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Enthalpic Interaction Coefficients of Glycine Betaine in Aqueous Sodium Chloride and Potassium Chloride Solutions at 298.15 K

Dashuang Fan,[†] Xueqin An,[‡] and Weiguo Shen*,[†,‡]

[†]Department of Chemistry, Lanzhou University, Lanzhou 730000, China

[‡]School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

ABSTRACT: The enthalpies of dilution were measured for glycine betaine in water and in aqueous solutions of sodium chloride or potassium chloride at 298.15 K in a range of salt molality up to 1.2 $\mathrm{mol \cdot kg^{-1}}$ using a flow−mixing microcalorimeter. The enthalpic interaction coefficients h_2 and h_3 were determined according to the McMillan−Mayer model and compared with that in glycine aqueous solutions. It was found that the enthalpic pairwise interaction coefficients h_2 of GB in both brine solutions are positive and increase with the molality of the salts. The value of h_2 in aqueous solutions of sodium chloride is larger than that in the aqueous solutions of potassium chloride with the same molality.

■ INTRODUCTION

Proteins are foundational materials of physiological activity in biological systems. Research on the structure and function of proteins has attracted great interest. Because of the complexity of their structure and the diversity of their interaction with the surrounding environment, it is extremely difficult to directly investigate the corresponding thermodynamic properties of proteins at present. Therefore, studies of the protein model compounds, such as amino acids, peptides, amides, and their derivatives, are the current key spots of the research. Most proteins exist in the complicated environment containing many organic and inorganic substances. Biological fluids of living organisms contain a quantity of ions, especially sodium, potassium, and chloride ions, which are indispensable for the metabolic processes of a living organism.[1] Therefore, investigation of the influence of electrolytes is important.[2−4] Glycine betaine (GB) is an analogue of glycine. It is present in most mammalian tissues, where it functions as a cell−volume regulator[5−7] and also as a reserve of methyl groups, potentially available for methionine synthesis through the enzyme betaine−homocysteine methyltransferase which is regulated both by the supply of methyl groups[8] and by osmotic stress.[9] It also acts like a chaperone to stabilize protein structure under denaturing conditions.[10] In this paper, we report the dilution enthalpies for GB in aqueous solutions of sodium chloride (NaCl) and potassium chloride (KCl) at 298.15 K. The experimental results are used to obtain the enthalpic interaction coefficients and discuss the nature of the interactions existing in the solutions.

■ EXPERIMENTAL SECTION

Reagents. GB (0.98 mass fraction) was purchased from J&K CHEMICAL, Ltd., and stored at (2 to 8) °C; NaCl (0.999 mass fraction) and KCl (0.999 mass fraction) were obtained from Tianjin Chemical Reagent Co. and stored over P_2O_5 in a vacuum desiccator for 72 h at room temperature prior to use. The water used throughout the experiment was deionized and twice distilled. All of the solutions were prepared by weighing using a Sartorius BS 224S balance with precision of ±0.1 mg. The molality range of the aqueous solutions of NaCl and KCl was (0 to 1.2) $\mathrm{mol \cdot kg^{-1}}$. All of the solutions were degassed with ultrasonic method and used within 12 h of preparation.

Calorimetric Measurements. The calorimetric measurements were performed with a mixing−flow microcalorimeter (2277 Thermal Activity Monitor manufactured in Sweden) at 298.15 K. Details of this apparatus and the standard experimental procedure has been reported in literature.[11−14] The solutions of GB and the solvents (water or aqueous solution of NaCl or KCl) were pumped through the flow−mixing vessel of the calorimeter using a 403U-VM2 50 rpm dual channel pump. The flow rates were determined from the mass of the samples delivered in 6 min, with a variation of less than 0.1 % both before and after a complete dilution experiment. Thermal effects of the dilution were obtained with a standard process.[15,16] The enthalpies of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ were calculated from the equation:

