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Thermochimica Acta 378 (2001) 1–8

thermochimica acta

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# Enthalpic interactions of glycine in aqueous sodium halide solutions

Li Yu[a,*], Xingen Hu[a], Ruisen Lin[a], Shuang Shao[b], Honglin Zhang[c]

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China*
[b]*Department of Chemistry, Zhejiang Educational College, Hangzhou 310000, PR China*
[c]*Department of Chemistry, Qufu Normal University, Qufu 273165, PR China*

Received 19 January 2001; received in revised form 25 April 2001; accepted 27 April 2001

## Abstract

Dilution enthalpies of glycine in aqueous NaF and NaI solutions of various molalities at 298.15 K have been determined, respectively, by mixing flow microcalorimetry. The results have been analyzed according to the modified McMillan–Mayer model to obtain homogeneous enthalpic interaction coefficients. The effect of the anions on enthalpic pair-wise interaction coefficients has been discussed from the point of view of electrostatic interaction and structural interaction. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Glycine; Sodium halide solution; Dilution enthalpy; Homogeneous enthalpic interaction coefficient

## 1. Introduction

The study of the thermodynamic stability of the native structure of proteins has proved quite challenging and still remains a subject of extensive investigations [1,2]. Owing to the complexities arising from a direct thermodynamic study on proteins, amino acids have been quite useful as models for understanding the thermodynamic behavior of peptides and proteins in aqueous solutions [3]. It is well known that salts can have marked effects on the stability of protein structures, and that some electrolytes have a tendency to disrupt some, at least, of the structural features of proteins, whereas other electrolytes show a propensity to buttress such structures [4]. It is quite effective to investigate the interaction between amino acids and electrolytes using enthalpic measurement method [5]. Much work has been done on this kind of interaction by measuring enthalpic effects [6–14].

In consequence, continuing our investigations on the enthalpic interactions of some typical amino acids in aqueous non-electrolyte binary solutions [15–19], we turn our attention to aqueous electrolyte solutions in the present work. Dilution enthalpy is recognized as a basic thermodynamic parameter to study the interactions between two solvated solute molecules in solutions. But most of the research works are focus on the dissolution or mixing enthalpies between amino acids and electrolytes [8–10,20,21]. A survey of the literatures indicates a lack of experimental data of the dilution enthalpies of amino acid in aqueous electrolyte solutions. The aim of this investigation is to explore the role of the anions in influencing the enthalpic interaction between two amino acid zwitter ions in aqueous electrolyte solutions. Glycine is the simplest amino acid of the smallest hydrocarbon

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[*] Corresponding author. Fax: +86-571-795-1846.
*E-mail address*: yl-mary@263.net (L. Yu).

0040-6031/01/$ – see front matter
PII: S0040-6031(01)00592-5

backbone. In this paper, the dilution enthalpies of glycine in aqueous sodium halide solutions of various molalities at 298.15 K and the homogeneous enthalpic interaction coefficients of glycine have been reported. The results are interpreted from the point of view of electrostatic interaction and structural interaction.

## 2. Experimental

### 2.1. Reagents

Glycine (biochemical reagent, >99.0%, from Shanghai Chem. Co.) was recrystallized from water–methanol mixture and dried under reduced pressure at 323 K. NaF and NaI (analytical reagents, >99.0%, from Shanghai Chem. Co.) were recrystallized from distilled water and dried under reduced pressure at 353 K. Both the salts and glycine 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 preparation of solutions.

Both the aqueous salt solutions, which were used as mixed solvents (water + sodium halide), and the amino acid solutions (glycine + sodium halide + water) were prepared by mass using a Mettler AE 200 balance precise to ±0.0001 g. The molality ranges of aqueous sodium fluoride and sodium iodide solutions are 0.1–0.6 and 0.2–1.0 mol $kg^{-1}$, respectively. The molality range of aqueous glycine solutions (glycine + sodium halide + water) is 0.2–1.0 mol $kg^{-1}$. All the solutions were degassed and used within 12 h after preparation.

