Thermochimica Acta 513 (2011) 68–74

Contents lists available at ScienceDirect

Thermochimica Acta

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

Partial molar volumes, expansibilities and compressibilities of glyglyglycine in aqueous sucrose and fructose solutions between 288.15 and 308.15 K

Amalendu Pal*, Nalin Chauhan

Department of Chemistry, Kurukshetra University, Kurukshetra 136119, India

A R T I C L E I N F O

Article history:
Received 8 September 2010
Received in revised form 2 November 2010
Accepted 8 November 2010
Available online 12 November 2010

Keywords:
Glyglyglycine
Transfer functions
Saccharides
Adiabatic
Partial molar expansion

A B S T R A C T

Apparent molar volumes (V_ϕ) and apparent molar adiabatic compressibilities ($K_{\phi,s}$) of triglycine (glyglyglycine) in aqueous and mixed aqueous solutions of fructose and sucrose (2, 4, and 6 mass%) have been determined at 288.15, 293.15, 298.15, 303.15, and 308.15 K. From these data, limiting partial molar volumes (V_ϕ^0) and limiting partial molar adiabatic compressibilities ($K_{\phi,s}^0$) for glyglyglycine in aqueous sucrose and fructose solutions have been evaluated, together with the standard partial molar properties of transfer $\Delta_{tr}Y$ of the glyglyglycine from water to aqueous saccharides solutions. Transfer parameters have been interpreted in terms of solute–cosolute interactions on the basis of a cosphere overlap model. Pair and triplet interaction coefficients have also been calculated from transfer parameter data. The partial molar volume at infinite dilution (V_ϕ^0) were used to obtain the partial molar expansion at infinite dilution, E_2^0, for glyglyglycine to examine the temperature dependence of such interactions.

1. Introduction

The stabilization of native confirmations of biological macromolecules is commonly related to several interactions including hydrogen bonding, electrostatic and hydrophobic interactions. These interactions are affected by the surrounding solutes and solvent of macromolecules; for this reason, the physico-chemical behaviours of proteins are strongly influenced by the presence of solutes. Volume and compressibility are fundamental thermodynamic observables that have been proven sensitive to solute hydration [1–4]. Volumetric measurements have been applied to characterizing conformational states of proteins, including the native, compact intermediate, fully and partially unfolded states [5–9]. Peptides are also among the building units of complex biomolecules such as proteins. Therefore the determination of various thermodynamic properties for aqueous and mixed aqueous solutions of peptides has occupied our attention [10–13]. The partial molar volume (V_ϕ^0) data at infinite dilution for the peptides are of particular interest because of their use in group additivity schemes to characterize the fully unfolded proteins [11,14].

Despite the significance of partial molar volume measurements, a complete understanding of such hydration phenomenon requires determination of the partial molar expansibility and compressibility. Such measurements are scarce [15–18]. In a recent paper [18], we described the partial molar volumes (V_ϕ^0) and partial molar adiabatic compressibilities ($K_{\phi,s}^0$) of glyglyglycine at infinite dilution in aqueous and mixed aqueous solutions of glucose from high precision density and sound speed measurements. In continuation of the previous study, the present paper reports partial molar volume (V_ϕ^0) and partial molar adiabatic compressibility ($K_{\phi,s}^0$) at infinite dilution of glyglyglycine (0.03–0.10 mol kg^{-1}) in pure water to 6 mass% of sucrose and fructose at temperatures: 288.15, 293.15, 298.15 K, 303.15 and 308.15 K. The corresponding transfer functions and partial molar expansions are also reported. These results were combined with the results of our previous work [18] to obtain a better understanding of the hydration of biological systems. The results have been discussed in terms of various solute–solvent and solute–solute interactions.

2. Experimental

The peptide triglycine (glyglyglycine) (G1377) (minimum assay 98.0%) of highest purity was obtained from Sigma Chemicals Co., and was used as such without further purification. However, before use this was dried over P_2O_5 under vacuum at room temperature. Analytical reagent grade saccharides: sucrose (minimum assay 98.0%) from Hi Media, Mumbai and fructose (minimum assay 98.0%) from Loba Chemie Pvt. Ltd., were used after drying at 333.15 K in a vacuum oven for a minimum of 48 h. All solutions were prepared by using deionized doubly glass-distilled water (having specific conductance less than 10^{-6} S) that had been freshly degassed by vacuum pump. Solutions of saccharides were pre-

* Corresponding author. Tel.: +91 1744 239765; fax: +91 1744 238277.
E-mail address: palchem@sify.com (A. Pal).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.11.013

pared by mass in the range 2–6% and used on the day they were prepared. Solutions of glyglyglycine in the concentration range 0.03–0.10 mol kg^{-1} were made by mass on the molality concentration scale with an accuracy of $\pm 1 \times 10^{-5}$. The weighings were done on an A&D Company, Limited electronic balance (Japan, Model GR-202) with a precision of ±0.01 mg. The uncertainties in the solution molalities were in the range $\pm 2 \times 10^{-5}$ mol kg^{-1}. Densities (ρ) and speeds of sound (u) of glyglyglycine in aqueous sucrose and fructose solutions at different temperatures were measured simultaneously and automatically, using an Anton Paar DSA 5000 instrument. Both speed of sound and density are extremely sensitive to temperature, so it is controlled to $\pm 1 \times 10^{-2}$ K by built-in-solid state thermostat. Before each series of measurements, the instrument was calibrated at temperatures: 288.15, 293.15, 298.15, 303.15, and 308.15 K with doubly distilled water and dry air. The sensitivity of instrument corresponded to a precision in density and speed of sound measurements of $\pm 1 \times 10^{-6}$ g cm^{-3} and $\pm 1 \times 10^{-2}$ m s^{-1}, respectively. The reproducibility of density and speed of sound was found to be better than $\pm 5 \times 10^{-6}$ g cm^{-3} and $\pm 5 \times 10^{-2}$ m s^{-1}, respectively.

