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Enthalpies of Dilution of *N*-Glycylglycine in Aqueous Sodium Chloride and Potassium Chloride Solutions at 298.15 K

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The enthalpies of dilution of *N*-glycylglycine in aqueous sodium chloride and potassium chloride solutions have been determined by using flow microcalorimetry at 298.15 K. The homogeneous enthalpic interaction coefficients (h_2, h_3, h_4) in the range of sodium chloride and potassium chloride molality, (0 to 0.6) $\text{mol}\cdot\text{kg}^{-1}$, have been calculated according to the McMillan−Mayer theory. It shows that the enthalpic pairwise interaction coefficients h_2 of *N*-glycylglycine in both electrolyte solutions are negative, and the value of h_2 in aqueous sodium chloride solutions is less than that in aqueous potassium chloride solutions of the same molality. The values of h_2 for *N*-glycylglycine in aqueous solutions of sodium chloride pass through a minimum at about 0.10 $\text{mol}\cdot\text{kg}^{-1}$, while the corresponding values of h_2 in aqueous potassium chloride solutions become less negative with an increase in the molality of potassium chloride. The results are discussed in terms of the solute−solute and solute−solvent interactions.

Introduction

For a globular protein to be functional in aqueous solution, the protein must fold into its unique three-dimensional native structure. Protein folding is the final step in the overall process of gene expression.[1] A thorough understanding of this folding process requires knowledge of the interactions that are responsible for stabilizing the native protein structure in aqueous solution. Interactions between the solvent and various functional groups on the protein, along with the various noncovalent bonding interactions among protein constituent groups, are very important factors that determine the folded conformation of a globular protein.[2] As proteins are large complex molecules, small solutes that incorporate some of the structural features found in proteins, such as amino acids, amides, and oligopeptides, have been used as models for specific aspects of proteins in aqueous solution. The investigation of solute−solute and solute−solvent interactions for these model compounds in aqueous solution can assist in the understanding of the important interactions that determine protein stability.[3−6]

Most of the previous studies on oligopeptides have been restricted to water.[7−10] However, biological fluids of living organisms contain a specified quantity of ions, especially sodium, potassium, and chloride ions, which are indispensable for the metabolic processes of a living organism to proceed.[11] nvestigating the influence of electrolytes is therefore important. Information is available on activity coefficients, enthalpies, partial molal adiabatic compressibilities, and partial molar volumes of aqueous oligopeptides in electrolytes.[12−16] Among the enthalpies studies, most of the research works are focused on the dissolution or mixing enthalpies between amino acids and electrolytes.[17,18] A survey of the literature indicates a lack of experimental data of the dilution enthalpies of oligopeptides in aqueous electrolyte solutions. As an extension to our previous study,[19] the present work is aimed at measuring the enthalpies of dilution of *N*-glycylglycine (diglycine) in aqueous sodium chloride and potassium chloride solutions by using flow microcalorimetry, and the homogeneous enthalpic interaction coefficients of diglycine in both electrolyte solutions of different molalities are obtained.

Experimental Section

Reagents. Diglycine was purchased from Tokyo Chemical Industry Co., Ltd. (Japan), and the purity is better than 99 %. It was used as received. Sodium chloride and potassium chloride were analytical reagents with mass fraction > 99 % obtained from Tianjin Kermel Chemical Reagent Co., Ltd. They were recrystallized from distilled water and dried under reduced pressure at 393 K. All the reagents were stored over P_2O_5 in a vacuum desiccator for 72 h at room temperature prior to use.

Twice distilled water was deionized by passing through a quartz sub-boiling purifier before use in the preparation of solutions. All the solutions were prepared by mass using a Mettler AG 135 balance with precision to ± 0.00001 g. The molality ranges of aqueous solutions of sodium chloride and potassium chloride were (0 to 0.60) $\text{mol}\cdot\text{kg}^{-1}$. The molality range of aqueous diglycine solution was (0.08 to 0.35) $\text{mol}\cdot\text{kg}^{-1}$. All the solutions were degassed with ultrasonic waves and used within 12 h of preparation.