### 2.2. Calorimetric procedure

The enthalpies of dilution for glycine in aqueous sodium halide solutions were measured with LKB-2277 BioActivity Monitor at 298.15 K. The solutions were pumped through the mixing-flow vessel of the calorimeter in different ratios using a pair of LKB-2132 microperpex peristaltic pumps. The variation in flow rates was less than 0.2%. The flow rates were determined by weighing samples delivered in 8 min. The variation in flow rates was less than 0.1% both before and after a complete dilution experiment. The details of the experimental technique have been described elsewhere [16,19].

The enthalpies of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ were calculated from the equation

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

in which $P$ is the dilution thermal power (μW), $M$ the molar mass of amino acid (mol $kg^{-1}$), and $f_2$ is the flow rate of amino acid solution (mg $s^{-1}$). The final molality $m_{\mathrm{f}}$ were calculated from the equation

$$m_{\mathrm{f}} = \frac{m_{\mathrm{i}}f_2}{f_1(m_{\mathrm{i}}M+1)+f_2} \tag{2}$$

in which $f_1$ is the flow rate of diluent (aqueous sodium halide solution).

## 3. Results and discussion

According to the McMillan–Mayer theory [22], all the thermodynamic properties of multi-components solutions can be expressed by using a virial expansion in $m$ which relates the non-ideal contributions of any total thermodynamic function to a series of interaction parameters. The thermodynamic procedures used have been previously described in detail [23–25] and only a summary will be given here.

The molar enthalpy change $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ on diluting a solution of non-electrolytic solute from an initial molality $m_{\mathrm{i}}$ to a final molality $m_{\mathrm{f}}$ can be written as

$$\begin{aligned}\Delta_{\mathrm{dil}}H_{\mathrm{m}} &= H_{\mathrm{m}}^{\mathrm{ex,o}}(m_{\mathrm{f}}) - H_{\mathrm{m}}^{\mathrm{ex,o}}(m_{\mathrm{i}}) \\ &= h_2(m_{\mathrm{f}}-m_{\mathrm{i}}) + h_3(m_{\mathrm{f}}^2-m_{\mathrm{i}}^2) \\ &\quad + h_4(m_{\mathrm{f}}^3-m_{\mathrm{i}}^3) + \cdots \end{aligned} \tag{3}$$

where $H_{\mathrm{m}}^{\mathrm{ex,o}}(m_{\mathrm{f}})$ and $H_{\mathrm{m}}^{\mathrm{ex,o}}(m_{\mathrm{i}})$ are the molar excess (relative apparent molar) enthalpies of the solute in the solutions before and after dilution, and $h_2$, $h_3$, $h_4$, etc. are the enthalpic coefficients representing pair-wise and, at least notionally, triplet, quartet and higher order interactions between solvated solute species.

In this paper, the aqueous sodium halide solutions are regarded wholly as "solvents". Tables 1 and 2 give the experimental values ($\Delta_{\mathrm{dil,exp}}H_{\mathrm{m}}$) and the calculated values ($\Delta_{\mathrm{dil,calc}}H_{\mathrm{m}}$) of dilution enthalpies, which were fitted to Eq. (3) by a least-squares procedure, together with the initial and final molality ($m_{\mathrm{i}}$ and $m_{\mathrm{f}}$) of glycine in various aqueous sodium halide solutions.