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}} = -P(m_{\mathrm{i}}M + 1)/m_{\mathrm{i}}f_2 \qquad (1)$$

where P is the dilution thermal power of solution (μW), m_{i} is the initial molality of GB ($\mathrm{mol \cdot kg^{-1}}$), M is the molar mass of GB ($\mathrm{kg \cdot mol^{-1}}$), and f_2 is the flow rate of GB solution ($\mathrm{mg \cdot s^{-1}}$). The uncertainties of P, m_{i}, f_2 were ±0.2 μW, ± 0.0001 $\mathrm{mol \cdot kg^{-1}}$, and ±0.002 $\mathrm{mg \cdot s^{-1}}$, respectively. The uncertainty of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ was estimated by repeating measurements at each initial molality and found to be about 1% of the value for the brine solutions, but up to 10% of the value for aqueous solutions because the heat effect is very small when the GB aqueous solution was diluted by the pure water.

The final molality m_{f} was calculated from the equation:

$$m_{\mathrm{f}} = m_{\mathrm{i}}f_2/[f_1(m_{\mathrm{i}}M + 1) + f_2] \qquad (2)$$

where f_1 is the flow rate of the solvent.

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Table 1. Molar Enthalpies of Dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ of GB in Water and Aqueous Solutions of NaCl at 298.15 K

m_{i}	m_{f}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}{}^{a}$	δ	m_{i}	m_{f}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}{}^{a}$	δ
$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$
$m(\mathrm{NaCl}) = 0.0000\ \mathrm{mol\cdot kg^{-1}}$							
0.3776	0.1848	−0.69	0.08	0.5174	0.2518	−2.09	−0.02
0.4003	0.1956	−0.95	−0.01	0.5478	0.2652	−2.41	0.03
0.4180	0.2041	−1.17	−0.08	0.5760	0.2784	−2.78	0.02
0.4482	0.2184	−1.35	0.01	0.6003	0.2901	−3.07	0.05
0.4784	0.2334	−1.65	0.00	0.6180	0.2985	−3.38	−0.01
0.4965	0.2414	−1.87	−0.02	0.6473	0.3125	−3.83	−0.03
$m(\mathrm{NaCl}) = 0.2000\ \mathrm{mol\cdot kg^{-1}}$							
0.1208	0.0601	−7.71	−0.07	0.2997	0.1478	−17.92	0.15
0.1493	0.0742	−9.40	−0.04	0.3192	0.1573	−19.12	0.02
0.1811	0.0899	−11.34	−0.08	0.3483	0.1713	−20.57	0.16
0.2010	0.0997	−12.49	−0.06	0.3780	0.1856	−22.35	−0.03
0.2195	0.1086	−13.34	0.19	0.3993	0.1961	−23.42	−0.02
0.2490	0.1232	−15.37	−0.16	0.4201	0.2060	−24.49	0.00
0.2794	0.1381	−16.96	−0.04	0.4475	0.2191	−25.96	−0.08
$m(\mathrm{NaCl}) = 0.4000\ \mathrm{mol\cdot kg^{-1}}$							
0.1493	0.0731	−15.80	−0.30	0.2978	0.1445	−28.91	0.32
0.1792	0.0876	−18.59	−0.20	0.3182	0.1543	−30.62	0.35
0.1996	0.0975	−20.37	−0.05	0.3464	0.1676	−33.05	0.30
0.2188	0.1066	−22.57	−0.42	0.3795	0.1836	−35.82	0.17
0.2480	0.1206	−25.04	−0.21	0.3958	0.1911	−37.57	−0.25
0.2780	0.1354	−26.91	0.51	0.4170	0.2011	−39.41	−0.43
$m(\mathrm{NaCl}) = 0.5000\ \mathrm{mol\cdot kg^{-1}}$							
0.1188	0.0568	−14.10	0.02	0.2792	0.1318	−32.40	0.08
0.1485	0.0708	−17.56	0.03	0.2954	0.1394	−34.41	−0.15
0.1808	0.0858	−21.42	−0.05	0.3184	0.1503	−36.83	−0.09
0.1950	0.0926	−22.79	0.17	0.3445	0.1620	−39.51	0.16
0.2185	0.1039	−25.68	−0.10	0.3761	0.1769	−43.10	−0.10
0.2482	0.1175	−29.01	−0.02	0.3984	0.1874	−45.26	0.07
$m(\mathrm{NaCl}) = 0.6000\ \mathrm{mol\cdot kg^{-1}}$							
0.1200	0.0582	−16.40	−0.16	0.2998	0.1439	−39.30	0.11
0.1507	0.0729	−20.34	−0.03	0.3173	0.1522	−41.44	0.13
0.1792	0.0867	−24.32	−0.32	0.3484	0.1667	−45.28	0.16
0.2199	0.1060	−28.99	0.31	0.3779	0.1805	−48.95	0.09
0.2483	0.1196	−33.02	−0.12	0.3985	0.1901	−51.43	0.11
0.2789	0.1340	−36.87	−0.07	0.4181	0.1994	−54.20	−0.35
$m(\mathrm{NaCl}) = 0.8000\ \mathrm{mol\cdot kg^{-1}}$							
0.0980	0.0488	−14.27	0.13	0.2993	0.1474	−44.64	−0.06
0.1211	0.0603	−17.89	−0.09	0.3185	0.1569	−47.14	0.30
0.1807	0.0896	−26.84	−0.15	0.3496	0.1718	−52.18	0.04
0.2193	0.1079	−32.92	−0.26	0.3791	0.1858	−56.68	0.11
0.2501	0.1235	−36.96	0.17	0.4210	0.2061	−63.27	−0.10
0.2791	0.1376	−41.54	−0.02	0.4278	0.2093	−64.35	−0.11
$m(\mathrm{NaCl}) = 1.0000\ \mathrm{mol\cdot kg^{-1}}$							
0.1181	0.0593	−21.36	−0.38	0.3174	0.1580	−56.20	−0.21
0.1483	0.0745	−26.12	0.15	0.3470	0.1721	−61.70	−0.41
0.1782	0.0892	−31.26	0.35	0.3757	0.1861	−66.26	0.03
0.1999	0.1002	−35.32	0.03	0.3969	0.1966	−70.21	−0.30
0.2182	0.1089	−38.40	0.29	0.4151	0.2052	−73.08	0.08
0.2784	0.1384	−49.28	0.05	0.4467	0.2206	−78.24	0.36