3. Results and discussion

3.1. Apparent molar volume and apparent molar adiabatic compressibility

Densities (ρ) and speeds of sound (u) of solutions are listed in Table 1. Apparent molar volumes (V_ϕ) and apparent molar adiabatic compressibilities ($K_{\phi,s}$) of glyglyglycine were calculated using accurate density and speed of sound data through the following equations:

$$V_\phi = \left\{\frac{M}{\rho}\right\} - \left\{\frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right\} \quad (1)$$

$$K_{\phi,s} = \left\{\frac{M\beta_s}{\rho}\right\} - \left\{\frac{1000(\beta_{s,0}\rho - \beta_s\rho_0)}{m\rho\rho_0}\right\} \quad (2)$$

where M is the molar mass of the solute (glyglyglycine), ρ_0, ρ, $\beta_{s,0}$ and β_s are the densities and coefficient of adiabatic compressibilities of saccharide + water and glyglyglycine + saccharide + water, respectively, and m is the molality of glyglyglycine in glyglyglycine + saccharide + water.

The coefficient of adiabatic compressibility (β_s) was determined from the sound speed (u) and density (ρ) data by using the equation:

$$\beta_s = \frac{1}{u^2\rho} \quad (3)$$

The results obtained using Eqs. (1) and (2) are listed in Table 2. Infinite dilution apparent molar volumes (V_ϕ^0) and apparent molar adiabatic compressibilities ($K_{\phi,s}^0$), which are equal to standard partial molar volumes and standard partial molar adiabatic compressibilities, were obtained by least squares fitting of experimental data to the following equation:

$$Y_\phi = Y_\phi^0 + S_Q m \quad (4)$$

where Y_ϕ^0 (denotes V_ϕ^0 or $K_{\phi,s}^0$) is the infinite dilution apparent molar property (equal to standard partial molar property) and S_Q (S_Q denotes S_V or S_K) is the experimental slope. The resulting values of V_ϕ^0, $K_{\phi,s}^0$, S_V and S_K are summarized in Table 3. At infinite dilution, the solute–solute interaction is negligible; therefore, the standard partial molar property and its temperature dependence provide valuable information of the solute–solvent interactions [19–21]. Table 3 shows that glyglyglycine has positive V_ϕ^0 and negative $K_{\phi,s}^0$ values in aqueous fructose and sucrose solutions as in case of glucose [18], which indicates the presence of strong solute–solvent interactions [22]. The V_ϕ^0 and $K_{\phi,s}^0$ values increase with increase in temperature in aqueous saccharide solutions, indicating the presence of strong solute–solvent interactions as the temperature of the solution increases. This may be due to the reduced electrostriction of water as a result of the zwitterionic groups of the glyglyglycine. The V_ϕ^0 values first increase up to 4 mass% of aqueous fructose solution and then decrease at higher mass percentages and reverse trend has been observed in aqueous sucrose solutions. The overall values of V_ϕ^0 in aqueous saccharide solutions follow the order: sucrose > fructose > glucose [18].

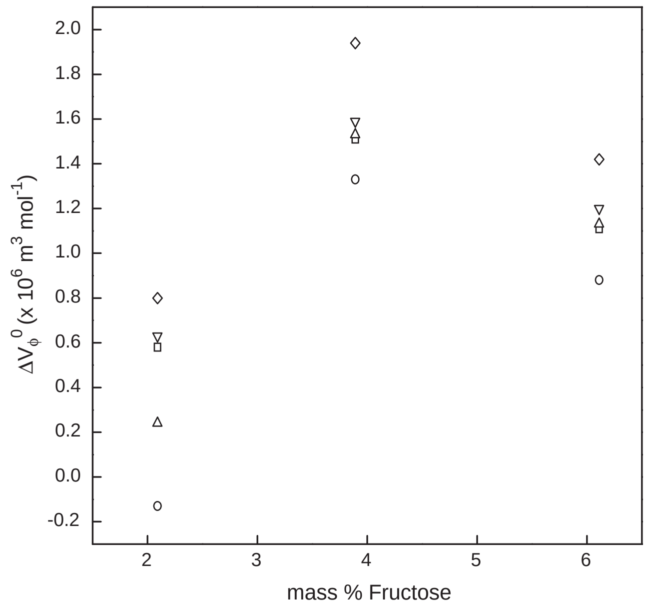

Fig. 1. Variation of partial molar volume of transfer at infinite dilution for glyglyglycine in aqueous fructose solution at: (□) 288.15 K, (○) 293.15 K, (△) 298.15 K, (▽) 303.15 K, and (◇) 308.15 K.

It indicates the presence of strong interaction of tripeptide with disaccharide sucrose as compared to monosaccharides glucose [18] and fructose.

The experimental slopes S_V values are influenced by number of effects [23]. The magnitude of the slope is related to the solute–solute interactions. As can be seen from Table 3 that the values of slope are negative in aqueous sucrose solutions and 4 mass% of fructose suggesting weak solute–solute interactions. $K_{\phi,s}^0$ values for glyglyglycine are negative in aqueous fructose and sucrose solutions and their magnitude are less than the corresponding values in water as for glucose solutions [18].

Partial molar properties of transfer at infinite dilution of glyglyglycine from water [18] to aqueous sachharide solutions were calculated from:

$$\Delta_{tr} Y = Y_\phi^0(\text{in aqueous saccharide solutions}) - Y_\phi^0(\text{in water}) \quad (5)$$

The values are given in Table 4 and represented in Figs. 1 and 2.

