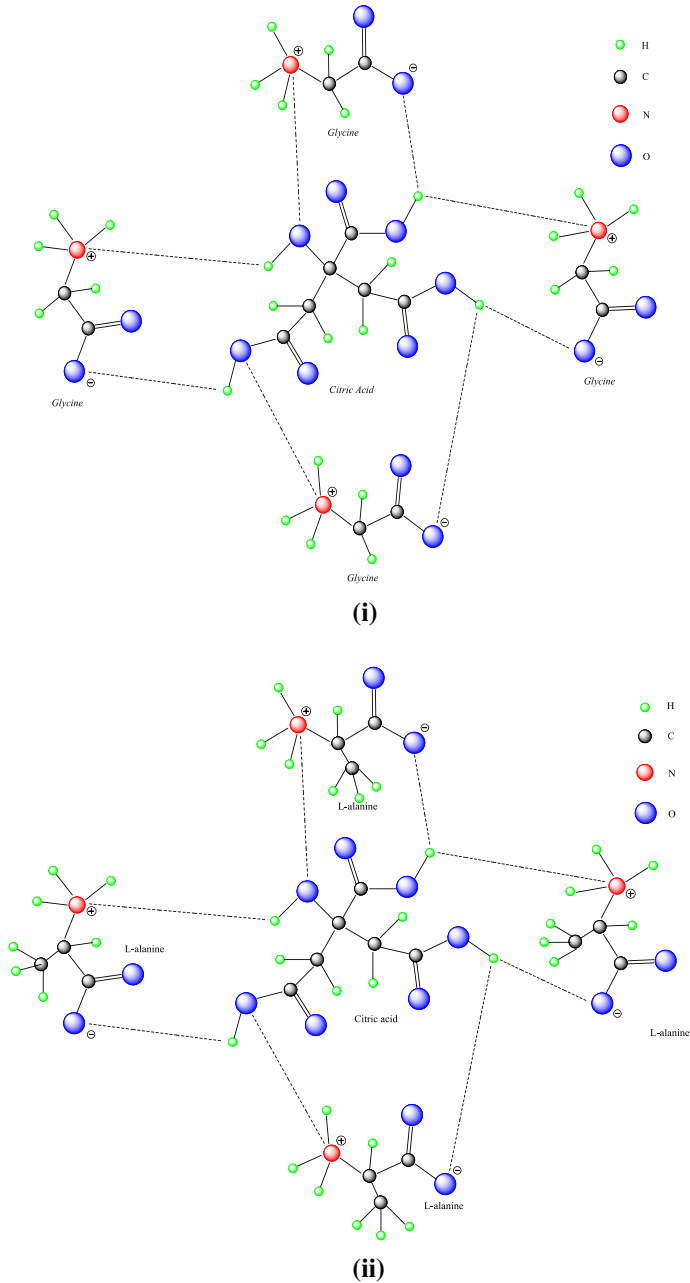


Fig. 10 Comparative plots of limiting partial molar volumes (ϕ_V^o) of L-alanine in water versus temperature, $T=(288.15\text{--}318.15)$ K

Hepler [46] used the following thermodynamic relation by which qualitative information regarding hydration of a solute can be evaluated from the thermal expansion:

$$(\partial C_p^o / \partial p)_T = -T(\partial^2 \phi_V^o / \partial T^2)_p \quad (7)$$

where C_p^o is the partial molar heat capacity. The sign of $(\partial C_p^o / \partial p)_T$ and its temperature dependence should provide a distinction between the structure making or breaking ability of solutes in solution. According to Eq. 7, a structure-breaking solute should have negative $(\partial^2 \phi_V^o / \partial T^2)_p$ values whereas positive $(\partial^2 \phi_V^o / \partial T^2)_p$ values suggest that the solute behaves as a structure maker. It can be seen from Table 5 that glycine predominantly acts as a structure breaker whereas L-alanine acts as a structure maker. It is concluded that the