Calorimetric Measurements. The calorimetric measurements were performed with a 2277-204 Measuring Cylinder and a Thermometric 2277 Thermal Activity Monitor (Thermometric, Sweden) at 298.15 K. Details of this apparatus, associated equipment, and the experimental procedure have been reported elsewhere.[20−23] The solutions of diglycine and their solvents were pumped through the mixing-flow vessel of the calorimeter using VS2-10R MIDI dual channel pumps. The flow rates were determined from the mass of the samples delivered in 6 min. The variation of flow rates was less than 0.1 % both before and

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Table 1. Molar Enthalpies of Dilution $\Delta_{dil}H_m$ of Glycylglycine in Water and Aqueous Sodium Chloride Solutions at 298.15 K[a]

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil}H_m$ / J·mol^{-1}	δ^* / J·mol^{-1}	m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil}H_m$ / J·mol^{-1}	δ^* / J·mol^{-1}
m(NaCl) = 0.0000 mol·kg^{-1}							
0.0800	0.0414	29.32 ± 0.26	−0.04	0.2200	0.1152	76.95 ± 0.69	0.00
0.1000	0.0517	36.60 ± 0.33	−0.03	0.2500	0.1327	85.27 ± 0.75	0.00
0.1200	0.0623	43.50 ± 0.39	−0.02	0.2800	0.1489	94.40 ± 0.85	0.00
0.1500	0.0789	53.24 ± 0.48	−0.02	0.3000	0.1589	101.04 ± 0.92	0.00
0.1800	0.0943	63.66 ± 0.57	−0.01	0.3200	0.1709	106.05 ± 0.95	−0.01
0.2000	0.1048	70.27 ± 0.60	0.00	0.3500	0.1866	115.14 ± 1.04	−0.02
m(NaCl) = 0.0500 mol·kg^{-1}							
0.0800	0.0412	24.52 ± 0.20	−0.03	0.2200	0.1125	76.72 ± 0.61	0.02
0.1000	0.0514	32.76 ± 0.26	−0.04	0.2500	0.1276	86.53 ± 0.69	0.01
0.1200	0.0616	40.79 ± 0.33	−0.02	0.2800	0.1427	95.81 ± 0.77	−0.01
0.1500	0.0768	52.36 ± 0.42	0.00	0.3000	0.1531	101.60 ± 0.81	−0.02
0.1800	0.0922	63.09 ± 0.50	0.01	0.3200	0.1632	107.41 ± 0.86	−0.04
0.2000	0.1024	69.95 ± 0.56	0.01	0.3500	0.1785	115.74 ± 0.93	−0.07
m(NaCl) = 0.1000 mol·kg^{-1}							
0.0800	0.0419	19.38 ± 0.16	−0.06	0.2200	0.1133	73.03 ± 0.62	0.46
0.1000	0.0520	28.52 ± 0.24	0.07	0.2500	0.1290	81.58 ± 0.69	0.05
0.1200	0.0623	36.89 ± 0.31	0.18	0.2800	0.1444	90.09 ± 0.77	−0.26
0.1500	0.0784	47.46 ± 0.40	−0.19	0.3000	0.1541	96.49 ± 0.82	−0.09
0.1800	0.0932	59.00 ± 0.50	0.09	0.3200	0.1643	102.45 ± 0.87	0.13
0.2000	0.1035	65.05 ± 0.55	−0.58	0.3500	0.1794	111.04 ± 0.94	0.01
m(NaCl) = 0.2000 mol·kg^{-1}							