3.2. Dependence of volumetric properties on saccharides

It can be seen from Figs. 1 and 2 that ΔV_ϕ^0 values are positive for glyglyglycine in aqueous fructose (except at T = 303.15 K in lower mass percentage) and sucrose solutions at all temperatures. A positive ΔV_ϕ^0 can be explained on the basis that the saccharides interact with the charged centers of tripeptide, thereby leading to a reduction in their electrostriction of the solvent and, hence, a positive volume of transfer. The values of ΔV_ϕ^0 first increase from 2 to 4 mass percentage of fructose and then

Table 1
Densities ρ and speeds of sound u of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

m^a (mol kg^{-1})	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
	ρ ($\times 10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times 10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times 10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times 10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times 10^{-3}$ kg m^{-3})	u (m s^{-1})
Glyglyglycine + 2.09 mass% fructose										
0.00000	1.007403	1476.23	1.006419	1492.03	1.005175	1505.64	1.003702	1517.31	1.002023	1527.00
0.04104	1.010597	1480.48	1.009580	1496.01	1.008312	1509.55	1.006819	1521.25	1.005116	1530.98
0.04714	1.011067	1481.10	1.010046	1496.58	1.008773	1510.12	1.007275	1521.83	1.005572	1531.55
0.06178	1.012195	1482.54	1.011162	1497.95	1.009874	1511.51	1.008365	1523.25	1.006663	1532.98
0.07040	1.012855	1483.52	1.011816	1498.80	1.010520	1512.33	1.009001	1524.08	1.007304	1533.81
0.07908	1.013520	1484.40	1.012471	1499.65	1.011164	1513.20	1.009638	1524.95	1.007946	1534.57
0.08839	1.014228	1485.36	1.013172	1500.54	1.011856	1514.78	1.010319	1525.87	1.008633	1535.51
Glyglyglycine + 3.89 mass% fructose										
0.00000	1.014620	1483.08	1.013563	1498.50	1.012262	1511.97	1.010732	1523.47	1.008998	1533.20
0.03985	1.017691	1487.61	1.016607	1502.90	1.015279	1516.20	1.013729	1527.56	1.011976	1537.10
0.04785	1.018309	1488.51	1.017218	1503.77	1.015886	1517.03	1.014331	1528.37	1.012575	1537.86
0.05874	1.019150	1489.74	1.018051	1504.95	1.016712	1518.13	1.015151	1529.46	1.013390	1538.89
0.06733	1.019815	1490.71	1.018709	1505.88	1.017366	1519.05	1.015798	1530.33	1.014034	1539.73
0.07757	1.020608	1491.83	1.019492	1506.98	1.018143	1520.16	1.016571	1531.35	1.014802	1540.74
0.08586	1.021251	1492.80	1.020127	1507.93	1.018774	1521.01	1.017194	1532.16	1.015422	1541.51
Glyglyglycine + 6.11 mass% fructose										
0.00000	1.023638	1492.81	1.022495	1507.75	1.021112	1520.76	1.019509	1531.80	1.017712	1540.98
0.04289	1.026911	1497.86	1.025741	1512.49	1.024331	1525.25	1.022707	1536.22	1.020891	1545.27
0.05189	1.027589	1498.92	1.026413	1513.48	1.025000	1526.19	1.023370	1537.14	1.021552	1546.15
0.06166	1.028323	1500.08	1.027142	1514.57	1.025724	1527.22	1.024087	1538.13	1.022267	1547.12
0.07099	1.029020	1501.20	1.027835	1515.60	1.026412	1528.20	1.024769	1539.05	1.022947	1548.05
0.07820	1.029555	1502.05	1.028367	1516.40	1.026942	1528.97	1.025295	1539.85	1.023471	1548.80
0.09139	1.030531	1503.60	1.029338	1517.83	1.027909	1530.32	1.026251	1541.18	1.024426	1550.10
Glyglyglycine + 2.14 mass% sucrose										
0.00000	1.007500	1473.09	1.006548	1489.01	1.005339	1503.01	1.003893	1515.09	1.002240	1525.30
0.04007	1.010602	1477.48	1.009616	1493.28	1.008377	1507.14	1.006905	1519.11	1.005234	1529.22
0.04992	1.011367	1478.55	1.010372	1494.32	1.009125	1508.15	1.007648	1520.09	1.005972	1530.16
0.05875	1.012052	1479.50	1.011050	1495.24	1.009797	1509.04	1.008315	1520.95	1.006634	1531.01
0.07073	1.012979	1480.80	1.011968	1496.50	1.010708	1510.26	1.009219	1522.14	1.007532	1532.14
0.08246	1.013892	1482.08	1.012872	1497.74	1.011602	1511.46	1.010108	1523.34	1.008414	1533.25
0.09093	1.014551	1482.96	1.013525	1498.60	1.012246	1512.32	1.010750	1524.17	1.009050	1534.05
Glyglyglycine + 4.19 mass% sucrose										
0.00000	1.015590	1479.35	1.014587	1495.07	1.013332	1508.79	1.011848	1520.52	1.010160	1530.44
0.03852	1.018578	1483.76	1.017541	1499.30	1.016258	1512.86	1.014754	1524.46	1.013046	1534.28
0.04968	1.019442	1485.03	1.018397	1500.51	1.017106	1514.03	1.015595	1525.60	1.013882	1535.37
0.05984	1.020230	1486.18	1.019178	1501.61	1.017880	1515.09	1.016360	1526.63	1.014642	1536.38
0.07144	1.021126	1487.50	1.020066	1502.87	1.018762	1516.29	1.017234	1527.80	1.015512	1537.51
0.08243	1.021975	1488.72	1.020910	1504.04	1.019596	1517.43	1.018061	1528.90	1.016334	1538.55
0.08791	1.022408	1489.34	1.021332	1504.62	1.020014	1517.99	1.018474	1529.43	1.016745	1539.10
Glyglyglycine + 6.14 mass% sucrose										
0.00000	1.023446	1486.32	1.022396	1501.82	1.021098	1515.29	1.019579	1526.84	1.017854	1536.67
0.04087	1.026586	1490.80	1.025501	1506.09	1.024171	1519.36	1.022628	1530.74	1.020885	1540.50
0.04931	1.027235	1491.71	1.026143	1506.96	1.024808	1520.18	1.023260	1531.53	1.021513	1541.26
0.05925	1.028001	1492.77	1.026901	1507.98	1.025559	1521.14	1.024004	1532.46	1.022254	1542.17
0.06889	1.028745	1493.80	1.027635	1508.95	1.026285	1522.08	1.024727	1533.35	1.022973	1543.05
0.06942	1.028786	1493.88	1.027676	1509.05	1.026326	1522.15	1.024767	1533.42	1.023013	1543.12
0.09012	1.030385	1496.05	1.029261	1511.15	1.027897	1524.12	1.026320	1535.29	1.024558	1544.95