Scheme 2 Different types of possible interactions **(i)** glycine–CA and **(ii)** L-alanine–CA at pH 2.12 and at $T=310.15$ K

structure-breaking and structure-making behavior of glycine and L-alanine in CA may be attributed to the absence of the caging effect [47]. Similar behavior for glycine in SA is observed for the $(\partial^2 \phi_V^0 / \partial T^2)_p$ values. Overall, the structure breaking tendency of glycine

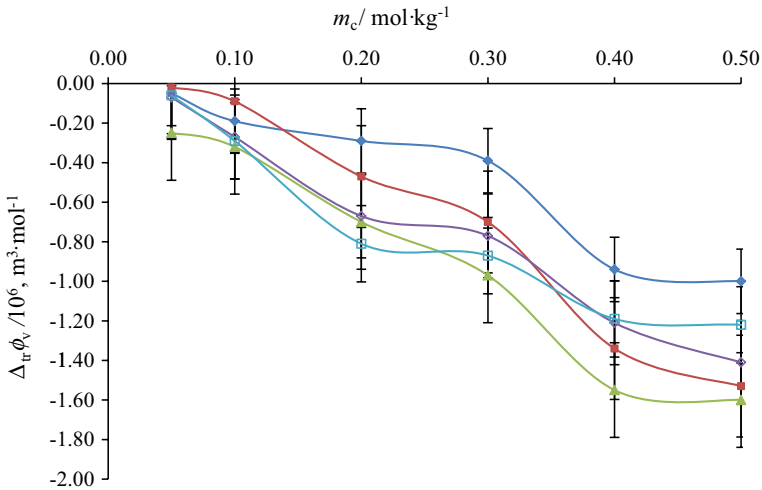


Fig. 11 Plots of partial molar volumes of transfer ($\Delta_{tr}\phi_V$) versus molalities (m_c) of CA of glycine at different temperatures: T =blue filled diamond, 288.15; red filled square, 298.15; Green filled triangle, 308.15; Violet open diamond, 310.15; blue open square, 318.15 K (Color figure online)

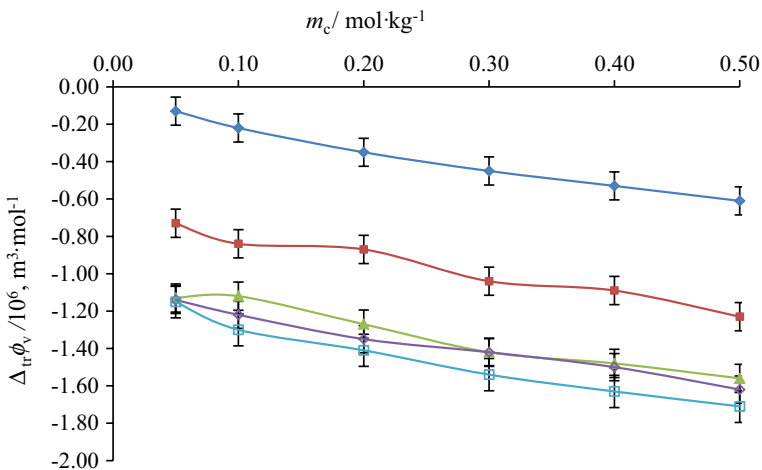


Fig. 12 Plots of partial molar volumes of transfer ($\Delta_{tr}\phi_V$) versus molalities (m_c) of CA of L-alanine at different temperatures: T =blue filled diamond, 288.15; red filled square, 298.15; Green filled triangle, 308.15; Violet open diamond, 310.15; blue open square, 318.15 K (Color figure online)

in the presence of CA is higher than for glycine in SA [23]. This may be attributed due to partial dissociation of CA which tends to destruct the hydrogen bonded structure of water, and then water behaves as a normal (*i.e.* non associated) liquid. The equilibrium of different water species (*i.e.*, a hydrogen bonded structure associated with a normal liquid) is temperature dependent. Elevation in temperature leads to the expansion of volume with increase in the fraction of non-associated water molecules. In addition, the water structure

Table 4 Pair (V_{AB}) and triplet (V_{ABB}) interaction coefficients of glycine/L-alanine in aqueous CA solutions at $T=(288.15$ to $318.15)$ K

