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Interactions of tripeptide with glucose in aqueous solutions at various temperatures: A volumetric and ultrasonic study

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ABSTRACT

Solution densities and speeds of sound of tripeptide (gly(gly)$_2$) in aqueous and aqueous glucose solutions have been determined at temperatures: 288.15, 293.15, 298.15, 303.15 and 308.15 K. These solution densities and speeds of sound were used to calculate apparent molar volume at infinite dilution (V_ϕ^0) transfer partial molar volume ($\Delta_{tr}V_\phi^0$) apparent molar adiabatic compressibility at infinite dilution ($K_{\phi,S}^0$), and its transfer values ($\Delta_{tr}K_{\phi,S}^0$), at infinite dilution. These parameters have been discussed in terms of solute–solvent interactions. We have also attempted to examine the temperature and concentration dependence of such interactions. Contributions of peptide group (–CONH–) to V_ϕ^0 and $K_{\phi,S}^0$ in aqueous solution at 298.15 K are also estimated by comparing with the data in the literature and of α,ω-amino acids. Also group contributions to transfer volumes at temperatures: 288.15, 298.15 and 308.15 K from water to aqueous glucose solutions have also calculated.

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1. Introduction

Development and design of new separation and purification processes for biomolecules require accurate knowledge of their thermodynamic properties in solution. The volumetric properties of aqueous solutions of small solutes that model specific structural features of proteins are of particular interest because of their use in group additivity schemes to evaluate the volumetric properties of fully unfolded proteins [1–4]. Peptides are also among the building units of complex biomolecules such as protein. Therefore, a systematic study of their thermodynamic properties can provide valuable information about their behaviour in solution as well as interactions of larger molecules in solution. Thermodynamic properties of peptides have been the subject of several studies in aqueous solution [5–11]. In previous studies we have shown the interactions between simple amino acid (L-alanine, glycine) and peptide (diglycine) with saccharides in aqueous solutions [12–15].

In this paper we report apparent molar volume at infinite dilution (V_ϕ^0) and apparent molar adiabatic compressibility at infinite dilution ($K_{\phi,S}^0$) of glyglyglyine (0.04–0.10 mol kg^{-1}) in pure water to 6 mass % of glucose at temperatures: 288.15, 293.15, 298.15, 303.15 and 308.15 K. Their corresponding transfer functions, pair interaction coefficients and partial molar expansions at infinite dilution are also reported. All these parameters are discussed in terms of solute–solvent and solute–solute interactions occurring in ternary (glyglyglyine + saccharide + water) system.

2. Experimental

The peptide glyglyglycine (G 1377) of highest purity was procured from Sigma Chemicals Co. and used as such without further purification. However, before use this was dried over P_2O_5 under vacuum at room temperature. The saccharide:glucose (S.D. Finechemicals, Mumbai, Analytical Grade), was used after drying at 333.15 K in a vacuum oven for a minimum of 48 h. All solutions were prepared using deionized glass-distilled water (having specific conductance less than 10^{-6} S) that had been freshly degassed by vacuum pump. Solutions of saccharide were prepared by mass in the range 2–6% and used on the day they were prepared. Solution of glyglyglyine in the concentration range 0.04–0.09 mol kg^{-1} was made by mass on the molality concentration scale with an accuracy of $\pm 1 \times 10^{-5}$. The weighing was 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) speeds of sound (u) of glyglyglyine in aqueous glucose solutions at different temperatures were measured simultaneously and automatically, using an Anton Paar DSA 5000 (oscillating U-tube density and speed of sound analyzer) 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-

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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

Densities (ρ) and speeds of sound (u) of glyglyglyine in aqueous solutions of glucose (mass percentage = 2, 4, and 6) are given in Table 1. These data were used to calculate the apparent molar volume (V_ϕ) and apparent molar adiabatic compressibility ($K_{\phi,s}$) using the equation:

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

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

where M is the solute molar mass, ρ_0, ρ, $\beta_{s,0}$ and β_s are the densities and coefficient of adiabatic compressibilities of pure solvent and solution, respectively, and m_s is the solution molality.

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 calculated values of apparent molar volume (V_ϕ) and apparent molar adiabatic compressibility ($K_{\phi,s}$) are given in Table 2. The variation of V_ϕ and $K_{\phi,s}$ vs. m were found to be linear in the concentration range studied in all cases with positive slopes. The V_ϕ values increases with increase in molality of tripeptide. This indicates that the solute–solvent interactions increase with the increase in the amount of the tripeptide in the solution. Negative value of $K_{\phi,s}$ imply that the water molecules around glyglyglycine molecules are less compressible than the water molecules in the bulk solution due to the hydrophobic interactions of a non-polar group resulting in the tightening of the water molecules around it. For the dilute solutions used in this study, the molality dependence of V_ϕ, and $K_{\phi,s}$ can be represented by the linear 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 limiting value of apparent partial molar property (equal to the infinite dilution partial molar property) and S_Q (S_Q denotes S_V or S_K) is the experimental or limiting slope indicative of solute–solute interactions arising from solute concentration effects. The evaluated values of V_ϕ^0 or $K_{\phi,s}^0$ and S_V or S_K with standard errors of the fitting Eq. (4) are given in Table 3 along with their standard deviation. The experimental values of V_ϕ^0, and $K_{\phi,s}^0$ for the tripeptide in water reported in literatures [6,16–22] are compared with our results in Table 3. These properties are important because at infinite dilution the interactions between the peptide molecules are negligible and these properties solely reflect the interactions between the peptide molecules and the mixed solvent. In Table 3, it can be seen that the tripeptide under study has positive V_ϕ^0 and negative $K_{\phi,s}^0$ values in aqueous glucose solutions at different temperatures thereby showing the presence of strong solute–solvent interactions [23]. The overall values of V_ϕ^0 and $K_{\phi,s}^0$ for the tripeptide are higher in aqueous glucose solutions than in water, and these values increases with the concentration of co-solute as well as with temperature. Hence,