[a] m stands for the molalities of peptide in aqueous solutions of saccharides which represents that the solutions of triglycine in (water + saccharide) were prepared on the molal basis (i.e. no. of moles of triglycine dissolved in 1000 g of aqueous saccharide solution) and mass% of saccharides in (water + saccharide) means that the solutions of saccharides in water were made by weight percentage. i.e. [{wt. of saccharide/total wt. of solution} × 100].

decrease slowly at higher concentration of fructose. Whereas in aqueous sucrose solutions ΔV_{ϕ}^{0} first decreases up to 4 mass percentage and then increases at higher concentration of sucrose. Further these results can be explained on the basis of cosphere overlap model [24,25]. A property of water molecules in the hydration cosphere depends on the nature of the solute species [26]. In ternary systems, glyglyglycine + saccharide + water, when the solute–cosolute molecules come close enough so that their cospheres overlap, following types of interactions are possible: (a) hydrophilic–ionic group interactions between the –OH group of the saccharides and the zwittreionic centers (COO^- and NH_3^+) of the glyglyglycine, (b) hydrophilic–hydrophilic group interactions between the –OH group of the saccharides and the $-NH_2$ group of the glyglyglycine meditated through the hydrogen bonding, and (c) Hydrophilic–hydrophobic group interactions between the –OH group of the saccharides and the non-polar group ($-CH_2$) of the glyglyglycine. According to this model, first two types of interactions would lead to a positive ΔV_{ϕ}^{0} whereas third type of interaction would lead to negative ΔV_{ϕ}^{0}. The observed positive transfer volume in both the saccharide solutions at all temperature suggests that the hydrophilic–ionic and hydrophilic–hydrophilic interactions are predominant over hydrophilic–hydrophobic group interactions. The same types of interactions are predominant in aqueous glucose solutions [18]. It is worth mentioning that overall values of ΔV_{ϕ}^{0} from water to aqueous saccharide solutions at all temperatures follow the sequence sucrose > fructose > glucose. This, in turn, suggests the sequence of the strength of hydrophilic–ionic and hydrophilic–hydrophilic interactions of glyglyglycine with the saccharides in the solution.

Table 2
Apparent molar volume V_ϕ and apparent molar adiabatic compressibilities $K_{\phi,s}$ of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