Table 1
Enthalpies of dilution of glycine in aqueous sodium fluoride solution at 298.15 K

| $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) | $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $b = 0.1003$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.0996 | 45.83 | 45.93 | 0.6001 | 0.3717 | 87.19 | 87.97 |
| 0.2000 | 0.0746 | 57.68 | 57.75 | 0.7991 | 0.3918 | 151.46 | 150.28 |
| 0.2000 | 0.1248 | 34.48 | 34.16 | 0.7991 | 0.4924 | 112.91 | 110.79 |
| 0.3989 | 0.1974 | 84.60 | 85.03 | 0.7991 | 0.2926 | 191.74 | 191.17 |
| 0.3989 | 0.2475 | 63.37 | 63.06 | 1.0051 | 0.4913 | 179.00 | 180.25 |
| 0.3989 | 0.1477 | 107.11 | 107.49 | 1.0051 | 0.3666 | 229.54 | 229.52 |
| 0.6001 | 0.2960 | 118.40 | 119.33 | 1.0051 | 0.6184 | 132.08 | 132.77 |
| 0.6001 | 0.2212 | 151.00 | 151.51 | | | | |
| $b = 0.1504$ mol kg$^{-1}$ | | | | | | | |
| 0.2023 | 0.0992 | 47.68 | 48.05 | 0.6000 | 0.3669 | 86.93 | 85.82 |
| 0.2023 | 0.0741 | 61.23 | 60.31 | 0.7997 | 0.3972 | 138.51 | 138.58 |
| 0.2023 | 0.1247 | 35.37 | 35.80 | 0.7997 | 0.4973 | 102.34 | 100.89 |
| 0.3999 | 0.2007 | 83.30 | 83.17 | 0.7997 | 0.2973 | 176.47 | 178.87 |
| 0.3999 | 0.2506 | 61.83 | 61.22 | 0.9999 | 0.4805 | 166.35 | 166.57 |
| 0.3999 | 0.1505 | 106.67 | 106.13 | 0.9999 | 0.3571 | 212.04 | 213.89 |
| 0.6000 | 0.2912 | 115.58 | 116.77 | 0.9999 | 0.6071 | 122.31 | 121.76 |
| 0.6000 | 0.2170 | 147.32 | 148.76 | | | | |
| $b = 0.3007$ mol kg$^{-1}$ | | | | | | | |
| 0.2026 | 0.0980 | 52.39 | 52.28 | 0.6049 | 0.3650 | 85.73 | 85.66 |
| 0.2026 | 0.0729 | 66.98 | 65.78 | 0.8000 | 0.4037 | 133.49 | 131.02 |
| 0.2026 | 0.1235 | 38.82 | 38.98 | 0.8000 | 0.5038 | 96.26 | 94.45 |
| 0.4000 | 0.2039 | 81.94 | 83.25 | 0.8000 | 0.3035 | 174.41 | 171.23 |
| 0.4000 | 0.2537 | 60.20 | 60.42 | 1.0001 | 0.4716 | 165.26 | 165.83 |
| 0.4000 | 0.1536 | 105.78 | 107.56 | 1.0001 | 0.3490 | 209.41 | 212.46 |
| 0.6049 | 0.2884 | 118.08 | 117.26 | 1.0001 | 0.5985 | 120.82 | 122.48 |
| 0.6049 | 0.2139 | 148.69 | 150.53 | | | | |
| $b = 0.3508$ mol kg$^{-1}$ | | | | | | | |
| 0.1974 | 0.0999 | 53.02 | 52.50 | 0.5975 | 0.3701 | 81.56 | 80.08 |
| 0.1974 | 0.0751 | 68.07 | 67.10 | 0.7999 | 0.3985 | 131.93 | 132.71 |
| 0.1974 | 0.1244 | 38.19 | 38.55 | 0.7999 | 0.2989 | 173.07 | 173.24 |
| 0.3999 | 0.2003 | 85.52 | 86.86 | 0.7999 | 0.4989 | 98.23 | 96.39 |
| 0.3999 | 0.1502 | 110.86 | 112.78 | 0.9990 | 0.4947 | 166.30 | 165.36 |
| 0.3999 | 0.2500 | 61.94 | 62.96 | 0.9990 | 0.3705 | 208.69 | 211.14 |
| 0.5975 | 0.2955 | 113.21 | 111.04 | 0.9990 | 0.6206 | 122.54 | 123.81 |
| 0.5975 | 0.2207 | 145.59 | 145.34 | | | | |
| $b = 0.4510$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.0985 | 54.62 | 54.59 | 0.6009 | 0.3676 | 79.33 | 79.04 |
| 0.2000 | 0.0736 | 70.67 | 69.37 | 0.8195 | 0.4061 | 131.14 | 128.61 |
| 0.2000 | 0.1236 | 39.71 | 40.31 | 0.8195 | 0.5090 | 94.71 | 92.94 |
| 0.4000 | 0.2004 | 85.15 | 85.61 | 0.8195 | 0.3042 | 172.03 | 168.83 |
| 0.4000 | 0.2504 | 62.48 | 61.76 | 0.9998 | 0.4811 | 156.85 | 158.62 |
| 0.4000 | 0.1505 | 110.61 | 111.39 | 0.9998 | 0.3573 | 202.77 | 203.60 |
| 0.6009 | 0.2922 | 107.88 | 109.88 | 0.9998 | 0.6069 | 117.38 | 118.70 |
| 0.6009 | 0.2177 | 141.30 | 143.91 | | | | |
| $b = 0.5121$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.0995 | 56.41 | 56.13 | 0.5996 | 0.3707 | 81.85 | 80.33 |
| 0.2000 | 0.0745 | 72.65 | 71.53 | 0.7992 | 0.3913 | 135.38 | 132.86 |
| 0.2000 | 0.1245 | 41.25 | 41.34 | 0.7992 | 0.2925 | 177.03 | 174.11 |