0.0800	0.0420	18.34 ± 0.17	0.21	0.2200	0.1148	63.25 ± 0.57	−0.54
0.1000	0.0524	24.95 ± 0.22	−0.43	0.2500	0.1305	72.57 ± 0.65	0.12
0.1200	0.0630	32.12 ± 0.29	0.01	0.2800	0.1460	81.81 ± 0.74	0.59
0.1500	0.0784	42.45 ± 0.38	0.20	0.3000	0.1574	85.90 ± 0.77	−0.37
0.1800	0.0939	51.79 ± 0.47	0.02	0.3200	0.1661	93.04 ± 0.84	−0.33
0.2000	0.1045	57.83 ± 0.52	0.11	0.3500	0.1815	102.50 ± 0.92	0.15
m(NaCl) = 0.3000 mol·kg^{-1}							
0.0800	0.0413	15.98 ± 0.14	0.08	0.2200	0.1126	60.65 ± 0.55	0.00
0.1000	0.0518	22.30 ± 0.20	−0.10	0.2500	0.1276	69.69 ± 0.64	0.00
0.1200	0.0618	29.20 ± 0.26	0.01	0.2800	0.1426	78.55 ± 0.71	−0.01
0.1500	0.0771	38.87 ± 0.35	0.02	0.3000	0.1533	83.81 ± 0.75	−0.01
0.1800	0.0924	48.31 ± 0.43	0.01	0.3200	0.1632	89.58 ± 0.81	0.00
0.2000	0.1026	54.42 ± 0.49	0.01	0.3500	0.1783	97.96 ± 0.88	0.02
m(NaCl) = 0.4000 mol·kg^{-1}							
0.0800	0.0415	19.50 ± 0.18	0.03	0.2200	0.1139	60.81 ± 0.55	0.01
0.1000	0.0521	25.51 ± 0.23	−0.05	0.2500	0.1295	69.03 ± 0.62	0.02
0.1200	0.0625	31.57 ± 0.28	−0.03	0.2800	0.1445	77.35 ± 0.70	0.01
0.1500	0.0776	40.85 ± 0.37	0.00	0.3000	0.1550	82.52 ± 0.74	0.01
0.1800	0.0937	49.20 ± 0.44	0.01	0.3200	0.1649	87.93 ± 0.79	0.03
0.2000	0.1040	54.93 ± 0.49	0.02	0.3500	0.1801	95.68 ± 0.86	0.04
m(NaCl) = 0.5000 mol·kg^{-1}							
0.0800	0.0400	16.28 ± 0.14	−0.11	0.2200	0.1100	55.33 ± 0.52	−0.01
0.1000	0.0501	22.38 ± 0.20	0.18	0.2500	0.1250	63.27 ± 0.57	0.06
0.1200	0.0604	27.81 ± 0.25	0.07	0.2800	0.1397	71.29 ± 0.65	0.11
0.1500	0.0748	36.51 ± 0.34	−0.06	0.3000	0.1502	76.17 ± 0.69	0.14
0.1800	0.0901	44.52 ± 0.42	−0.07	0.3200	0.1593	81.52 ± 0.73	−0.17
0.2000	0.1000	50.01 ± 0.47	−0.05	0.3500	0.1743	89.43 ± 0.81	0.08
m(NaCl) = 0.6000 mol·kg^{-1}							
0.0800	0.0410	13.19 ± 0.12	−0.03	0.2200	0.1120	49.00 ± 0.44	0.00
0.1000	0.0512	18.59 ± 0.17	0.03	0.2500	0.1270	56.28 ± 0.51	0.01
0.1200	0.0613	23.86 ± 0.21	0.02	0.2800	0.1420	63.44 ± 0.57	0.01
0.1500	0.0767	31.51 ± 0.28	0.01	0.3000	0.1523	67.90 ± 0.61	0.01
0.1800	0.0918	39.16 ± 0.35	0.01	0.3200	0.1626	72.34 ± 0.65	0.00
0.2000	0.1019	44.13 ± 0.40	0.01	0.3500	0.1776	79.10 ± 0.71	−0.01

[a] m_i and m_f are the initial and final molalities of the glycylglycine, respectively. $\delta^* = \Delta_{dil}H_m - \Delta_{dil}H_m(\text{cal})$, where $\Delta_{dil}H_m(\text{cal})$ was calculated from eq 5 with coefficients for this equation.