$T(K)$	$10^6 \times V_{AB} (\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg})$	$10^6 \times V_{ABB} (\text{m}^3 \cdot \text{mol}^{-3} \cdot \text{kg}^2)$
Glycine		
288.15	$-0.33 (-12.28)_{SA}$	$-1.62 (12.69)_{SA}$
298.15	$0.19 (-11.68)_{SA}$	$-5.07 (3.82)_{SA}$
308.15	$-1.40 (0.64)_{SA}$	$-1.69 (-33.95)_{SA}$
310.15	$-1.40 (0.91)_{SA}$	$-0.22 (-35.34)_{SA}$
318.15	$-1.64 (1.22)_{SA}$	$-0.59 (-39.19)_{SA}$
L-Alanine		
288.15	-1.32	1.75
298.15	-5.82	13.51
308.15	-8.35	19.42
310.15	-8.99	21.48
318.15	-9.25	21.58

$()_{SA}$ are the V_{AB} and V_{ABB} values of glycine in aqueous SA solutions [23]

changes from the combined effects of increased temperature and with increase in the CA concentration [19].

3.2 Hydration Number

The hydration number (n_H) reflects the electrostriction effect of the charge centers of amino acids on nearby water molecules. Millero et al. [48] reported a relationship between the limiting electrostriction contribution to the partial molar volume and hydration number of the non-electrolytes as:

$$\phi_{V, \text{elect}} = n_H(\phi_{V, e}^{\circ} - \phi_{V, b}^{\circ}) \quad (8)$$

where $\phi_{V, e}^{\circ}$ is the limiting molar volume of electrostricted water and $\phi_{V, b}^{\circ}$ is the molar volume of bulk water. For every water molecule taken from the bulk phase to the region near an AA, the $(\phi_{V, e}^{\circ} - \phi_{V, b}^{\circ})$ values are -2.9 , -3.3 and $-4.0) \times 10^{-2} \text{ m}^3 \cdot \text{mol}^{-1}$ at $T=(288.15$, 298.15 and $308.15)$ K, respectively [48]. The n_H values of glycine/L-alanine in water and in aqueous CA solutions are summarized in Table 6. The n_H values of glycine/L-alanine in water are in good agreement with the literature values and are shown in Figs. 13 and 14 [26–28, 49]. The n_H values of glycine and L-alanine increase with increase in the concentration of CA, which further suggests that water in the immediate vicinity of charged centers of glycine/L-alanine in aqueous CA solutions is highly electrostricted leading to higher n_H values. The decrease in n_H values with increases in temperature may be attributed to the weakening of the electrostriction effect of charged centers, which then leads to stronger interactions between glycine–CA and L-alanine–CA. It also shows that CA exerts a dehydration effect in the present systems.

Lower n_H values for glycine/L-alanine in water than in CA indicate that glycine/L-alanine are more hydrated in the presence of CA. Also, the higher n_H values for glycine in SA than in CA further suggests that SA has a strong dehydrating effect on glycine. This may be due to the presence of hydrophilic groups (*i.e.*, $-\text{OH}$ and $-\text{COOH}$ in CA) which leads to the formation of hydrogen bonding.

Table 5 Limiting partial molar expansibilities $(\partial\phi_V^0/\partial T)_p$ and their second-order derivatives $(\partial^2\phi_V^0/\partial T^2)_p$ for glycine/L-alanine in water and in aqueous CA solutions at $T=(288.15$ to $318.15)$ K