Table 1 (*Continued*)

| $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) | $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.3999 | 0.1982 | 88.37 | 89.99 | 0.7992 | 0.4923 | 97.74 | 95.89 |
| 0.3999 | 0.1482 | 114.96 | 116.86 | 0.9993 | 0.4853 | 161.40 | 162.90 |
| 0.3999 | 0.2481 | 64.49 | 65.13 | 0.9993 | 0.3612 | 206.77 | 209.39 |
| 0.5996 | 0.2958 | 112.73 | 111.97 | 0.9993 | 0.6110 | 120.44 | 121.66 |
| 0.5996 | 0.2210 | 144.35 | 147.28 | | | | |
| $b = 0.5521$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.0988 | 55.35 | 54.83 | 0.5997 | 0.3676 | 79.89 | 78.34 |
| 0.2000 | 0.0739 | 70.94 | 69.70 | 0.7998 | 0.3944 | 127.73 | 125.30 |
| 0.2000 | 0.1239 | 39.90 | 40.39 | 0.7998 | 0.4949 | 91.76 | 90.01 |
| 0.4000 | 0.1997 | 85.27 | 86.38 | 0.7998 | 0.2947 | 168.66 | 165.38 |
| 0.4000 | 0.2497 | 61.35 | 62.33 | 1.0035 | 0.4827 | 152.75 | 154.45 |
| 0.4000 | 0.1495 | 111.22 | 112.51 | 1.0035 | 0.3590 | 196.56 | 199.29 |
| 0.5997 | 0.2918 | 109.59 | 109.50 | 1.0035 | 0.6102 | 113.38 | 114.45 |
| 0.5997 | 0.2175 | 141.16 | 143.65 | | | | |
| $b = 0.6013$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.1003 | 57.59 | 57.12 | 0.5999 | 0.3707 | 74.57 | 73.20 |
| 0.2000 | 0.0751 | 74.23 | 73.36 | 0.7983 | 0.3882 | 123.28 | 120.96 |
| 0.2000 | 0.1251 | 41.82 | 41.85 | 0.7983 | 0.4888 | 88.65 | 86.98 |
| 0.4000 | 0.1971 | 86.39 | 87.95 | 0.7983 | 0.2884 | 164.01 | 160.92 |
| 0.4000 | 0.2474 | 61.83 | 62.91 | 0.9989 | 0.4857 | 149.65 | 151.30 |
| 0.4000 | 0.1471 | 113.35 | 115.36 | 0.9989 | 0.3619 | 191.75 | 194.17 |
| 0.5999 | 0.2951 | 105.07 | 103.76 | 0.9989 | 0.6116 | 113.24 | 114.37 |
| 0.5999 | 0.2208 | 135.97 | 138.25 | | | | |

Tables 3 and 4 list the coefficients of Eq. (3) which were obtained from least-squares analysis of these results. Since it is difficult to interpret the higher $h$ coefficients, only the enthalpic pair-wise coefficient $h_2$ is discussed here.