Table 1. Continued

m_i $\mathrm{mol \cdot kg^{-1}}$	m_f $\mathrm{mol \cdot kg^{-1}}$	$\Delta_{\mathrm{dil}}H_\mathrm{m}{}^{a}$ $\mathrm{J \cdot mol^{-1}}$	δ $\mathrm{J \cdot mol^{-1}}$	m_i $\mathrm{mol \cdot kg^{-1}}$	m_f $\mathrm{mol \cdot kg^{-1}}$	$\Delta_{\mathrm{dil}}H_\mathrm{m}{}^{a}$ $\mathrm{J \cdot mol^{-1}}$	δ $\mathrm{J \cdot mol^{-1}}$
			$m(\mathrm{NaCl}) = 1.2000\ \mathrm{mol \cdot kg^{-1}}$				
0.0974	0.0483	−19.31	0.08	0.2956	0.1450	−58.32	−0.13
0.1458	0.0722	−28.80	0.12	0.3134	0.1537	−61.27	0.32
0.1904	0.0938	−37.97	−0.20	0.3426	0.1675	−66.70	0.61
0.2160	0.1062	−43.29	−0.48	0.3726	0.1819	−72.59	0.47
0.2439	0.1201	−48.20	−0.09	0.3938	0.1920	−77.64	−0.52
0.2738	0.1344	−53.92	0.08	0.4083	0.1987	−80.27	−0.30

[a] $\delta = \Delta_{\mathrm{dil}}H_\mathrm{m} - \Delta_{\mathrm{dil}}H_{\mathrm{m(calcd)}}$, where $\Delta_{\mathrm{dil}}H_{\mathrm{m(calcd)}}$ was calculated from eq 5 with the coefficients listed in Table 3.