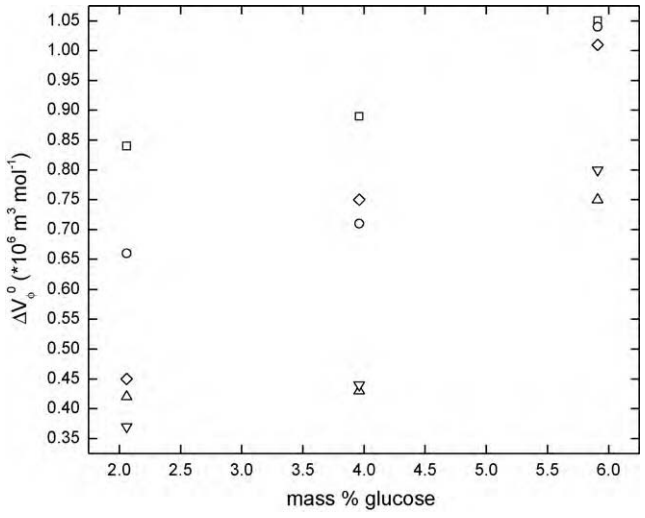

Fig. 1. Partial molar volume of transfer at infinite dilution for triglycine in aqueous glucose solution: (□) at 288.15 K, (○) at 293.15 K, (Δ) at 298.15 K, (▽) at 303.15 K, (◊) at 308.15 K.

the solute–solvent interactions are increasing with the concentration of co-solute and with increase of temperature. The values of experimental slopes (S_V) which are considered as a measure of homogeneous solute–solute interactions, are found to be generally positive. S_V is influenced by a number of effects [24]. The experimental S_V values in Table 3 for tripeptide are found to be positive but smaller than V_ϕ^0 values, suggesting that solute–solute interactions are weaker than solute–solvent interactions in the system under study.

The V_ϕ^0 and $K_{\phi,s}^0$ data in water and in aqueous additive solutions have been used to calculate corresponding transfer functions at infinite dilution ($\Delta_{tr}V_\phi^0$ and $\Delta_{tr}K_{\phi,s}^0$) by the equation:

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

The calculated results are given in Table 4 and illustrated in Fig. 1. The values of $\Delta_{tr}V_\phi^0$ is by definition free from solute–solute interactions and therefore provides information regarding solute–solvent interactions. As can be seen in Table 4, the values $\Delta_{tr}V_\phi^0$ for glyglyglycine are positive and increase with the mass % of glucose at each temperature. A positive $\Delta_{tr}V_\phi^0$ can be explained on the basis that the saccharide interact directly with the solute (triglycine) through electrostatic interactions with the charged centers of the solute, thereby leading to a reduction in their electrostriction of the solvent and hence, a positive volume of transfer. The ion–hydrophilic and hydrophilic–hydrophilic group interactions leads to a positive $\Delta_{tr}V_\phi^0$ and hydrophilic–hydrophobic interactions leads to a negative $\Delta_{tr}V_\phi^0$. The observed increasing positive transfer partial molar volumes at infinite dilution in saccharide mixed solvents suggests that in ternary solutions, the ion–hydrophilic and hydrophilic–hydrophilic group interactions are predominant over hydrophilic–hydrophobic group interactions. It can also be seen from Fig. 1 that the transfer partial molar volume at infinite dilution increases with the increasing concentration of glucose. It may be inferred that in the ternary solution, the increased concentrations of the glucose lead to the greater ion–hydrophilic and hydrophilic–hydrophilic interactions that are not influenced by hydrophilic–hydrophobic interactions. Table 4 shows that $\Delta_{tr}K_{\phi,s}^0$ values are positive in case of glucose solutions. Similar observations have also been shown by Banipal and Sehgal [21] for the same tripeptide in 1 M aqueous glucose solution at 298.15 K. The $\Delta_{tr}K_{\phi,s}^0$ value increases with increasing mass % of