after a complete dilution experiment. The details of the thermodynamic procedures have been described elsewhere.[24,25]

The enthalpies of dilution $\Delta_{dil}H_m$ were calculated from the equation[26]

$$\Delta_{dil}H_m = -P(1 + m_iM)/m_if_2 \tag{1}$$

where P is the dilution thermal power of the solute; m_i and M are the initial molality and the molar mass of diglycine, respectively; and f_2 is the flow rate of diglycine solutions. The uncertainty of P, m_i, and f_2 is ± 0.2 μW, ± 0.0001 mol·kg^{-1}, and ± 0.002 mg·s^{-1}, respectively. The relative mean deviations of all $\Delta_{dil}H_m$ values owing to duplicate runs at each initial molality are within 1 %.

The final molality m_f after diluting was calculated from the equation

$$m_f = m_if_2/[f_1(1 + m_iM) + f_2] \tag{2}$$

in which f_1 is the flow rate of diluents (water or aqueous solution of sodium chloride or potassium chloride).

Table 2. Molar Enthalpies of Dilution $\Delta_{dil}H_m$ of Glycylglycine in Aqueous Potassium Chloride Solutions at 298.15 K

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil}H_m$ / J·mol^{-1}	δ^* / J·mol^{-1}	m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil}H_m$ / J·mol^{-1}	δ^* / J·mol^{-1}
m(KCl) = 0.0500 mol·kg^{-1}							
0.0800	0.0402	27.72 ± 0.25	−0.05	0.2200	0.1095	74.71 ± 0.67	0.00
0.1000	0.0502	34.68 ± 0.31	−0.03	0.2500	0.1243	84.28 ± 0.76	−0.01
0.1200	0.0600	41.68 ± 0.38	−0.02	0.2800	0.1391	93.69 ± 0.84	−0.02
0.1500	0.0749	51.76 ± 0.47	−0.01	0.3000	0.1492	99.80 ± 0.90	−0.03
0.1800	0.0896	61.86 ± 0.56	0.00	0.3200	0.1589	106.12 ± 0.96	−0.04
0.2000	0.0996	68.25 ± 0.61	0.00	0.3500	0.1734	115.56 ± 1.04	−0.06
m(KCl) = 0.1000 mol·kg^{-1}							
0.0800	0.0419	39.27 ± 0.35	−0.03	0.2200	0.1149	84.09 ± 0.76	−0.32
0.1000	0.0523	45.90 ± 0.41	−0.01	0.2500	0.1305	93.96 ± 0.85	0.07
0.1200	0.0628	52.48 ± 0.47	0.01	0.2800	0.1461	103.45 ± 0.92	0.06
0.1500	0.0784	62.24 ± 0.56	0.04	0.3000	0.1566	109.75 ± 0.99	0.05
0.1800	0.0940	71.86 ± 0.65	0.06	0.3200	0.1671	116.07 ± 1.04	0.03
0.2000	0.1045	78.19 ± 0.70	0.07	0.3500	0.1826	125.70 ± 1.13	−0.03
m(KCl) = 0.2000 mol·kg^{-1}							
0.0800	0.0424	30.73 ± 0.28	0.03	0.2200	0.1161	71.95 ± 0.65	−0.01
0.1000	0.0529	36.81 ± 0.33	−0.07	0.2500	0.1319	80.07 ± 0.72	−0.01