RESULTS AND DISCUSSION

According to the McMillan–Mayer theory,[17] the molar excess enthalpy of a solution with molality m can be expressed as a power series of m:

$$H_\mathrm{m}^\mathrm{E} = h_2 m + h_3 m^2 + h_4 m^3 + ... \tag{3}$$

where h_2, h_3, h_4, ... are the pairwise, triplet, quarter, and higher-order enthalpic interaction coefficients mediated by the solvent. The molar enthalpy of dilution $\Delta_{\mathrm{dil}}H_\mathrm{m}$, for diluting a solution from an initial molality m_i to a final molality m_f is

$$\Delta_{\mathrm{dil}}H_\mathrm{m} = H_\mathrm{m}^\mathrm{E}(m_\mathrm{f}) - H_\mathrm{m}^\mathrm{E}(m_\mathrm{i}) \tag{4}$$

Combining eqs 3 and 4 yields

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

From the McMillan–Mayer theory, the relative partial molar enthalpy L_2 with molality m can be written as

$$L_2 = 2h_2 m + 3h_3 m^2 + ... \tag{6}$$

The experimental values ($\Delta_{\mathrm{dil}}H_\mathrm{m}$) together with the initial and final molalities (m_i and m_f) of GB in various aqueous solutions of NaCl and KCl are listed in Tables 1 and 2, which were fitted to eq 5 to obtain the interaction coefficients h_2 and h_3. Tables 3 and 4 list the values of h_2 and h_3, together with their standard errors, and the standard deviations SD of the fitting. It was found that although the standard deviations for the fits with the term of h_3 were significantly smaller than that for the fits without the term of h_3, the uncertainties of the optimal values of h_3 are large as shown in Tables 3 and 4 because of both the experimental uncertainties and the correlations between h_2 and h_3; thus the values of h_3 and its physical meaning are unreliable. In fact, it is very difficult to elucidate the complicated interaction contributions from h_3; therefore, we only pay attention to h_2 here. Figure 1 shows the plots of h_2 versus the molality of NaCl and KCl in aqueous solutions.

The relationship between relative partial molar enthalpy L_2 and the molality m for aqueous solutions of NaCl or KCl calculated by eq 6 is shown in Figures 2 and 3, respectively. From Figures 2 and 3, we can find that the relative partial molar enthalpy L_2 is nearly linear with the salt molality m in the experimental molality ranges, which indicates that the interaction between two GB molecules is dominating in these dilute solutions, and the higher order enthalpic interaction coefficients representing the interactions of multiple molecules are negligible.

It is generally believed that the pair enthalpic interaction coefficient h_2 gives the measure of the interaction between two solvated solute molecules, which consists of the electrostatic interaction and the structural interaction.[16,18,19] In the system we studied, the electrostatic interaction is caused by the attractions between two polar parts of GB, which is exothermic and leads a negative contribution to h_2. The structural interaction is caused by the partial dehydration of the hydrated solutes when two GB molecules interact with each other, which is endothermic and leads a positive contribution to h_2. The partial dehydration causes relaxation of some water molecules from the hydrated shell of GB to the bulk solvent.