Table 1
Densities ρ and speeds of sound u of glyglyglyine peptide in aqueous glucose 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 ($\times10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times10^{-3}$ kg m^{-3})	u (m s^{-1})	ρ ($\times10^{-3}$ kg m^{-3})	u (m s^{-1})
Glyglyglycine + water										
0.00000	0.999122	1466.72	0.998219	1482.98	0.997050	1497.20	0.995645	1509.46	0.994020	1519.91
0.03587	1.001940	1470.60	1.001005	1486.68	0.999808	1500.76	0.998381	1512.93	0.996783	1523.31
0.04684	1.002791	1471.63	1.001846	1487.80	1.000644	1501.81	0.999208	1513.96	0.997565	1524.27
0.05855	1.003689	1472.95	1.002735	1489.02	1.001523	1502.98	1.000083	1515.10	0.998435	1525.41
0.06301	1.004027	1473.42	1.003070	1489.40	1.001856	1503.39	1.000413	1515.48	0.998760	1525.78
0.07743	1.005130	1474.99	1.004160	1490.84	1.002932	1504.78	1.001540	1516.82	0.999825	1527.30
0.09073	1.006130	1476.48	1.005151	1492.56	1.003919	1506.02	1.002458	1518.38	1.000793	1528.55
0.10162	1.006948	1477.68	1.005962	1493.44	1.004733	1507.33	1.003256	1519.31	1.001582	1529.49
Glyglyglycine + 2.06 mass % glucose										
0.00000	1.007045	1475.58	1.006081	1491.75	1.004858	1505.54	1.003409	1517.30	1.001751	1527.01
0.03981	1.010144	1479.76	1.009148	1495.85	1.007902	1509.35	1.006429	1521.03	1.004753	1530.66
0.05105	1.011012	1480.86	1.010007	1496.97	1.008755	1510.40	1.007274	1522.06	1.005593	1531.69
0.06045	1.011735	1481.80	1.010724	1497.87	1.009464	1511.28	1.007978	1522.93	1.006293	1532.55
0.06879	1.012374	1482.50	1.011357	1498.68	1.010092	1511.96	1.008601	1523.66	1.006910	1533.30
0.08072	1.013289	1483.41	1.012261	1499.90	1.010988	1512.57	1.009488	1524.31	1.007790	1534.14
0.09081	1.014060	1484.74	1.013021	1500.90	1.011740	1513.73	1.010235	1525.43	1.008531	1535.22
0.10119	1.014849	1485.68	1.013801	1501.89	1.012512	1514.68	1.011001	1526.35	1.009291	1536.17
Glyglyglycine + 3.96 mass % glucose										
0.00000	1.014534	1482.17	1.013517	1497.74	1.012251	1511.34	1.010764	1523.05	1.009084	1532.99
0.04046	1.017655	1486.61	1.016601	1502.02	1.015315	1515.47	1.013801	1527.12	1.012098	1536.80
0.05200	1.018536	1487.88	1.017474	1503.24	1.016178	1516.65	1.014657	1528.20	1.012945	1537.89
0.06050	1.019180	1488.82	1.018111	1504.14	1.016807	1517.52	1.015283	1529.07	1.013563	1538.70
0.07170	1.020027	1490.05	1.018945	1505.35	1.017631	1518.92	1.016098	1530.15	1.014373	1539.76
0.08128	1.020747	1491.10	1.019655	1506.35	1.018338	1519.64	1.016795	1531.05	1.015065	1540.63
0.09094	1.021468	1492.20	1.020361	1507.38	1.019036	1520.57	1.017489	1531.95	1.015755	1541.54
0.10302	1.022347	1493.60	1.021227	1508.77	1.019898	1521.82	1.018349	1533.23	1.016612	1542.75
Glyglyglycine + 5.91 mass % glucose										
0.00000	1.022208	1489.97	1.021131	1505.14	1.019812	1518.44	1.018273	1529.87	1.016540	1539.53
0.04088	1.025348	1494.46	1.024234	1509.48	1.022892	1522.60	1.021326	1533.92	1.019572	1543.47
0.04989	1.026028	1495.46	1.024909	1510.44	1.023557	1523.52	1.021992	1534.80	1.020234	1544.33
0.06001	1.026788	1496.59	1.025662	1511.53	1.024305	1524.52	1.022733	1535.78	1.020972	1545.23
0.07200	1.027691	1497.87	1.026555	1512.81	1.025190	1525.80	1.023612	1537.01	1.021845	1546.43
0.07945	1.028245	1498.64	1.027106	1513.54	1.025736	1526.51	1.024154	1537.67	1.022383	1547.16
0.08861	1.028928	1499.71	1.027782	1514.49	1.026405	1527.52	1.024819	1538.66	1.023043	1548.04
0.09872	1.029678	1500.73	1.028525	1515.60	1.027135	1528.62	1.025548	1539.76	1.023768	1549.02