Fig. 1 shows the variations of $h_2$ coefficients for glycine with the increasing molalities of aqueous sodium halide solution. There is a relatively good linear relation between the pair-wise coefficients $h_2$ for glycine and the molalities of the aqueous sodium halide solution in which glycine is diluted. The relations were obtained with the method of least-squares as follows:

$$h_2 = -458.22 - 480.92b \quad (\mathrm{Gly{-}NaF{-}H_2O,\ S.D.} = 26.17) \tag{4}$$

$$h_2 = -469.35 + 232.52b \quad (\mathrm{Gly{-}NaI{-}H_2O,\ S.D.} = 17.20) \tag{5}$$

The enthalpic pair-wise interaction coefficients of glycine at infinite dilution obtained from the two linear equations, −458.22 and −469.35 J kg mol$^{-2}$, are in good agreement with the literature values of −465.29 [16], and −472.40 J kg mol$^{-2}$ [18]. From Fig. 1, it can be seen that $h_2$ is negative over the whole molality ranges of salt solutions investigated, and that in aqueous solutions of NaF, the values of $h_2$ increase negatively along with the increase of electrolyte molality; while the values of $h_2$ decrease negatively following increasing NaI molality in aqueous solutions.

For a better understanding of the interactions taking place in aqueous electrolyte solutions, it is necessary to obtain the homogeneous enthalpic pair-wise interaction coefficients of glycine in the electrolyte solutions. These values are the measurement of the interaction energy between a pair of glycine molecules, that takes place with participation of dissociated electrolyte and water molecules. It is generally believed that the interaction of non-electrolyte with electrolyte consists of electrostatic and structural interactions. For the enthalpic functions, the structural interaction consists principally of the partial desolvation of solute and the solvent reorganization in the

Table 2
Enthalpies of dilution of glycine in aqueous sodium iodide solution at 298.15 K