GB is the substance that three methyl groups replace the hydrogen atoms of glycine. It was reported that the values of h_2 for glycine in water and aqueous solutions of NaCl and KCl are all negative.[18−20] The value of h_2 for glycine in pure water is −439 $\mathrm{J \cdot kg \cdot mol^{-2}}$, while the value of h_2 in 0.2 $\mathrm{mol \cdot kg^{-1}}$ aqueous solutions of NaCl or KCl is −424.2 $\mathrm{J \cdot kg \cdot mol^{-2}}$ or −443.5 $\mathrm{J \cdot kg \cdot mol^{-2}}$, respectively. It indicates that electrostatic interactions in glycine aqueous solutions dominate the value of h_2. However, according to Tables 3 and 4, the value of h_2 for GB in pure water is −6.47 $\mathrm{J \cdot kg \cdot mol^{-2}}$, while the values of h_2 in aqueous solutions of NaCl and KCl are all positive. This illustrated that the structural interactions for GB are predominant and stronger than those for glycine. The replacement of the hydrogen in glycine by the methyl groups brings about the stronger hydrophobic interaction. The hydrophobic interaction causes the increase of the number of water molecules in the hydration shell. The structure of water in the hydration layer is more ordered and contains lower energy. Furthermore, the electrostatic interaction is weakened by the steric effect of the three methyl groups. Both effects give rise to the positive contributions to h_2. The value of h_2 for GB in pure water is negative, which indicates that the structural interaction of GB does not surpass over the electrostatic interactions and the energy decreases when two GB molecules in the pure water approach each other.

From Tables 3 and 4 and Figure 1, it can be seen that the values of the pair enthalpic interaction coefficient h_2 for GB increase with the concentration of salts. In the GB brine solution, the hydration shell of GB contains not only the water molecules but also the ions of the salt. The hydration cosphere overlap between two hydrated GB molecules may cause the partial removal of water molecules and the ions from the hydration layer to the bulk solvent. This procedure absorbs more heats than that of dehydration with no ions because of the interactions between the ions and the $\mathrm{N^+}$ and $\mathrm{COO^-}$ of GB. The higher of the

Table 2. Molar Enthalpies of Dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ of GB in Aqueous Solutions of KCl at 298.15 K