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

Table 2
Apparent molar volume V_ϕ and apparent molar adiabatic compressibilities $K_{\phi,s}$ of glyglyglyine peptide in aqueous glucose 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 (×10^6 m^3 mol^{-1})	$K_{\phi,s}$ (×10^6 m^3 mol^{-1} GPa^{-1})	V_ϕ (×10^6 m^3 mol^{-1})	$K_{\phi,s}$ (×10^6 m^3 mol^{-1} GPa^{-1})	V_ϕ (×10^6 m^3 mol^{-1})	$K_{\phi,s}$ (×10^6 m^3 mol^{-1} GPa^{-1})	V_ϕ (×10^6 m^3 mol^{-1})	$K_{\phi,s}$ (×10^6 m^3 mol^{-1} GPa^{-1})	V_ϕ (×10^6 m^3 mol^{-1})	$K_{\phi,s}$ (×10^6 m^3 mol^{-1} GPa^{-1})
Glyglyglycine + water										
0.03587	110.33	−53.81	111.25	−48.69	112.08	−43.86	112.74	−40.89	113.17	−39.23
0.04684	110.46	−51.49	111.39	−47.83	112.14	−43.16	112.86	−40.33	113.31	−37.59
0.05855	110.69	−52.18	111.60	−47.72	112.38	−43.13	113.03	−40.26	113.49	−37.86
0.06301	110.81	−52.00	111.70	−46.82	112.46	−42.74	113.12	−39.70	113.63	−37.27
0.07743	110.94	−52.06	111.84	−46.37	112.65	−42.28	113.31	−39.85	113.77	−38.37
0.09073	111.18	−52.22	112.05	−48.56	112.80	−42.06	113.47	−40.84	113.98	−38.00
0.10162	111.32	−52.18	112.17	−46.77	112.96	−43.05	113.58	−39.89	114.13	−37.27
Glyglyglycine + 2.06 mass % glucose										
0.03981	110.74	−48.81	111.57	−45.34	112.19	−39.46	112.84	−37.00	113.36	−34.91
0.05105	110.79	−47.74	111.60	−44.80	112.22	−39.08	112.90	−36.62	113.41	−34.80
0.06045	110.83	−47.31	111.63	−44.13	112.28	−38.83	112.94	−36.47	113.45	−34.70
0.06879	110.87	−46.46	111.67	−43.74	112.32	−37.81	112.97	−36.01	113.52	−34.48
0.08072	110.88	−43.55	111.70	−43.77	112.36	−34.13	113.04	−32.74	113.60	−32.63
0.09081	110.90	−45.81	111.75	−43.54	112.43	−35.80	113.10	−34.15	113.67	−33.68
0.10119	110.95	−45.07	111.80	−43.11	112.49	−35.77	113.15	−34.01	113.73	−33.64
Glyglyglycine + 3.96 mass % glucose										
0.04046	111.17	−49.09	112.01	−44.52	112.63	−40.87	113.27	−37.83	113.97	−34.08
0.05200	111.25	−48.97	112.06	−44.41	112.74	−40.73	113.44	−37.65	114.11	−33.93
0.06050	111.34	−48.90	112.15	−44.29	112.88	−40.58	113.54	−37.78	114.25	−33.86
0.07170	111.43	−48.73	112.28	−44.30	113.05	−40.50	113.74	−37.23	114.42	−33.68
0.08128	111.51	−48.56	112.40	−44.03	113.11	−40.24	113.85	−36.82	114.52	−33.33
0.09094	111.62	−48.65	112.58	−43.87	113.30	−39.68	114.01	−36.32	114.67	−33.17
0.10302	111.91	−48.69	112.89	−44.13	113.58	−39.51	114.23	−36.60	114.85	−33.36
Glyglyglycine + 5.91 mass % glucose										
0.04088	111.21	−46.81	112.12	−42.61	112.71	−38.68	113.41	−35.93	113.98	−33.55
0.04989	111.37	−46.73	112.21	−42.51	112.83	−38.51	113.47	−35.70	114.03	−33.38
0.06001	111.52	−46.68	112.35	−42.48	113.01	−38.09	113.60	−35.36	114.12	−32.60
0.07200	111.58	−46.20	112.41	−42.37	113.08	−38.45	113.66	−35.62	114.19	−32.94
0.07945	111.68	−45.73	112.47	−41.83	113.14	−38.01	113.73	−35.00	114.27	−32.95
0.08861	111.75	−46.06	112.54	−41.60	113.22	−38.38	113.80	−35.44	114.34	−32.85
0.09872	111.83	−45.40	112.61	−41.73	113.36	−38.56	113.89	−35.84	114.42	−32.78

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

Mass % (glucose)	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
0.00	109.79 (±0.04)	110.76 (±0.04)	111.56 (±0.04) 111.69,[a] 111.81 (±0.01),[b] 111.96 (±0.06),[c] 112.11 (±0.03),[d] 112.51 (±0.03)[e,f]	112.27 (±0.03)	112.64 (±0.04)	15.24 (±0.64)	14.17 (±0.54)	13.86 (±0.63)	13.17 (±0.38)	14.71 (±0.52)
2.06	110.63 (±0.02)	111.42 (±0.01)	111.98 (±0.02)	112.64 (±0.01)	113.09 (±0.02)	3.16 (±0.28)	3.66 (±0.18)	4.93 (±0.23)	5.05 (±0.14)	6.27 (±0.25)
3.96	110.68 (±0.09)	111.47 (±0.12)	111.99 (±0.07)	112.71 (±0.05)	113.39 (±0.02)	10.98 (±1.18)	12.97 (±1.58)	14.70 (±0.99)	14.40 (±0.67)	14.07 (±0.26)
5.91	110.84 (±0.06)	111.80 (±0.03)	112.31 (±0.05)	113.07 (±0.02)	113.65 (±0.01)	10.27 (±0.77)	8.32 (±0.49)	10.59 (±0.69)	8.24 (±0.31)	7.71 (±0.21)
Mass % (glucose)	$K_{\phi,S}^0$ ($\times 10^6$ 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
0.00	−53.03 (±0.91)	−48.65 (±1.11)	−44.07 (±0.60) −44.36 (±0.80),[f] −44.10 (±0.13),[g] −44.9 (±0.01)[h]	−40.70 (±0.61)	−38.90 (±0.82)	11.08 (±12.75)	16.50 (±15.60)	17.31 (±8.43)	6.63 (±8.52)	14.13 (±11.53)
2.06	−51.06 (±1.49)	−46.42 (±0.340)	−42.81 (±1.67)	−39.68 (±1.34)	−36.14 (±0.82)	66.32 (±20.39)	33.48 (±4.71)	78.74 (±22.34)	62.42 (±18.27)	28.73 (±11.23)
3.96	−49.34 (±0.14)	−44.84 (±0.18)	−41.92 (±0.22)	−38.99 (±0.35)	−34.67 (±0.19)	7.56 (±1.89)	8.62 (±2.43)	22.74 (±2.92)	25.39 (±4.68)	14.57 (±2.61)
5.91	−47.92 (±0.30)	−43.47 (±0.26)	−38.56 (±0.37)	−35.85 (±0.47)	−33.79 (±0.38)	24.16 (±4.19)	18.65 (±3.59)	2.53 (±5.16)	4.19 (±6.54)	11.22 (±5.20)