m (mol kg^{-1})	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
	V_ϕ ($\times 10^6$ m^3 mol^{-1})	$K_{\phi,s}$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})	V_ϕ ($\times 10^6$ m^3 mol^{-1})	$K_{\phi,s}$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})	V_ϕ ($\times 10^6$ m^3 mol^{-1})	$K_{\phi,s}$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})	V_ϕ ($\times 10^6$ m^3 mol^{-1})	$K_{\phi,s}$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})	V_ϕ ($\times 10^6$ m^3 mol^{-1})	$K_{\phi,s}$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})
Glyglyglycine + 2.09 mass% fructose										
0.04104	110.74	−47.79	111.57	−41.70	112.19	−39.13	112.73	−38.32	113.38	−37.63
0.04714	110.79	−47.55	111.60	−41.37	112.25	−38.91	112.83	−38.13	113.40	−37.47
0.06178	110.82	−46.71	111.64	−40.83	112.39	−38.69	113.03	−38.04	113.46	−37.49
0.07040	110.87	−47.46	111.68	−40.95	112.46	−38.60	113.16	−37.89	113.48	−37.39
0.07908	110.89	−47.24	111.73	−40.96	112.57	−38.78	113.29	−37.98	113.52	−36.76
0.08839	110.94	−47.11	111.78	−40.81	112.64	−38.73	113.42	−37.95	113.56	−36.98
Glyglyglycine + 3.89 mass% fructose										
0.03985	111.25	−51.23	111.95	−47.23	112.65	−43.08	113.21	−39.86	113.74	−36.27
0.04785	111.15	−51.14	111.88	−47.07	112.56	−42.89	113.13	−39.75	113.65	−36.04
0.05874	111.04	−51.10	111.77	−46.90	112.45	−42.42	113.03	−39.54	113.55	−35.80
0.06733	110.93	−51.08	111.67	−46.81	112.33	−42.63	112.94	−39.52	113.45	−35.89
0.07757	110.80	−50.82	111.58	−46.68	112.24	−42.88	112.83	−39.39	113.34	−36.05
0.08586	110.70	−51.09	111.50	−46.96	112.14	−42.75	112.77	−39.19	113.27	−35.84
Glyglyglycine + 6.11 mass% fructose										
0.04289	111.62	−50.38	112.26	−44.39	112.92	−39.66	113.46	−37.64	113.96	−35.17
0.05189	111.70	−50.23	112.36	−44.21	112.97	−39.55	113.53	−37.46	114.00	−34.89
0.06166	111.77	−50.19	112.41	−44.20	113.01	−39.52	113.61	−37.21	114.04	−34.77
0.07099	111.86	−50.20	112.47	−44.07	113.07	−39.44	113.68	−36.82	114.09	−34.70
0.07820	111.94	−50.06	112.53	−44.00	113.11	−39.46	113.72	−37.18	114.13	−35.00
0.09139	112.07	−49.81	112.63	−43.65	113.18	−39.13	113.82	−36.87	114.19	−34.62
Glyglyglycine + 2.14 mass% sucrose										
0.04007	111.15	−51.41	112.03	−47.26	112.81	−43.32	113.51	−40.27	114.02	−37.82
0.04992	111.02	−51.34	111.91	−47.18	112.70	−43.29	113.37	−40.23	113.90	−37.61
0.05875	110.93	−51.20	111.80	−47.01	112.59	−43.14	113.25	−40.05	113.79	−37.56
0.07073	110.84	−51.12	111.70	−46.93	112.46	−43.10	113.12	−40.05	113.66	−37.33
0.08246	110.69	−51.18	111.54	−46.98	112.32	−43.14	112.95	−40.34	113.51	−37.23
0.09093	110.60	−51.10	111.43	−46.78	112.24	−43.10	112.84	−40.28	113.42	−37.16
Glyglyglycine + 4.19 mass% sucrose										
0.03852	110.73	−52.42	111.62	−47.34	112.38	−43.16	112.95	−39.97	113.52	−37.49
0.04968	110.67	−52.29	111.53	−47.18	112.28	−43.07	112.87	−39.95	113.43	−37.26
0.05984	110.58	−52.18	111.42	−47.07	112.16	−43.00	112.81	−39.86	113.36	−37.27
0.07144	110.53	−52.10	111.34	−46.99	112.06	−42.85	112.72	−39.76	113.25	−37.14
0.08243	110.47	−51.82	111.24	−46.80	111.98	−42.75	112.65	−39.63	113.17	−36.84
0.08791	110.33	−51.79	111.18	−46.71	111.92	−42.68	112.60	−39.47	113.12	−36.92
Glyglyglycine + 6.14 mass% sucrose										
0.04087	111.15	−46.89	112.01	−41.86	112.81	−37.47	113.43	−33.99	113.93	−32.19
0.04931	111.07	−46.72	111.92	−41.74	112.69	−37.29	113.32	−33.88	113.82	−31.91
0.05925	110.95	−46.50	111.79	−41.64	112.56	−37.12	113.20	−33.79	113.68	−31.84
0.06889	110.83	−46.38	111.70	−41.40	112.48	−37.04	113.08	−33.65	113.56	−31.79
0.06942	110.82	−46.57	111.69	−41.77	112.46	−37.20	113.07	−33.81	113.54	−31.95
0.09012	110.58	−46.10	111.40	−41.54	112.16	−36.88	112.84	−33.36	113.30	−31.52

Table 3
Limiting partial molar properties V_ϕ^0 and $K_{\phi,s}^0$ and experimental slopes S_V and S_K of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

Mass% (saccharide)	V_ϕ^0 ($\times 10^6$ m^3 mol^{-1})					S_V ($\times 10^6$ m^3 L$^{1/2}$ mol$^{-3/2}$)				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Fructose										
2.09	110.59 (±0.02)	111.39 (±0.02)	111.80 (±0.01)	112.14 (±0.01)	113.22 (±0.01)	3.91 (±0.30)	4.30 (±0.29)	9.60 (±0.24)	14.52 (±0.13)	3.75 (±0.13)
3.89	111.73 (±0.01)	112.35 (±0.01)	113.09 (±0.02)	113.60 (±0.01)	114.15 (±0.01)	−11.92 (±0.21)	−9.92 (±0.17)	−11.06 (±0.25)	−9.74 (±0.20)	−10.31 (±0.19)
6.11	111.21 (±0.02)	111.96 (±0.02)	112.69 (±0.01)	113.15 (±0.01)	113.75 (±0.01)	9.26 (±0.30)	7.32 (±0.33)	5.38 (±0.13)	7.38 (±0.16)	4.80 (±0.11)
Sucrose										
2.14	111.56 (±0.03)	112.49 (±0.02)	113.26 (±0.01)	114.02 (±0.02)	114.49 (±0.01)	−10.51 (±0.38)	−11.55 (±0.36)	−11.32 (±0.16)	−13.01 (±0.24)	−11.81 (±0.13)
4.19	111.02 (±0.06)	111.96 (±0.01)	112.73 (±0.02)	113.22 (±0.01)	113.83 (±0.01)	−7.27 (±0.91)	−8.81 (±0.23)	−9.25 (±0.30)	−6.99 (±0.14)	−8.09 (±0.15)
6.14	111.64 (±0.01)	112.52 (±0.03)	113.33 (±0.03)	113.91 (±0.01)	114.45 (±0.02)	−11.75 (±0.20)	−12.25 (±0.47)	−12.83 (±0.55)	−12.01 (±0.21)	−12.89 (±0.28)