m_{i}	m_{f}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}{}^{a}$	δ	m_{i}	m_{f}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}{}^{a}$	δ
mol·kg^{-1}	mol·kg^{-1}	J·mol^{-1}	J·mol^{-1}	mol·kg^{-1}	mol·kg^{-1}	J·mol^{-1}	J·mol^{-1}
m(KCl) = 0.2000 mol·kg^{-1}							
0.1198	0.0587	−7.48	−0.20	0.2983	0.1463	−17.46	−0.05
0.1474	0.0721	−9. 07	−0.15	0.3163	0.1549	−18.39	0.03
0.1790	0.0875	−10.84	−0.07	0.3474	0.1693	−19.98	0.20
0.1984	0.0976	−11.70	0.11	0.3769	0.1835	−21.70	0.07
0.2199	0.1083	−13.07	−0.06	0.3983	0.1932	−23.09	−0.12
0.2471	0.1217	−14.44	0.09	0.4181	0.2029	−24.12	−0.13
0.2758	0.1352	−16.05	0.14				
m(KCl) = 0.4000 mol·kg^{-1}							
0.1493	0.0736	−13.53	−0.57	0.3166	0.1544	−27.29	0.29
0.1776	0.0874	−16.00	−0.58	0.3491	0.1699	−30.76	−0.33
0.1971	0.0969	−17.03	0.09	0.3757	0.1826	−32.80	−0.04
0.2189	0.1075	−18.70	0.32	0.3946	0.1916	−34.44	−0.03
0.2485	0.1218	−21.33	0.27	0.4173	0.2024	−36.55	−0.15
0.2768	0.1354	−23.91	0.17	0.4464	0.2162	−38.94	0.01
0.2987	0.1458	−25.71	0.31				
m(KCl) = 0.5000 mol·kg^{-1}							
0.0999	0.0496	−11.57	−0.26	0.2478	0.1222	−27.12	0.17
0.1190	0.0591	−13.67	−0.26	0.3189	0.1564	−34.98	−0.26
0.1510	0.0748	−17.04	−0.11	0.3504	0.1716	−37.88	0.04
0.1774	0.0877	−19.64	0.17	0.3759	0.1840	−40.29	0.15
0.2008	0.0993	−21.95	0.34	0.3984	0.1947	−42.72	−0.02
0.2184	0.1077	−24.26	−0.04	0.4168	0.2033	−44.64	−0.08
m(KCl) = 0.6000 mol·kg^{-1}							
0.1781	0.0877	−20.67	0.03	0.3157	0.1541	−36.55	0.07
0.1995	0.0979	−23.40	−0.18	0.3475	0.1694	−40.05	0.21
0.2189	0.1075	−25.75	−0.33	0.3769	0.1833	−44.15	−0.48
0.2463	0.1206	−28.25	0.38	0.3971	0.1930	−46.27	−0.31
0.2801	0.1371	−32.53	−0.04	0.4156	0.2020	−48.12	−0.08
0.2965	0.1449	−34.02	0.38	0.4464	0.2164	−51.26	0.35
m(KCl) = 0.8000 mol·kg^{-1}							
0.0986	0.0483	−14.25	0.01	0.2887	0.1396	−42.27	−0.23
0.1158	0.0567	−16.35	0.40	0.3102	0.1501	−45.50	−0.38
0.1745	0.0850	−25.20	0.12	0.3356	0.1623	−48.99	−0.19
0.1944	0.0947	−28.05	0.14	0.3654	0.1761	−53.12	0.14
0.2099	0.1026	−30.45	−0.12	0.3847	0.1855	−55.93	0.08
0.2682	0.1301	−38.94	0.03	0.4045	0.1946	−58.77	0.22
m(KCl) = 1.0000 mol·kg^{-1}							
0.0977	0.0485	−16.29	−0.12	0.2767	0.1360	−45.15	0.19
0.1188	0.0590	−19.95	−0.34	0.2943	0.1446	−47.76	0.39
0.1502	0.0744	−24.41	0.36	0.3420	0.1675	−56.14	−0.31
0.1966	0.0971	−32.83	−0.48	0.3723	0.1821	−60.37	0.27
0.2149	0.1060	−35.60	−0.26	0.3955	0.1931	−64.53	−0.16
0.2462	0.1212	−40.03	0.39	0.4116	0.2009	−67.00	−0.12
m(KCl) = 1.2000 mol·kg^{-1}							
0.0963	0.0471	−16.88	0.20	0.2744	0.1330	−49.37	−0.13
0.1166	0.0570	−20.59	0.11	0.2930	0.1416	−53.12	−0.38
0.1454	0.0709	−25.91	−0.03	0.3121	0.1508	−55.92	0.28
0.1750	0.0853	−31.24	−0.06	0.3725	0.1794	−67.00	0.35
0.1942	0.0946	−34.48	0.15	0.3884	0.1871	−70.00	0.23
0.2435	0.1183	−43.82	−0.25	0.4094	0.1967	−74.59	−0.36

[a] $\delta = \Delta_{\mathrm{dil}}H_{\mathrm{m}} - \Delta_{\mathrm{dil}}H_{\mathrm{m(calcd)}}$,where $\Delta_{\mathrm{dil}}H_{\mathrm{m(calcd)}}$ was calculated from eq 5 with the coefficients listed in Table 4.