0.1200	0.0634	43.07 ± 0.39	0.02	0.2800	0.1474	88.24 ± 0.79	0.00
0.1500	0.0789	52.19 ± 0.47	0.01	0.3000	0.1578	93.55 ± 0.84	0.00
0.1800	0.0951	60.62 ± 0.55	0.00	0.3200	0.1676	99.08 ± 0.89	0.01
0.2000	0.1053	66.54 ± 0.60	0.00	0.3500	0.1827	107.01 ± 0.96	0.02
m(KCl) = 0.3000 mol·kg^{-1}							
0.0800	0.0424	19.69 ± 0.18	0.03	0.2200	0.1160	51.55 ± 0.46	−0.03
0.1000	0.0530	24.49 ± 0.22	−0.14	0.2500	0.1319	57.54 ± 0.52	−0.02
0.1200	0.0635	29.47 ± 0.27	0.00	0.2800	0.1469	63.83 ± 0.57	−0.01
0.1500	0.0793	36.58 ± 0.33	0.17	0.3000	0.1563	68.32 ± 0.61	0.13
0.1800	0.0951	43.04 ± 0.39	−0.03	0.3200	0.1684	71.11 ± 0.64	0.02
0.2000	0.1056	47.32 ± 0.43	−0.03	0.3500	0.1843	76.48 ± 0.69	−0.04
m(KCl) = 0.4000 mol·kg^{-1}							
0.0800	0.0435	25.04 ± 0.22	−0.03	0.2200	0.1160	61.22 ± 0.55	−0.01
0.1000	0.0543	30.11 ± 0.27	0.06	0.2500	0.1324	68.32 ± 0.61	0.00
0.1200	0.0651	35.05 ± 0.32	−0.03	0.2800	0.1466	76.50 ± 0.69	0.00
0.1500	0.0795	43.46 ± 0.39	−0.03	0.3000	0.1577	81.09 ± 0.73	0.00
0.1800	0.0947	51.36 ± 0.46	−0.02	0.3200	0.1679	86.09 ± 0.77	0.00
0.2000	0.1059	56.00 ± 0.50	−0.01	0.3500	0.1855	92.36 ± 0.83	−0.01
m(KCl) = 0.5000 mol·kg^{-1}							
0.0800	0.0427	41.78 ± 0.38	−0.06	0.2200	0.1165	69.36 ± 0.62	0.02
0.1000	0.0533	45.90 ± 0.41	−0.05	0.2500	0.1321	75.08 ± 0.68	0.02
0.1200	0.0638	50.20 ± 0.45	0.17	0.2800	0.1485	80.44 ± 0.72	0.03
0.1500	0.0795	55.89 ± 0.50	−0.11	0.3000	0.1579	84.71 ± 0.76	0.03
0.1800	0.0956	61.70 ± 0.56	0.00	0.3200	0.1693	88.12 ± 0.79	0.03
0.2000	0.1061	65.51 ± 0.59	0.01	0.3500	0.1838	94.43 ± 0.85	0.00
m(KCl) = 0.6000 mol·kg^{-1}							
0.0800	0.0425	23.64 ± 0.21	−0.02	0.2200	0.1165	54.10 ± 0.49	0.01
0.1000	0.0534	27.75 ± 0.25	−0.01	0.2500	0.1322	60.98 ± 0.55	0.01
0.1200	0.0643	31.87 ± 0.29	0.00	0.2800	0.1480	68.04 ± 0.61	0.00
0.1500	0.0798	38.49 ± 0.35	0.00	0.3000	0.1580	73.06 ± 0.66	0.00
0.1800	0.0956	45.06 ± 0.41	0.01	0.3200	0.1685	77.91 ± 0.70	0.00
0.2000	0.1061	49.51 ± 0.45	0.01	0.3500	0.1841	85.52 ± 0.77	−0.01

The performance of the apparatus and the reliability of the method were checked by measuring the enthalpy of diglycine in water. The homogeneous enthalpic pairwise parameter of diglycine in pure water is −797.3 J·kg·mol^{-2}, which is in good agreement with those obtained by Lilley et al. (−796 J·kg·mol^{-2}).[17]