[a] Ref. [16].
[b] Ref. [17].
[c] Ref. [6].
[d] Ref. [18].
[e] Ref. [19].
[f] Ref. [20].
[g] Ref. [21].
[h] Ref. [22].

saccharide at each temperature. The increasing $\Delta_{tr}K_{\phi,s}^0$ values suggest the disruption of the hydration sphere of charged end centers, thereby dominating ionic–hydrophilic interactions.

Kozak et al. [25] proposed a theory based on the McMillan–Mayer [26] theory of solutions. This has further been discussed by Friedman and Krishnan [27] and Frank et al. [28] in order to include solute–co-solute interactions in the solvation spheres. According to this treatment, a thermodynamic transfer function at infinite dilution can be expressed as:

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

where $\Delta_{tr}Y_\phi^0$ denotes $\Delta_{tr}V_\phi^0$ or $\Delta_{tr}K_{\phi,s}^0$. A stands for peptide and B denotes co-solute, and m_B is the molality of co-solute. Constants Y_{AB} and Y_{ABB} are pair and triplet interaction coefficients. The ΔY_ϕ^0 data have been fitted to Eq. (6) to obtain Y_{AB} and Y_{ABB}. The corresponding parameters V_{AB} and V_{ABB} for volumes and K_{AB} and K_{ABB} for adiabatic compressibilities, estimated from $\Delta_{tr}V_\phi^0$ and $\Delta_{tr}K_{\phi,s}^0$ respectively, are summarized in Table 5.

The pair interaction coefficient (V_{AB}) is positive, whereas K_{AB} is also positive at all temperatures. The triplet interaction parameter (V_{ABB}) is negative in all the cases and K_{ABB} is negative except at temperatures: 298.15 and 303.15 K in case of glucose solutions. The maximum positive values of pair interaction coefficient (K_{AB}) in case of glyglyglycine with glucose at higher temperature suggests

Table 4
Transfer partial molar volumes $\Delta_{tr}V_\phi^0$ and transfer partial molar adiabatic compressibilities $\Delta_{tr}K_{\phi,S}^0$ of glyglyglycine peptide in aqueous glucose solutions at different temperatures.

Mass % (glucose)	$\Delta_{tr}V_\phi^0$ ($\times 10^6$ m^3 mol^{-1})					$\Delta_{tr}K_{\phi,S}^0$ ($\times 10^6$ 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
2.06	0.84	0.66	0.42	0.37	0.45	1.97	2.23	1.26	1.02	2.76
3.96	0.89	0.71	0.43	0.44	0.75	3.69	3.81	2.15	1.71	4.23
5.91	1.05	1.04	0.75	0.80	1.01	5.11	5.18	5.51	4.85	5.11

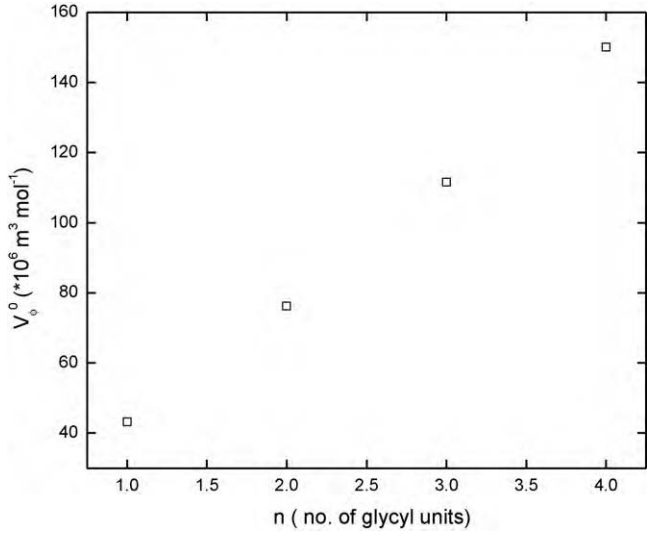

Fig. 2. Partial molar volume at infinite dilution of glycyl peptides vs. *n*, the number of residues in the polypeptides: (□) at 298.15 K.

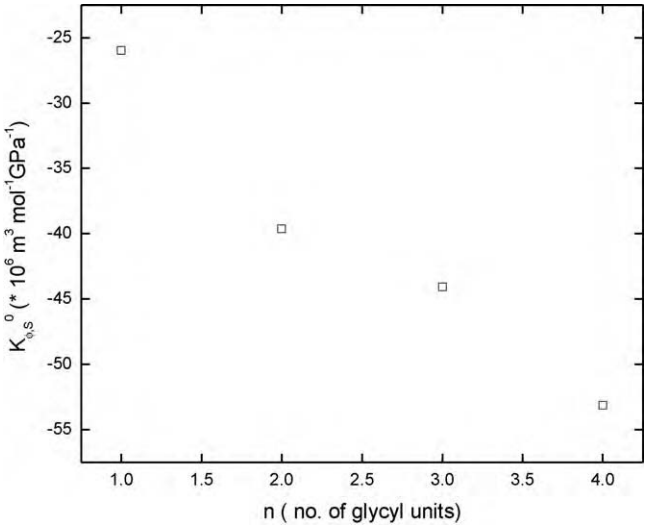

Fig. 3. Partial molar adiabatic compressibility at infinite dilution of glycyl peptides vs. *n*, the number of residues in the polypeptides: (□) at 298.15 K.

that interaction occur due to the overlap of hydration spheres of solute–co-solute molecules.