Mass% (saccharide)	$K_{\phi,s}^0$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})					S_K ($\times 10^6$ kg m^3 mol^{-2} GPa^{-1})				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Fructose										
2.09	−48.03 (±0.58)	−42.18 (±0.33)	−39.29 (±0.23)	−38.52 (±0.15)	−38.30 (±0.33)	11.15 (±8.69)	16.63 (±5.01)	7.45 (±3.56)	7.18 (±2.23)	15.61 (±4.98)
3.89	−51.40 (±0.19)	−47.45 (±0.24)	−43.06 (±0.40)	−40.39 (±0.08)	−36.37 (±0.25)	5.22 (±2.91)	8.07 (±3.77)	4.53 (±6.16)	13.57 (±1.19)	6.13 (±3.93)
6.11	−50.82 (±0.13)	−44.99 (±0.13)	−40.08 (±0.13)	−38.22 (±0.32)	−35.38 (±0.28)	10.25 (±1.87)	13.67 (±1.99)	9.32 (±1.98)	15.54 (±4.65)	7.88 (±4.19)
Sucrose										
2.14	−51.60 (±0.09)	−47.57 (±0.11)	−43.46 (±0.09)	−40.12 (±0.21)	−38.29 (±0.07)	5.70 (±1.41)	8.32 (±1.59)	4.29 (±1.30)	−1.26 (±3.12)	12.85 (±1.04)
4.19	−52.94 (±0.08)	−47.81 (±0.05)	−43.56 (±0.03)	−40.41 (±0.10)	−37.93 (±0.13)	12.97 (±1.22)	12.17 (±0.74)	9.81 (±0.45)	9.76 (±1.45)	12.03 (±1.88)
6.14	−47.48 (±0.15)	−42.06 (±0.24)	−37.86 (±0.14)	−34.50 (±0.13)	−32.58 (±0.18)	15.14 (±2.28)	6.34 (±3.66)	11.00 (±2.11)	11.99 (±2.06)	11.29 (±2.84)

Table 4 shows that $\Delta K_{\phi,s}^0$ values are also positive in aqueous fructose and sucrose solutions as in the case of glucose solution [18]. These positive values of transfer again suggest the presence of hydrophilic–ionic and hydrophilic–hydrophilic interactions between glyglyglycine and saccharides in aqueous solutions. The positive contribution to the $\Delta K_{\phi,s}^0$ values is due to the transfer of electrostricted from the hydration sphere of these ions to the bulk, which is more compressible [27–29].

3.3. Pair and triplet interaction parameters

Thermodynamic transfer functions at infinite dilution are expressed as [30–33]:

$$\Delta_{\mathrm{tr}} Y_\phi^0(\text{water to aqueous cosolute solution}) = 2Y_{AB}m_B + 3Y_{ABB}m_B^2 + \ldots \quad (6)$$

where $\Delta_{\mathrm{tr}} Y_\phi^0$ denotes $\Delta_{\mathrm{tr}} V_\phi^0$ or $\Delta_{\mathrm{tr}} K_{\phi,s}^0$. A stands for peptide and B denotes cosolute, and m_B is the molality of cosolute. Constants Y_{AB} and Y_{ABB} are pair and triplet interaction coefficients. The corresponding parameters V_{AB} and V_{ABB} for volumes and K_{AB} and K_{ABB} for adiabatic compressibilities, estimated from $\Delta_{\mathrm{tr}} V_\phi^0$ and $\Delta_{\mathrm{tr}} K_{\phi,s}^0$, respectively, are summarized in Table 5.

The pair interaction coefficients V_{AB} are positive, whereas triplet interaction coefficients V_{ABB} are negative, calculated from transfer partial molar volume as in case of glyglyglycine in aqueous glucose [18] solutions at the same temperatures. The positive V_{AB} values show that interactions between saccharides and tripeptide are mainly pairwise. The higher magnitude for these interaction coefficients in case of sucrose further suggest that interactions between glyglyglycine-disaccharide (sucrose) are stronger than glyglyglycine-monosaccharides (glucose and fructose) and thus glyglyglycine has a stronger dehydration effect on sucrose. The

Table 4
Transfer partial molar volumes ΔV_ϕ^0 and transfer partial molar adiabatic compressibilities $\Delta K_{\phi,s}^0$ of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

Mass% (saccharide)	ΔV_ϕ^0 ($\times 10^6$ m^3 mol^{-1})					$\Delta K_{\phi,s}^0$ ($\times 10^6$ m^3 mol^{-1} GPa^{-1})				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Fructose										
2.09	0.80	0.63	0.24	−0.13	0.58	5.00	6.47	4.78	2.18	0.60
3.89	1.94	1.59	1.53	1.33	1.51	1.63	1.20	1.01	0.31	2.53
6.11	1.42	1.20	1.13	0.88	1.11	2.21	3.66	3.99	2.48	3.52
Sucrose										
2.14	1.77	1.73	1.70	1.75	1.85	1.43	1.08	0.61	0.58	0.61
4.19	1.23	1.20	1.17	0.95	1.19	0.09	0.84	0.51	0.29	0.97
6.14	1.85	1.76	1.77	1.64	1.81	5.55	6.59	6.21	6.20	6.32

Table 5
Pair Y_{AB} and triplet Y_{ABB} interaction coefficients of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

T (K)	From volume		From compressibility	
	V_{AB} ($\times 10^6$ m^3 mol^{-2} kg)	V_{ABB} ($\times 10^6$ m^3 mol^{-3} kg^2)	K_{AB} ($\times 10^6$ m^3 mol^{-2} kg GPa^{-1})	K_{ABB} ($\times 10^6$ m^3 mol^{-3} kg^2 GPa^{-1})
Fructose				
288.15	6.125	−7.458	17.247	−27.556
293.15	4.886	−5.766	18.454	−26.834
298.15	3.587	−3.428	12.093	−13.762
303.15	2.205	−1.432	4.093	−2.067
308.15	4.626	−5.518	4.123	1.682
Sucrose				
288.15	12.196	−27.339	−7.594	72.557
293.15	12.059	−27.623	−9.063	88.276
298.15	11.675	−26.195	−12.666	97.763
303.15	11.223	−26.135	−14.005	102.072
308.15	12.621	−29.339	−10.547	91.987

pair interaction coefficients K_{AB} are positive in aqueous fructose solutions similar to glucose [18] and negative in aqueous sucrose solutions. The triplet interaction coefficients K_{ABB} are negative except at higher temperature in aqueous fructose solutions and positive in aqueous sucrose solutions.