Results and Discussion

The thermodynamic formula used to treat the enthalpies of dilution is based on the excess enthalpy concept.[27] According to the McMillan−Mayer theory,[28−30] thermodynamic properties of multicomponent solutions can be expressed using a viral expansion in molality that relates the nonideal contributions of any total thermodynamic function to a series of interaction parameters. If aqueous sodium chloride or potassium chloride solution is regarded as the "solvent", the molar excess enthalpy of a solution with molality m can be written as a power series of m with coefficients h_n by[31]

$$H_m^E = H^E/m = L_{2\phi} = h_2m + h_3m^2 + h_4m^3 + ... \quad (3)$$

where h_2, h_3, h_4, etc. are the enthalpic coefficients representing pairwise, triplet, quart, etc. higher-order interactions between solvated solute species, and $L_{2\phi}$ is the relative apparent molar enthalpy. According to the relationship $L_2 = L_{2\phi} + m(\partial L_{2\phi}/\partial_m)_{T,P,n_1}$, we can get hold of the relative partial molar enthalpy L_2.

$$L_2 = 2h_2m + 3h_3m^2 + 4h_4m^3 + ... \quad (4)$$

The molar enthalpy change ($\Delta_{dil}H_m$) on diluting a solution of nonelectrolytic solute from an initial molality m_i to a final molality m_f can be written as

$$\Delta_{\text{dil}}H_{\text{m}} = H_{\text{m}}^{\text{E}}(m_{\text{f}}) - H_{\text{m}}^{\text{E}}(m_{\text{i}}) = h_2(m_{\text{f}} - m_{\text{i}}) + h_3(m_{\text{f}}^2 - m_{\text{i}}^2) + h_4(m_{\text{f}}^3 - m_{\text{i}}^3) + ... \quad (5)$$

in which $H_{\text{m}}^{\text{E}}(m_{\text{i}})$ and $H_{\text{m}}^{\text{E}}(m_{\text{f}})$ are the molar excess enthalpies of the solute in the solutions before and after dilution.

Tables 1 and 2 give the experimental values of enthalpies of dilution ($\Delta_{\text{dil}}H_{\text{m}}$), together with the difference between the experimental values and the corresponding calculated values along with the initial and final molalities (m_{i} and m_{f}) of diglycine in various aqueous sodium chloride or potassium chloride solutions.

Tables 3 and 4 list the coefficients of eq 5 that were obtained from least-squares analysis of the above results. Quite large different deviations can be observed from the two tables for the values of h_3 and h_4 at different molalities of sodium/potassium chloride. This may be due to the fact that covariance in the multiple linear regression is too high and must be taken into account in the error calculation. Figures 1 and 2 show the relationship between relative partial molar enthalpy L_2 and molality *m* of sodium chloride or potassium chloride in aqueous solutions, respectively. The relationship between L_2 and salt molality *m* is nearly linear in smaller molality ranges, which indicates that the interactions between diglycine molecules make the dominate role in these solutions.[32] In addition, due to the complexities of the interaction among three or four solute molecules, it is difficult to display their regularities with increasing molalities of aqueous salt solutions.[33−35] So only the enthalpic pairwise coefficients h_2 are discussed here.

From Tables 3 and 4, it can be seen that the values of pairwise enthalpic coefficients h_2 for diglycine in both electrolyte solutions are negative, and the value of h_2 for diglycine in aqueous sodium chloride solutions is less than that in aqueous potassium chloride solutions of the same molality. This could be attributed to the cooperative effects of partial dehydration of the hydration shell (positive contribution to h_2), dipole−dipole interactions and electrostatic interactions between diglycine molecules (negative contribution to h_2), and electrostatic interactions between diglycine molecules and ions of electrolyte (negative contribution to h_2). The negative values of h_2 testify to the predominance of dipole−dipole interaction and electrostatic interaction over the partial dehydration of the hydration shell. In addition, Marcus specified that K^+ is a structure-breaking ion while Na^+ is a borderline ion.[36] In other words, the larger size of K^+ makes the interaction between it and the water molecule weaker than that between Na^+ and the water molecule. Therefore, the dehydration of diglycine molecules in aqueous potassium chloride solutions is more difficult than that in aqueous sodium chloride solutions, which leads to the value of h_2 for diglycine in aqueous sodium chloride solutions being less than that in aqueous potassium chloride solutions of the same molality.