| $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) | $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $b = 0.2020$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.0999 | 38.35 | 38.18 | 0.5999 | 0.2172 | 123.37 | 125.46 |
| 0.2000 | 0.0750 | 48.04 | 48.11 | 0.7993 | 0.3913 | 121.68 | 122.98 |
| 0.2000 | 0.1250 | 28.81 | 28.37 | 0.7993 | 0.4918 | 92.35 | 90.78 |
| 0.3950 | 0.1948 | 68.41 | 69.69 | 0.7993 | 0.2919 | 155.91 | 156.60 |
| 0.3950 | 0.2444 | 51.78 | 51.63 | 1.0000 | 0.4819 | 151.64 | 150.15 |
| 0.3950 | 0.1455 | 86.74 | 88.24 | 1.0000 | 0.6081 | 110.51 | 111.61 |
| 0.5999 | 0.2916 | 100.69 | 98.95 | 1.0000 | 0.3581 | 188.76 | 190.29 |
| 0.5999 | 0.3672 | 74.57 | 73.17 | | | | |
| $b = 0.4071$ mol kg$^{-1}$ | | | | | | | |
| 0.1999 | 0.0991 | 34.51 | 34.44 | 0.6002 | 0.3708 | 64.44 | 64.72 |
| 0.1999 | 0.0744 | 42.92 | 43.26 | 0.8000 | 0.3936 | 112.23 | 110.20 |
| 0.1999 | 0.1243 | 25.73 | 25.61 | 0.8000 | 0.4941 | 82.86 | 81.34 |
| 0.4028 | 0.2000 | 63.73 | 63.01 | 0.8000 | 0.2939 | 139.27 | 140.41 |
| 0.4028 | 0.2506 | 47.02 | 46.58 | 1.0002 | 0.4878 | 132.98 | 134.08 |
| 0.4028 | 0.1497 | 80.00 | 79.91 | 1.0002 | 0.3640 | 169.54 | 169.96 |
| 0.6002 | 0.2955 | 86.09 | 87.69 | 1.0002 | 0.6136 | 99.54 | 99.61 |
| 0.6002 | 0.2207 | 109.73 | 111.52 | | | | |
| $b = 0.5111$ mol kg$^{-1}$ | | | | | | | |
| 0.2001 | 0.0987 | 31.74 | 31.77 | 0.5995 | 0.3684 | 61.04 | 60.23 |
| 0.2001 | 0.0739 | 40.21 | 39.87 | 0.7998 | 0.3961 | 101.42 | 100.39 |
| 0.2001 | 0.1238 | 23.39 | 23.71 | 0.7998 | 0.4961 | 74.86 | 73.87 |
| 0.3995 | 0.1962 | 58.66 | 58.41 | 0.7998 | 0.2963 | 126.12 | 128.29 |
| 0.3995 | 0.1464 | 74.76 | 73.80 | 0.9999 | 0.4791 | 123.90 | 123.52 |
| 0.3995 | 0.2461 | 43.48 | 43.44 | 0.9999 | 0.3562 | 153.58 | 156.59 |
| 0.5995 | 0.2927 | 80.12 | 81.57 | 0.9999 | 0.6066 | 91.73 | 91.21 |
| 0.5995 | 0.2184 | 102.92 | 103.41 | | | | |
| $b = 0.6156$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.1001 | 29.23 | 29.32 | 0.6000 | 0.3719 | 52.35 | 52.12 |
| 0.2000 | 0.0751 | 37.36 | 37.05 | 0.7999 | 0.3899 | 88.50 | 88.95 |
| 0.2000 | 0.1252 | 21.71 | 21.72 | 0.7999 | 0.4906 | 65.89 | 65.33 |
| 0.3998 | 0.1971 | 52.45 | 52.77 | 0.7999 | 0.2908 | 113.66 | 113.89 |
| 0.3998 | 0.2472 | 39.05 | 38.92 | 1.0002 | 0.4884 | 105.93 | 105.75 |
| 0.3998 | 0.1472 | 66.83 | 67.13 | 1.0002 | 0.3652 | 134.27 | 134.90 |
| 0.6000 | 0.2963 | 72.47 | 71.24 | 1.0002 | 0.6154 | 77.73 | 77.86 |
| 0.6000 | 0.2220 | 89.69 | 91.15 | | | | |
| $b = 0.6679$ mol kg$^{-1}$ | | | | | | | |
| 0.1999 | 0.1006 | 28.14 | 28.59 | 0.6002 | 0.3731 | 50.32 | 50.22 |
| 0.1999 | 0.0756 | 36.79 | 36.21 | 0.7991 | 0.3867 | 87.90 | 86.41 |
| 0.1999 | 0.1256 | 21.13 | 21.14 | 0.7991 | 0.4851 | 64.64 | 63.94 |
| 0.4001 | 0.1959 | 52.07 | 51.89 | 0.7991 | 0.2857 | 113.01 | 111.25 |
| 0.4001 | 0.2450 | 38.57 | 38.61 | 0.9991 | 0.4893 | 99.27 | 101.18 |
| 0.4001 | 0.1450 | 66.71 | 66.29 | 0.9991 | 0.3657 | 128.84 | 129.59 |
| 0.6002 | 0.2972 | 67.70 | 68.90 | 0.9991 | 0.6160 | 74.73 | 74.33 |
| 0.6002 | 0.2222 | 86.84 | 88.43 | | | | |
| $b = 0.7214$ mol kg$^{-1}$ | | | | | | | |
| 0.1999 | 0.1006 | 24.33 | 24.62 | 0.6001 | 0.3744 | 47.82 | 48.18 |
| 0.1999 | 0.0755 | 31.39 | 31.01 | 0.7992 | 0.3869 | 83.38 | 84.27 |
| 0.1999 | 0.1256 | 18.07 | 18.30 | 0.7992 | 0.4877 | 63.46 | 62.30 |