3.4. Partial molar expansions

The temperature variation of V_ϕ^0 can be expressed as:

$$V_\phi^0 = a + b(T - T_m) + c(T - T_m)^2 \quad (7)$$

where T_m represents the midpoint temperature of the range used (T_m = 298.15 K). Least-square fitting of Eq. (7) was done to obtain a, b and c parameters, which are listed in Table 6 along with their uncertainties. Differentiation of Eq. (7) with respect to temperature at constant pressure was done to calculate partial molar isobaric expansions:

$$E_2^0 = \left(\frac{\partial V_2^0}{\partial T}\right)_P = b + 2c(T - T_m) \quad (8)$$

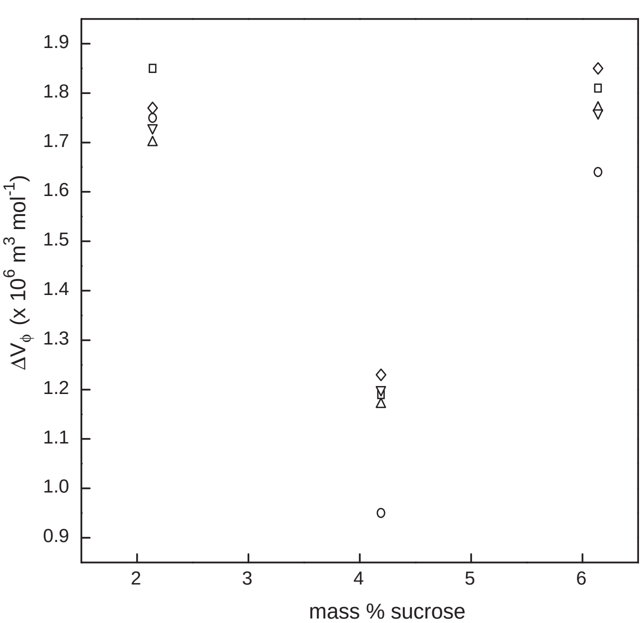

Fig. 2. Variation of partial molar volume of transfer at infinite dilution for glyglyglycine in aqueous sucrose solution at: (□) 288.15 K, (○) 293.15 K, (△) 298.15 K, (▽) 303.15 K, and (◊) 308.15 K.

Table 6
Coefficients of Eq. (7) for glyglyglycine peptide in aqueous saccharide solutions.

Mass% (saccharide)	a ($\times 10^6$ m^3 mol^{-1})	b ($\times 10^6$ m^3 mol^{-1} K^{-1})	c ($\times 10^{10}$ m^3 mol^{-1} K^{-2})
Fructose			
2.09	111.76(±0.18)	0.1202(±0.0162)	14.0(±27.4)
3.89	113.04(±0.04)	0.1218(±0.0035)	−10.6(±5.9)
6.11	112.63(±0.05)	0.1254(±0.0042)	−16.3(±7.1)
Sucrose			
2.14	113.30(±0.03)	0.1478(±0.0029)	−26.6(±4.9)
4.19	112.69(±0.05)	0.1376(±0.0049)	−26.9(±8.3)
6.14	113.30(±0.02)	0.1402(±0.0019)	−26.0(±3.2)

It follows from Eq. (8) that the quantity $b + 2c(T - T_m)$ is equivalent to E_2^0 at a temperature of 298.15 K. The calculated values of partial molar expansion (E_2^0) are given in Table 7. It can be seen from Table 7 that E_2^0 values are decreasing with increase in temperature (except in lower mass percentage of fructose), which is similar as in case of glucose [18]. Here also the E_2^0 values of glyglyglycine in fructose and sucrose solutions are lower than the E_2^0 values of glyglyglycine in water [18]. It can be seen from Table 7 and E_2^0 values of glyglyglycine in aqueous glucose solutions [18] that E_2^0 values of glyglyglycine in aqueous saccharide solutions are in the order: sucrose > glucose > fructose.

3.5. Structure making and breaking ability

Hepler [34] proposed a useful thermodynamic relation, which provides qualitative information on structure making and breaking ability of a solute in aqueous solution:

$$\left(\frac{\partial c_P^0}{\partial P}\right)_T = -T\left(\frac{\partial^2 V_\phi^0}{\partial T^2}\right)_P \quad (9)$$

Table 7
Partial molar expansions at infinite dilution of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

Mass% (saccharide)	E_2^0 ($\times 10^6$ m^3 mol^{-1} K^{-1})				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Fructose					
2.09	0.092	0.106	0.120	0.134	0.148
3.89	0.143	0.132	0.122	0.111	0.101
6.11	0.158	0.142	0.125	0.109	0.093
Sucrose					
2.14	0.201	0.174	0.148	0.121	0.095
1.49	0.191	0.164	0.138	0.111	0.084
6.14	0.192	0.166	0.140	0.114	0.088

Table 8
Values of $(\partial^2 V_\phi{}^o/\partial T^2)_P$ and $(\partial c_p{}^o/\partial P)_T$ of glyglyglycine peptide in aqueous saccharide solutions at different temperatures.