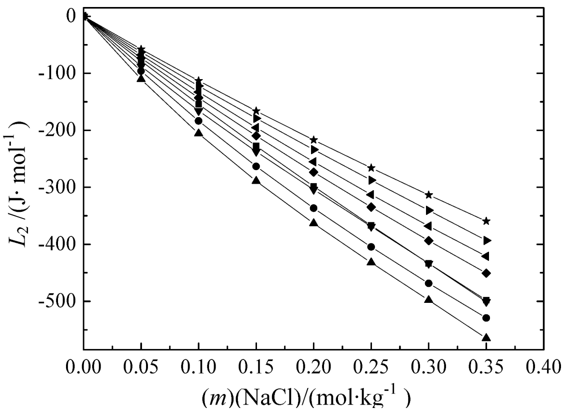

Figure 1. Relative partial molar enthalpy L_2 of glycylglycine versus the molality *m* of sodium chloride in aqueous solutions at 298.15 K. ■, *m*(NaCl) = 0.0000 mol·kg^{-1}; ●, *m*(NaCl) = 0.0500 mol·kg^{-1};▲, *m*(NaCl) = 0.1000 mol·kg^{-1}; ▼, *m*(NaCl) = 0.2000 mol·kg^{-1}; ◆, *m*(NaCl) = 0.3000 mol·kg^{-1}; solid triangle pointing left, *m*(NaCl) = 0.4000 mol·kg^{-1}; solid triangle pointing right, *m*(NaCl) = 0.5000 mol·kg^{-1}; ★, *m*(NaCl) = 0.6000 mol·kg^{-1}.

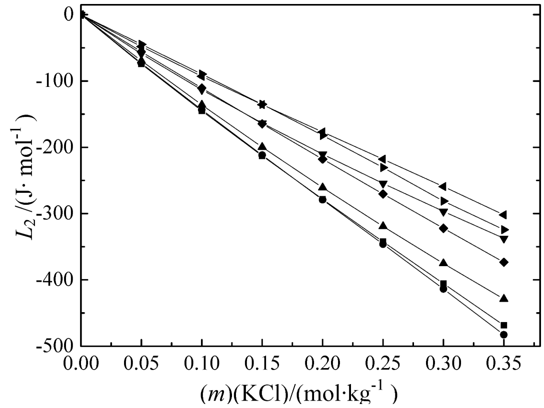

Figure 2. Relative partial molar enthalpy L_2 of glycylglycine versus the molality *m* of potassium chloride in aqueous solutions at 298.15 K. ■, *m*(KCl) = 0.0500 mol·kg^{-1}; ●, *m*(KCl) = 0.1000 mol·kg^{-1}; ▲, *m*(KCl) = 0.2000 mol·kg^{-1}; ▼, *m*(KCl) = 0.3000 mol·kg^{-1}; ◆, *m*(KCl) = 0.4000 mol·kg^{-1}; solid triangle pointing left, *m*(KCl) = 0.5000 mol·kg^{-1}; solid triangle pointing right, *m*(KCl) = 0.6000 mol·kg^{-1}.

Table 3. Enthalpic Interaction Coefficients of Glycylglycine in Water and Aqueous Sodium Chloride Solutions at 298.15 K

m(NaCl)	h_2	h_3	h_4	SD
mol·kg^{-1}	J·kg·mol^{-2}	J·kg^2·mol^{-3}	J·kg^3·mol^{-4}	J·mol^{-1}
0.0000	−797.3 ± 4.0[a]	179.9 ± 13.0[a]	−35.1 ± 17.0[a]	0.02
0.0500	−1008.4 ± 6.6[a]	655.9 ± 22.0[a]	−376.2 ± 29.1[a]	0.04
0.1000	−1192.0 ± 51.0[a]	1225.5 ± 169.0[a]	−1055.0 ± 221.5[a]	0.30
0.2000	−929.2 ± 65.4[a]	771.2 ± 216.1[a]	−780.5 ± 283.1[a]	0.39
0.3000	−750.0 ± 10.4[a]	245.7 ± 34.8[a]	−92.8 ± 45.8[a]	0.06
0.4000	−690.6 ± 3.2[a]	180.6 ± 10.6[a]	−23.4 ± 13.9[a]	0.02
0.5000	−644.6 ± 18.8[a]	254.7 ± 63.0[a]	−208.2 ± 83.4[a]	0.12
0.6000	−590.3 ± 3.6[a]	176.5 ± 11.9[a]	−64.5 ± 15.7[a]	0.02

[a] The values are the standard errors, which are given by the computer during the multiple linear regression analysis. SD = standard derivation.