Table 3. Enthalpic Interaction Coefficients of GB in Water and Aqueous Solutions of NaCl at 298.15 K

m(NaCl)	h_2	h_3	SD
$\text{mol}\cdot\text{kg}^{-1}$	$\text{J}\cdot\text{kg}\cdot\text{mol}^{-2}$	$\text{J}\cdot\text{kg}^{2}\cdot\text{mol}^{-3}$	$\text{J}\cdot\text{mol}^{-1}$
0.0000	−6.47 ± 0.31	18.57 ± 0.38	0.04
0.2000	130.44 ± 0.80	−25.66 ± 1.50	0.11
0.4000	216.17 ± 3.02	−57.69 ± 5.99	0.35
0.5000	233.36 ± 0.97	−31.60 ± 2.06	0.11
0.6000	269.57 ± 1.82	−37.85 ± 3.59	0.21
0.8000	292.29 ± 1.42	2.69 ± 2.71	0.17
1.0000	360.17 ± 2.37	−18.76 ± 4.33	0.29
1.2000	399.26 ± 3.40	−29.18 ± 6.75	0.37

Table 4. Enthalpic Interaction Coefficients of GB in Aqueous Solutions of KCl at 298.15 K

m(KCl)	h_2	h_3	SD
$\text{mol}\cdot\text{kg}^{-1}$	$\text{J}\cdot\text{kg}\cdot\text{mol}^{-2}$	$\text{J}\cdot\text{kg}^{2}\cdot\text{mol}^{-3}$	$\text{J}\cdot\text{mol}^{-1}$
0.2000	122.35 ± 1.07	−17.50 ± 2.13	0.13
0.4000	172.18 ± 2.57	−4.53 ± 4.86	0.33
0.5000	229.92 ± 1.73	−34.24 ± 3.36	0.21
0.6000	231.98 ± 2.57	−11.48 ± 4.79	0.31
0.8000	284.42 ± 2.07	−5.68 ± 4.17	0.23
1.0000	332.27 ± 2.89	−24.22 ± 5.71	0.33
1.2000	346.59 ± 2.23	3.98 ± 4.50	0.26

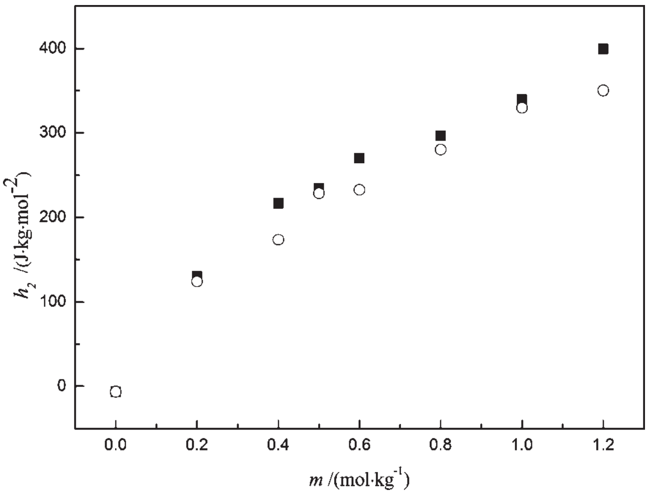

Figure 1. Enthalpic pairwise interaction coefficient h_2 of GB versus the molality of the salt in aqueous solutions at 298.15 K. ■, NaCl; ○, KCl.