m_c (mol·kg ⁻¹)	$(\partial\phi_V^0/\partial T)_p$ (m ³ ·mol ⁻¹ ·K ⁻¹)					$(\partial^2\phi_V^0/\partial T^2)_p$ (m ³ ·mol ⁻¹ ·K ⁻²)
	T(K): 288.15	298.15	308.15	310.15	318.15	
Glycine						
0.00	0.096 ^a (0.097) ^b	0.072 ^a (0.072) ^b (0.071) ^c	0.049 ^a (0.047) ^b	0.044 ^a	0.025 ^a (0.022) ^b	-0.0024 ^a (-0.0025) ^b
0.05	0.084	0.067	0.049	0.046	0.032	-0.0018
0.10	0.097 (0.125) _{SA}	0.071 (0.093) _{SA}	0.044 (0.061) _{SA}	0.039 (0.054) _{SA}	0.018 (0.029) _{SA}	-0.0026 (-0.0032) _{SA}
0.20	0.075	0.054	0.033	0.029	0.012	-0.0021
0.30	0.056 (0.486) _{SA}	0.048 (0.416) _{SA}	0.041 (0.346) _{SA}	0.040 (0.332) _{SA}	0.034 (0.276) _{SA}	-0.0007 (-0.0074) _{SA}
0.40	0.041	0.049	0.057	0.058	0.065	0.0008
0.50	0.027 (-0.219) _{SA}	0.045 (-0.149) _{SA}	0.063 (-0.079) _{SA}	0.067 (-0.065) _{SA}	0.081 (-0.009) _{SA}	0.0018 (0.0075) _{SA}
L-Alanine						
0.00	0.079	0.060 (0.062) ^d	0.040	0.036	0.021	-0.0019
0.05	0.008	0.010	0.020	0.022	0.029	-0.0010
0.10	0.004	0.010	0.017	0.018	0.024	0.0007
0.20	0.012	0.013	0.014	0.014	0.015	0.0001
0.30	0.009	0.012	0.015	0.016	0.018	0.0003
0.40	0.010	0.013	0.015	0.015	0.017	0.0002
0.50	0.007	0.011	0.015	0.016	0.019	0.0004

(_{SA}) are the $(\partial\phi_V^0/\partial T)_p$ and $(\partial^2\phi_V^0/\partial T^2)_p$ values of glycine in aqueous SA solutions [23]

^aPresent work

^bReference [27]

^cReference [28]

^dReference [34]

3.3 Apparent Specific Volumes and Taste Quality

CA and inorganic citrates are active ingredients in many dosage forms. It is a natural preservative which is used to add an acidic or sour taste to foods and drinks. The taste behavior can be verified on the basis of the apparent specific volumes (v_ϕ) which gives a direct measure of the dislocation of water molecule by the solute and reflects its compatibility with water. v_ϕ has been calculated by using the following equation [50]:

$$v_\phi = \phi_V/M \quad (9)$$

where ϕ_V is the apparent molar volume and M is the molar mass of glycine/L-alanine and $v_\phi \times 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$ bears a relationship to taste quality in the order salt $< \sim 0.33$, sour ~ 0.33 to ~ 0.52 , sweet ~ 0.52 to ~ 0.71 , and bitter ~ 0.71 to ~ 0.93 [51]. The v_ϕ values for CA in water, glycine/L-alanine in water, in aqueous CA and glycine in aqueous SA solutions are

Table 6 Hydration number (n_H) of glycine/L-alanine in water and in aqueous CA solutions at $T=(288.15, 298.15$ and $308.15)$ K

m_c (mol·kg ⁻¹)	n_H		
	$T(K): 288.15$	298.15	308.15
Glycine			
0.00	3.27 ^a (3.26 ^b , 3.27 ^c , 3.28 ^d)	2.64 ^a (2.58 ^b , 2.60 ^c , 2.61 ^d)	2.00 ^a (2.02 ^{b,c} , 1.97 ^d)
0.05	3.29	2.64	2.06
0.10	3.34 (3.97) _{SA}	2.66 (3.20) _{SA}	2.08 (2.55) _{SA}
0.20	3.37	2.78	2.18
0.30	3.41 (5.83) _{SA}	2.85 (4.37) _{SA}	2.24 (2.38) _{SA}
0.40	3.60	3.04	2.39
0.50	3.62 (6.53) _{SA}	3.10 (5.27) _{SA}	2.40 (4.32) _{SA}
L-Alanine			
0.00	4.17 ^a (4.17 ^d)	3.45 ^a (3.45 ^b)	2.73 ^a (2.68 ^b , 2.72 ^d)
0.05	4.21	3.68	3.01
0.10	4.24	3.71	3.03
0.20	4.29	3.72	3.05
0.30	4.32	3.77	3.08
0.40	4.35	3.78	3.10
0.50	4.38	3.83	3.12