3.1. Partial molar expansions

The temperature dependence of V_ϕ^0 for the glyglyglyine peptide can be expressed by the equation:

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

where T_m represents the midpoint temperature of the range used (T_m = 298.15 K for glyglyglycine), was fitted to the V_ϕ^0 data. The values of *a*, *b*, and *c* can be obtained by using the least-squares fitting method to Eq. (7) given in Table 6 together with their uncertainties. For the tripeptide, the value of the coefficient *c* was not statistically significant; hence a linear function was used in the least-squares analysis. The partial molar isobaric expansion for the peptide at infinite dilution (E_2^0) was derived from the polynomial coefficient given in Table 6. Differentiation of Eq. (7) with respect to temperature at constant pressure gives:

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

The quantity $\{b + 2c(T - T_m)\}$ in Eq. (8) is equivalent to E_2^0 at temperatures: 288.15, 293.15, 298.15, 303.15 and 308.15 K. The E_2^0 values for the tripeptide (glyglyglycine) are given in Table 7. The uncertainty for each E_2^0 estimated by the application of propagation of errors [29] to Eq. (8) is listed in Table 7. It can be seen from Table 7 that the E_2^0 values for triglycine are decreasing with increase in temperature and also with increasing mass % of glucose (up to 4 mass % of glucose) and then increase. But the values of E_2^0 triglycine in glucose solutions are lower than the E_2^0 values of triglycine in water.

3.2. Group contribution (in aqueous solution at 298.15 K)

Partial molar volumes (V_ϕ^0) and adiabatic compressibilities ($K_{\phi,s}^0$) of the peptides are plotted in Figs. 2 and 3, as a function of *n*, the number of glycyl residues in a particular homologue at 298.15 K. It is observed that our results show a linear relationship between V_ϕ^0 and no. of glycyl units which agrees well with the previously reported values [18] and nonlinear relationship between $K_{\phi,s}^0$ and no. of glycyl units which agrees well with the previously reported values [21,22]. The non-linear relationship is due to the end-group hydration of the amino acids and short chain peptides in aqueous solution which interferes with the hydration of all the intervening chain because of the overlap of cospheres [22]. The values of V_ϕ^0 and $K_{\phi,s}^0$ for glycine, diglycine and tetraglycine are taken from Refs. [13,18,30]. We have attempted to estimate the contribution of V_ϕ^0 and $K_{\phi,s}^0$ of the peptide group (–CONH–) by combining the present data with the previous data on α,ω-amino acids [31]. A comparison of peptides and α,ω-amino acids of the same carbon chain length is useful in deriving such contribution since both types of molecules are similar in structure except that in peptides the –CONH– group replaces the two methylene (–CH_2) groups of the α,ω-amino acid. The result is that the V_ϕ^0 and $K_{\phi,s}^0$ values are lower for the peptides in comparison to their α,ω-amino acid analogues. This implies that the replacement of two –CH_2– groups with one –CONH– group causes a considerable decrease in the volume and compressibility of the molecule.

The calculation of the peptide group contribution using the following equation:

$$\Delta V_\phi^0(\text{–CH}_2\text{CH}_2\text{–} \rightarrow \text{–CONH–}) = V_\phi^0(\text{peptide}) - V_\phi^0(\alpha, \omega\text{-amino acid}) \quad (9)$$

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

T (K)	From volume		From compressibility	
	V_{AB} (×10^6 m^3 mol^{-2} kg)	V_{ABB} (×10^6 m^3 mol^{-3} kg^2)	K_{AB} (×10^6 m^3 mol^{-2} kg GPa^{-1})	K_{ABB} (×10^6 m^3 mol^{-3} kg^2 GPa^{-1})
288.15	3.7987	−4.5086	9.2683	−3.6864
293.15	2.6586	−2.3528	10.4062	−5.7395
298.15	1.4801	−0.8710	1.5709	11.7442
303.15	1.2540	−0.2829	0.5326	11.9258
308.15	2.1026	−1.2633	13.6015	−12.0829

Table 6
Coefficients of Eq. (7) for glyglyglycine peptide in aqueous glucose solution.