Mass% (saccharide)	$(\partial^2 V_\phi{}^o/\partial T^2)_P$ (cm^6 mol^{-2} K^{-2})	$(\partial c_p{}^o/\partial P)_T$ (cm^3 mol^{-2} K^{-1})				
		288.15	293.15	298.15	303.15	308.15
Fructose						
2.09	0.0028	−0.807	−0.821	−0.835	−0.849	−0.863
3.89	−0.0021	0.611	0.621	0.632	0.643	0.653
6.11	−0.0032	0.939	0.956	0.972	0.988	1.004
Sucrose						
2.14	−0.0053	1.533	1.559	1.586	1.613	1.639
4.19	−0.0054	1.550	1.577	1.604	1.631	1.658
6.14	−0.0052	1.498	1.524	1.550	1.576	1.602

where c_P^0 is the heat capacity of the solute at infinite dilution. In this expression, $(\partial c_P^0/\partial P)_T$ values should be negative for structure-making solutes, whereas, positive for structure-breaking solutes. This suggests that $(\partial^2 V_\phi^0/\partial T^2)_P$ values are positive for structure-making solutes and negative for structure-breaking solutes [34,35]. It can be seen from Table 8 that glyglyglycine has negative $(\partial^2 V_\phi^0/\partial T^2)_P$ values (except in lower mass% of fructose) and, hence positive $(\partial c_P^0/\partial P)_T$ values. It indicates that glyglyglycine behaves as structure-breaker in aqueous fructose and sucrose solutions. The same type of behaviour is also observed from the results of ΔV_ϕ^0 which suggest that glyglyglycine act as a structure-breaker in aqueous fructose as well as sucrose solutions.

Acknowledgement

Financial support for this work sanction letter no. 01 (2187)/07/EMR–II by the Government of India through the Council of Scientific and Industrial Research (CSIR), New Delhi is gratefully acknowledged.

References

[1] T.V. Chalikian, R.B. Macgregor, Phys. Life Rev. 4 (2007) 91–115.
[2] H. Hoiland, H.–J. Hinz (Eds.), Springer–Verlag, Berlin, 1986, pp. 129–147.
[3] A.P. Sarvazyan, Annu. Rev. Biophys. Biophys. Chem. 20 (1991) 321–342.
[4] A.A. Zamyatnin, Annu. Rev. Biophys. Bioeng. 13 (1984) 145–165.
[5] R. Kitahara, H. Yamada, K. Akasaka, P.E. Wright, J. Mol. Biol. 320 (2002) 311–319.
[6] N. Taulier, T.V. Chalikain, Biochim. Biophys. Acta 1595 (2002) 48–70.
[7] R. Filfil, T.V. Chalikain, J. Mol. Biol. 299 (2000) 827–842.
[8] D.P. Kharakhoz, V.E. Bychkova, Biochemistry 36 (1997) 1882–1890.
[9] B. Nolting, S.G. Sligar, Biochemistry 32 (1993) 12319–12323.
[10] M.A. Schwitzer, G.R. Hedwig, J. Solution Chem. 34 (2005) 801–821.
[11] M. Hackel, H.J. Hinz, G.R. Hedwig, Biophys. Chem. 82 (1999) 35–50.
[12] C.J. Downes, G.R. Hedwig, Biophys. Chem. 55 (1995) 279–288.
[13] J.F. Reading, G.R. Hedwig, J. Chem. Soc., Faraday Trans. 86 (1990) 3117–3123.
[14] G.R. Hedwig, H.-J. Hinz, Biophys. Chem. 100 (2003) 239–260.
[15] T.V. Chalikain, A.P. Sarvazyan, K.J. Breslauer, J. Phys. Chem. 97 (1993) 13017.
[16] A.A. Yayanos, J. Phys. Chem. 97 (1993) 13027.
[17] T.S. Banipal, G. Sehgal, Thermochim. Acta 262 (1995) 175–183.
[18] A. Pal, N. Chauhan, S. Kumar, Thermochim. Acta 509 (2010) 24–32.
[19] T.S. Banipal, P. Kapoor, J. Indian Chem. Soc. 76 (1999) 431–437.
[20] F. Franks, Aqueous Solutions of Amphiphiles and Macromolecules, vol. 4, Plenum Press, New York, 1975.
[21] C.M. Romero, F. Negrete, Phys. Chem. Liq. 42 (2004) 261–267.
[22] K. Belibagli, E. Ayranci, J. Solution Chem. 19 (1990) 867–882.
[23] Z. Yan, J.–J. Wang, H. Zheng, D. Liu, J. Solution Chem. 27 (1998) 473–483.
[24] R.W. Gurney, Ionic Process in Solutions, vol. 3, McGraw-Hill, New York, 1953 (chapter 1).
[25] H.S. Frank, M.W. Evans, J. Chem. Phys. 13 (1945) 507–532.
[26] H.L. Friedman, C.V. Krishnan, in: F. Franks (Ed.), Water-A Comprehensive Treatise, vol. 3, Plenum, New York, 1973 (chapter 1).
[27] G.R. Hedwig, H. Hoiland, Biophys. Chem. 49 (1994) 175–181.
[28] B.E. Conway, R.E. Verrall, J. Phys. Chem. 70 (1966) 3952–3965.
[29] S. Cabani, G. Conti, M. Matteoli, J. Solution Chem. 8 (1979) 11–23.
[30] J.J. Kozak, W.S. Knight, W. Kauzmann, J. Chem. Phys. 48 (1968) 675–690.
[31] W.G. McMillan Jr., J.E. Mayer, J. Chem. Soc. 13 (1945) 276–305.
[32] H.L. Friedman, C.V. Krishnan, J. Solution Chem. 2 (1973) 37–51.
[33] F. Franks, M. Pedley, D.S. Reid, J. Chem. Soc., Faraday Trans. I 72 (1976) 359–367.
[34] L.G. Hepler, Can. J. Chem. 47 (1969) 4613–4617.
[35] A. Pal, S. Kumar, J. Mol. Liq. 109 (2004) 23–31.