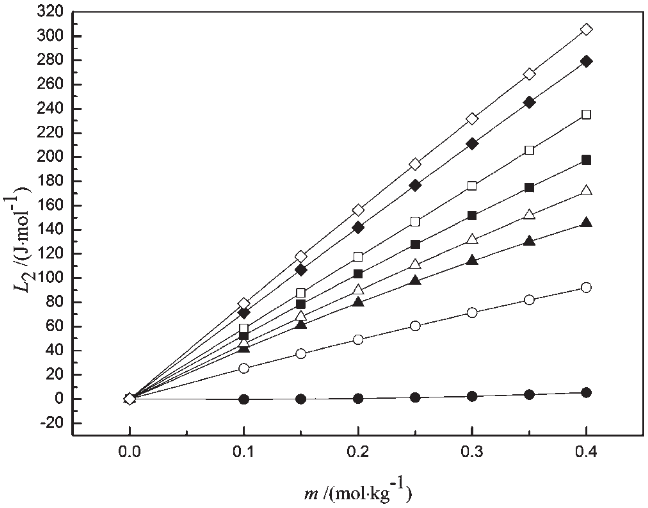

Figure 2. Relative partial molar enthalpy L_2 of GB versus the molality m of GB in aqueous solutions at 298.15 K. ●, m(NaCl) = 0.0000 mol·kg^{-1}; ○, m(NaCl) = 0.2000 mol·kg^{-1} ; ▲, m(NaCl) = 0.4000 mol·kg^{-1}; Δ, m(NaCl) = 0.5000 mol·kg^{-1}; ■, m(NaCl) = 0.6000 mol·kg^{-1}; □, m(NaCl) = 0.8000 mol·kg^{-1}; ♦, m(NaCl) = 1.0000 mol·kg^{-1}; ◊, m(NaCl) = 1.2000 mol·kg^{-1}.

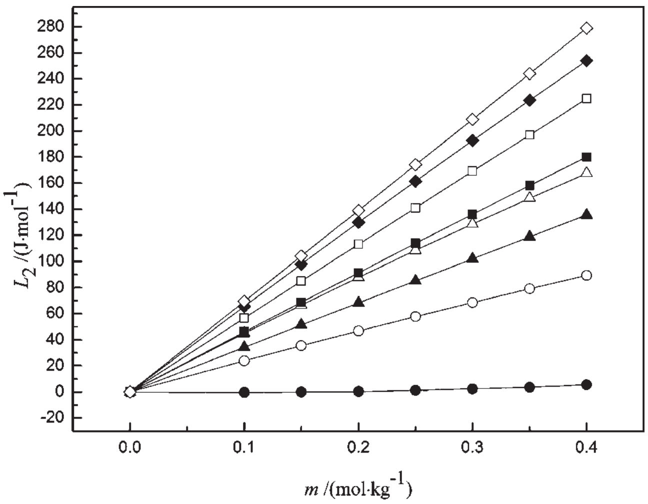

Figure 3. Relative partial molar enthalpy L_2 of GB versus the molality m of GB in aqueous solutions at 298.15 K. ●, m(KCl) = 0.0000 mol·kg^{-1}; ○, m(KCl) = 0.2000 mol·kg^{-1} ; ▲, m(KCl) = 0.4000 mol·kg^{-1}; Δ, m(KCl) = 0.5000 mol·kg^{-1}; ■, m(KCl) = 0.6000 mol·kg^{-1}; □, m(KCl) = 0.8000 mol·kg^{-1}; ♦, m(KCl) = 1.0000 mol·kg^{-1}; ◊, m(KCl) = 1.2000 mol·kg^{-1}.

molality of the ions is, the stronger is the interaction due to increase of the number of ions in the hydration layer.

Finally, the data in Tables 3 and 4 show that the values of h_2 in the NaCl aqueous solutions are larger than that in the KCl aqueous solutions with the same molalities. The same behavior was also found in glycine solutions.[19,20] This may be attributed to the fact that the electrostatic interaction between GB and Na^+ is stronger than that between GB and K^+ because of the smaller radius of Na^+. In other words, the process of removal of a part of Na^+ absorbs more heats than that of K^+ from the hydration layer to the bulk solvent when two GB molecules closing up.

■ CONCLUSIONS

The molar dilution enthalpies of GB have been measured in pure water and the NaCl aqueous solutions and KCl aqueous solutions at 298.15 K by a flow−mixing microcalorimeter. The enthalpic interaction coefficients h_2 and h_3 were obtained according to the McMillan−Mayer model. The results showed that the replacement of the hydrogen in glycine by the methyl groups and addition of Na^+ or K^+ increase the value of h_2. It may be attributed to the significant increases of the energy of the system to partly remove the water molecules and the cations from the hydration layer when two GB molecules close up.

AUTHOR INFORMATION

Corresponding Author

*Phone: +86−21−64250804. Fax: +86−21−64252510. E-mail: shenwg@lzu.edu.cn.

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