Mass % (glucose)	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})
0.00	111.59 (±0.03)	0.1442 (±0.0030)	−16.6 (±5.8)
2.06	112.03 (±0.04)	0.1228 (±0.0034)	−0.57 (±8.4)
3.96	112.05 (±0.05)	0.1332 (±0.0050)	−14.6 (±12.1)
5.91	112.41 (±0.08)	0.1378 (±0.0071)	−36.9 (±5.0)

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

Mass % (glucose)	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
0.00	0.218	0.181	0.144 (±0.003)0.156 (±0.003) [11]	0.107	0.070
2.06	0.156	0.139	0.123(±0.003)	0.106	0.090
3.96	0.134	0.134	0.133(±0.005)	0.133	0.132
5.96	0.167	0.152	0.138(±0.003)	0.123	0.109

$$\Delta K^0_{\phi,s}(\text{–CH}_2\text{CH}_2\text{–} \rightarrow \text{–CONH–}) = K^0_{\phi,s}(\text{peptide}) - K^0_{\phi,s}(\alpha,\omega\text{-amino acid}) \quad (10)$$

The difference between, the data for 5-aminopentanoic acid ($V^0_\phi = 88.3 \pm 0.3 \times 10^{-6}$ m^3 mol^{-1} [31], $K^0_{\phi,s} = (-34.3 \pm 5) \times 10^{-6}$ m^3 mol^{-1} GPa^{-1} [31]) and that of diglycine gives V^0_ϕ and $K^0_{\phi,s}$ values for one such substitution while a similar differences between the values of 8-aminooctanoic acid [31] and triglycine provides values for two such substitutions. From these two cases, an average value of ΔV^0_ϕ for a single substitution was found to be -12.05×10^{-6} m^3 mol^{-1}. The corresponding value of $\Delta K^0_{\phi,s}$ was found to be -3.41×10^{-6} m^3 mol^{-1} GPa^{-1}. From these data the values of V^0_ϕ (–CONH–) and $K^0_{\phi,s}$ (–CONH–) were estimated with the relationship:

$$\Delta V^0_\phi(\text{–CH}_2\text{CH}_2\text{–} \rightarrow \text{–CONH–}) = V^0_\phi(\text{–CONH–}) - V^0_\phi(\text{–CH}_2\text{CH}_2\text{–}) \quad (11)$$

$$\Delta K^0_{\phi,s}(\text{–CH}_2\text{CH}_2\text{–} \rightarrow \text{–CONH–}) = K^0_{\phi,s}(\text{–CONH–}) - K^0_{\phi,s}(\text{–CH}_2\text{CH}_2\text{–}) \quad (12)$$

Using the V^0_ϕ and $K^0_{\phi,s}$ values that is 16×10^{-6} m^3 mol^{-1} [32,33] and -1.9×10^{-6} m^3 mol^{-1} GPa^{-1} [34], respectively for the –CH$_2$– group, V^0_ϕ and $K^0_{\phi,s}$ values of the peptide group was obtained from Eqs. (11) and (12). The calculated value of V^0_ϕ (–CONH–) is 19.95×10^{-6} m^3 mol^{-1} which is in good agreement with the previously reported values: 20 [35], 22.3 [33], 19.3 [17], and 20.61×10^{-6} m^3 mol^{-1} [18]. However, there is only one value of $K^0_{\phi,s}$ (–CONH–) -12.4×10^{-6} m^3 mol^{-1} GPa^{-1} [18] available for the comparison with our calculated values of -7.21×10^{-6} m^3 mol^{-1} GPa^{-1}. The replacement of two –CH$_2$– group with one –CONH– groups creates a greater shrinkage of the hydration shell around the solute molecule due to the inclusion of two hydrogen bonding sites in the peptide molecule. The decrease in the volume and compressibility of the peptide is due to this shrinkage and also due to the degradation of the salvation shells surrounding the –CONH– group and the adjacent –CH$_2$– group due to the vicinal disturbance.

The V^0_ϕ and $K^0_{\phi,s}$ data of these peptides was used in different ways to calculate the contribution of a single glycyl residue to these properties. Analyses of the data were carried out by using curve-fitting procedures. The data were analyzed as follows:

i. The contribution of single glycyl residue is calculated by fitting of V^0_ϕ and $K^0_{\phi,s}$ values of glycyl peptides to the following equations [18]:

$$V^0_\phi = \overline{V}^0_0 + \left(\frac{\partial V^0_\phi}{\partial n}\right)_T \{n\} \quad (13)$$

$$K^0_{\phi,s} = \overline{K}^0_0 + \left(\frac{\partial K^0_{\phi,s}}{\partial n}\right)_T \{n\} \quad (14)$$

ii. The second method involves the plotting of glycyl residue: $\overline{V}^0_h$ (gly) and $\overline{K}^0_h$ (gly) against $1/n$. Estimates of the properties $\overline{V}^0_\infty$ (gly) and $\overline{K}^0_\infty$ (gly) were obtained by extrapolating the least square fitting of the following two equations:

$$\overline{V}^0_h(\text{gly}) = \overline{V}^0_\infty(\text{gly}) + a\{1/n\} + b\{1/n\}^2 \quad (15)$$

$$\overline{K}^0_h(\text{gly}) = \overline{K}^0_\infty(\text{gly})a\{1/n\} + b\{1/n\}^2 \quad (16)$$

where a and b are the coefficients of the fitting data.

iii. The final method involves the concept that hydration of terminal groups and the intervening chain in peptides produce non-uniform volume and compressibility effects. Amino acids and peptides exist in zwitterionic form in the aqueous solution. The end groups of amino acids and peptides are electostrictively solvated due to hydrophilic interactions while the intervening chain experiences non-electrostrictive interactions with the solvent mainly hydrophobic and hydrogen bonding. It is believed that short length peptides are fully solvated due to the absence of secondary structure and due to the free access of solvent to all parts of the solute molecule as a result of their conformational flexibility. The electrostriction effects of the end groups in amino acids and peptides interfere with the hydration effects of intervening chain due to the overlap of salvation sheaths as studied previously [6,34–38].