(_{SA}) are the n_H values of glycine in aqueous SA solutions [23]

^aPresent work

^bReference [28]

^cReference [27]

^dReference [49]

Fig. 13 Comparison plots of hydration number (n_H) of glycine in water at different temperatures, $T=(288.15, 298.15$ and $308.15)$ K

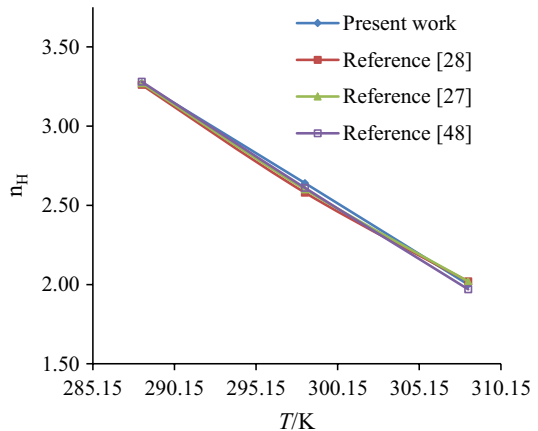
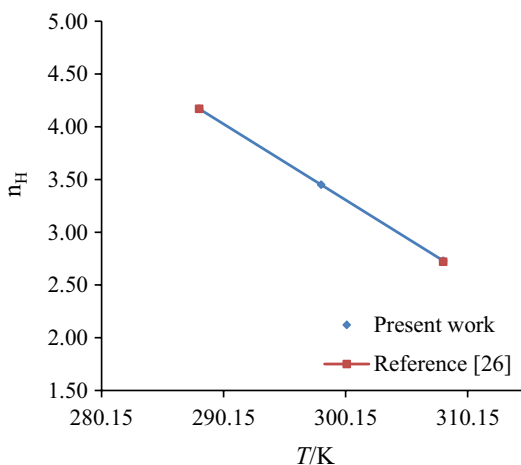


Fig. 14 Comparison plots of hydration number (n_H) of L-alanine in water at different temperatures, $T = (288.15, 298.15$ and $308.15)$ K



given in Table S2. It is observed from Table S2 that the v_ϕ values of glycine/L-alanine in water and in aqueous CA solutions (range from 0.55 to 0.69) fall in the sweet taste behavior range (except for L-alanine at $m_c = 0.05 \text{ mol}\cdot\text{kg}^{-1}$), which may be due to hydrophobic interactions occurring in these ternary systems. The result obtained from the v_ϕ values also supports $\Delta_{tr}\phi_V$ data, which further strengthens the view that hydrophobic interactions are dominating in these systems. In the case of SA, the v_ϕ values of glycine tend to show sour-to-sweet taste behavior (ranges from 0.47 to 0.61) with increase in concentration and temperature. The obtained trend in SA may due to the displacement of a large number of water molecules by hydrophobic groups [52].

4 Conclusions

The negative $\Delta_{tr}\phi_V$ values obtained for glycine/L-alanine in aqueous CA solutions suggest the dominance of hydrophilic–hydrophobic and hydrophobic–hydrophobic interactions in these systems. Triplet interactions dominate over pair interactions in the case of L-alanine compared to glycine in CA, which indicates that L-alanine interacts more strongly with CA. At low concentrations of CA, glycine/L-alanine act as structure breakers whereas at high concentrations of CA, glycine/L-alanine act as structure makers. Also, it is evident that CA has a dehydration effect on amino acids. The results obtained for v_ϕ values suggest that CA enhances the sweet taste behavior of glycine/L-alanine with rise in temperatures. Comparative studies of glycine in aqueous CA and aqueous SA solutions show that the stronger interactions exist between glycine–CA than for glycine–SA, which is attributed due to the presence of additional hydrophilic groups in CA that leads to the formation of hydrogen bonds.

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