Table 4. Enthalpic Interaction Coefficients of Glycylglycine in Aqueous Potassium Chloride Solutions at 298.15 K

m(KCl)	h_2	h_3	h_4	SD
mol·kg^{-1}	J·kg·mol^{-2}	J·kg^2·mol^{-3}	J·kg^3·mol^{-4}	J·mol^{-1}
0.0500	−763.0 ± 4.6	283.4 ± 15.6	−225.1 ± 20.7	0.03
0.1000	−747.9 ± 23.1	242.6 ± 76.1	−282.5 ± 99.5	0.13
0.2000	−709.8 ± 7.6	202.5 ± 25.1	−37.8 ± 32.6	0.05
0.3000	−615.3 ± 16.0	356.5 ± 53.1	−220.0 ± 69.5	0.09
0.4000	−562.9 ± 3.2	67.0 ± 10.8	−23.4 ± 14.3	0.02
0.5000	−498.1 ± 12.2	263.7 ± 40.5	−292.3 ± 53.2	0.07
0.6000	−446.3 ± 2.8	11.2 ± 9.3	−151.9 ± 12.2	0.02

The data in Tables 3 and 4 also show that the values of h_2 for diglycine in aqueous sodium chloride solutions become less negative with an increase in the molality of sodium chloride. In contrast, the values of h_2 for diglycine in aqueous sodium chloride solutions pass through a minimum at about 0.10 mol·kg^{-1}. This can be attributed to the influence of salt on the enthalpic pairwise interaction. In the diglycine−alkali chloride−water system, hydration sheaths with defined water molecules are formed around dissolved molecules or ions. Mutual interaction between the molecules or ions of the electrolyte may cause some water molecules to be squeezed out from the hydration sheaths into the typical bulk water.[37] With the increase of salt molality, the direct interactions between diglycine molecules and salt ions strengthen, which gives a negative contribution to

h_2. At the same time, the partial dehydration of solute molecules and salt ions gives a positive contribution to h_2. The discrepancy in the change trend of h_2 in aqueous sodium chloride and potassium chloride solutions with an increase of salt molality is mainly due to the different ion radius of Na^+ and K^+. The larger size of K^+ makes the dehydration of diglycine molecules in aqueous potassium chloride solutions more difficult than that in aqueous sodium chloride solutions. The higher the molality of potassium chloride is, the stronger the dehydration effects are, and the more positive the contribution to the enthalpy will be. But the dominant thermal effect is still the direct interaction. Consequently, the values of h_2 for diglycine in aqueous potassium chloride solutions are all negative over the whole molalities of the salt aqueous solutions investigated and become less negative with an increase of salt molality. As for the diglycine−sodium chloride−water system, with the increase of sodium chloride molality, the direct interactions are most prevailing at about $0.10\ \text{mol}\cdot\text{kg}^{-1}$, leading to a minimum of h_2 coefficients. We can deduce from the above results that with an increase in the molality of potassium chloride the dehydration effects are strengthened, the hydration sheaths between protein molecules are broken more strongly, which is unfavorable to the stabilization of protein structure. As for sodium chloride, the direct interactions between solute molecules are prevailing when sodium chloride molality is less than $0.10\ \text{mol}\cdot\text{kg}^{-1}$, which makes protein structure stabilized. However, when the molality of sodium chloride continues to increase, the dehydration effects dominate over the direct interactions, which is detrimental to the stabilization of protein structure.

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