For the calculation of the standard contribution of an intervening glycyl unit, for example $\overline{V}^0_h$(gly), the V^0_ϕ of the entire peptide structure can be regarded as a composite of the separate contribution from the intervening chain V^0_ϕ(int) and the end group electrostriction V^0_ϕ(el):

$$V^0_\phi = V^0_\phi(\text{int}) + V^0_\phi(\text{el}) \quad (17)$$

assuming that each residue contributes a constant factor, so that:

$$V^0_\phi(\text{int}) = n\overline{V}^0_h(\text{gly}) \quad (18)$$

Table 8
Estimated values of V_ϕ^0 and $K_{\phi,s}^0$ for a glycyl residue in aqueous solution for various polyglycines at 298.15 K.

Peptide length, n	$\overline{V}_h^0$(gly) ($\times 10^6$ m^3 mol^{-1}), by method		$\overline{K}_h^0$(gly) ($\times 10^6$ m^3 mol^{-1} GPa^{-1}), by method	
	i and ii	iii	i and ii	iii
1	43.19	30.19	−25.97	+3.73
2	38.11	30.01	−19.82	−4.97
3	37.19	31.79	−14.69	−4.79
4	37.49	33.44	−13.28	−5.86
∞[a]	35.57[b], 37.99[c]	39.07[d]	−8.59[b], −3.99[c]	−3.94[d]

[a] Derived values correspond to a peptide of infinite length.
[b] From method i.
[c] From method ii.
[d] From method iii.

Table 9
Transfer volumes of glycine, glyglycine and glyglyglycine from water to aqueous glucose solutions at different temperatures.

Amino acids	$\Delta_{tr}V_\phi^0$ ($\times 10^6$ m^3 mol^{-1})								
	Water → 2.06 mass % glucose			Water → 3.96 mass % glucose			Water → 5.91 mass % glucose		
	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K
Glycine [30]	1.65	1.32	0.72	1.82	1.50	1.10	2.00	1.67	1.50
Glyglycine [13]	0.67	0.55	0.49	0.88	0.67	0.59	1.52	1.13	0.88
Glyglyglycine	0.84	0.42	0.45	0.89	0.43	0.75	1.05	0.75	1.01

Table 10
Group contributions to transfer volume at different temperatures.

Group	$\Delta_{tr}V_\phi^0$ ($\times 10^6$ m^3 mol^{-1})								
	Water → 2.06 mass % glucose			Water → 3.96 mass % glucose			Water → 5.91 mass % glucose		
	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K	288.15 K	298.15 K	308.15 K
–NH–CO–CH_2–[a]	−0.98	−0.77	−0.23	−0.94	−0.83	−0.51	−0.48	−0.54	−0.62
(–NH–CO–CH_2–)$_2$[b]	−0.81	−0.90	−0.27	−0.93	−1.07	−0.35	−0.95	−0.92	−0.49

[a] Digly–gly.
[b] Trigly–gly.

Substituting the expression for V_ϕ^0(int), we obtains:

$$\overline{V}_h^0(\text{gly}) = \frac{V_\phi^0 - V_\phi^0(\text{el})}{n} \tag{19}$$

The same expression can be obtained for the compressibilities:

$$\overline{K}_h^0(\text{gly}) = \frac{K_{\phi,s}^0 - K_{\phi,s}^0(\text{el})}{n} \tag{20}$$

To calculate the values of $\overline{V}_h^0$(gly) and $\overline{K}_h^0$(gly), the electrostrictive components of these properties are required. The values of V_ϕ^0(el) were obtained by comparing the data of the amino acids and their uncharged isomers [36]. For shorter molecules, these values were found to be a function of the chain length the molecule. The V_ϕ^0(el) values for the monomeric amino acid was estimated as 13×10^{-6} m^3 mol^{-1} [36,38] and was used for calculating $\overline{V}_h^0$(gly) in the present calculations. It was found that a constant value [32,39] of V_ϕ^0(el) is 16.2×10^{-6} m^3 mol^{-1} where the minimum separation between the end groups is five or more covalent bonds in case of solutes. It follows that for diglycine and higher peptides; the value of 16.2×10^{-6} m^3 mol^{-1} is a reasonable estimate of the volume of electrostriction and can be used in Eq. (19). With respect to compressibility data, the value of $K_{\phi,s}^0$(el) for monomeric amino acids was found to be -29.7×10^{-6} m^3 mol^{-1} GPa^{-1} [36]. This value is used directly in Eq. (20). Table 8 shows a comparison of the data obtained from the methods discussed above.

3.3. Group contribution to transfer volumes

The values of $\Delta_{tr}V_\phi^0$ for glycine [30] and diglycine [13] are taken from the references and included in Table 9. From the difference in $\Delta_{tr}V_\phi^0$ values of glycine, diglycine and triglycine the group contribution of a peptide backbone unit (–CH_2CONH–)$_n$ has been calculated and reported in Table 10. The $\Delta_{tr}V_\phi^0$ of a peptide backbone unit (–CH_2CONH–)$_n$ has been calculated from the difference in the $\Delta_{tr}V_\phi^0$ of successive glycine oligopeptides. It is seen from Table 10 that $\Delta_{tr}V_\phi^0$ for the peptide backbone unit –CH_2CONH– is negative. The negative $\Delta_{tr}V_\phi^0$ values of the –CONH– group can be rationalized in terms of a increase in the hydrogen bonding interactions with water as a result of decrease in the interactions with the –OH group of the saccharide.

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