Table 2 (*Continued*)

| $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) | $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil,exp}H_m$ (J mol$^{-1}$) | $\Delta_{dil,calc}H_m$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.4002 | 0.1956 | 48.04 | 47.45 | 0.7992 | 0.2879 | 105.44 | 106.82 |
| 0.4002 | 0.2461 | 35.79 | 35.35 | 0.9999 | 0.4934 | 96.65 | 97.40 |
| 0.4002 | 0.1460 | 59.85 | 59.64 | 0.9999 | 0.3687 | 124.82 | 124.66 |
| 0.6001 | 0.2988 | 64.74 | 65.41 | 0.9999 | 0.6198 | 71.74 | 71.22 |
| 0.6001 | 0.2238 | 83.53 | 83.09 | | | | |
| $b = 0.8275$ mol kg$^{-1}$ | | | | | | | |
| 0.2000 | 0.1003 | 25.09 | 24.86 | 0.6004 | 0.3806 | 42.79 | 42.12 |
| 0.2000 | 0.0754 | 31.95 | 31.40 | 0.8003 | 0.3804 | 77.30 | 75.86 |
| 0.2000 | 0.1254 | 18.11 | 18.40 | 0.8003 | 0.4816 | 55.60 | 55.66 |
| 0.3997 | 0.1996 | 43.62 | 44.20 | 0.8003 | 0.2819 | 96.08 | 97.05 |
| 0.3997 | 0.1497 | 55.59 | 56.38 | 0.9999 | 0.5018 | 82.72 | 82.89 |
| 0.3997 | 0.2497 | 32.34 | 32.46 | 0.9999 | 0.3776 | 105.55 | 107.53 |
| 0.6004 | 0.3067 | 58.78 | 57.87 | 0.9999 | 0.6276 | 60.29 | 59.98 |
| 0.6004 | 0.2308 | 74.79 | 75.03 | | | | |
| $b = 1.0429$ mol kg$^{-1}$ | | | | | | | |
| 0.1998 | 0.0982 | 20.27 | 20.37 | 0.6003 | 0.3654 | 33.63 | 33.92 |
| 0.1998 | 0.0733 | 25.72 | 25.69 | 0.8042 | 0.3979 | 54.09 | 53.09 |
| 0.1998 | 0.1232 | 15.21 | 15.15 | 0.8042 | 0.4993 | 38.62 | 38.00 |
| 0.3999 | 0.2004 | 34.92 | 34.39 | 0.8042 | 0.2986 | 69.53 | 69.39 |
| 0.3999 | 0.2505 | 25.54 | 25.09 | 1.0004 | 0.4760 | 60.73 | 61.89 |
| 0.3999 | 0.1506 | 43.51 | 44.11 | 1.0004 | 0.3531 | 79.52 | 80.79 |
| 0.6003 | 0.2893 | 46.03 | 46.68 | 1.0004 | 0.6035 | 45.11 | 44.46 |
| 0.6003 | 0.2151 | 59.20 | 60.07 | | | | |

neighborhood of hydrophobic groups of the non-electrolyte [26,27].

Gallardo et al. [28] have measured the homogeneous enthalpic pair-wise parameters of some amino acids in water and given two modules of the association for the α-amino acids. One is in a side-by-side manner and the other in a head-on-fashion. For glycine, two solvated zwitter ions will take the head-on-fashion to associate strongly mutually with electrostatic interaction and hence render $h_2$ large negative value. The structural interaction, arising from the side group on the α-carbon, will make positive contribution to $h_2$. The exact contribution will depend on the nature of the side-groups involved. Since the apolar part of glycine is shortest, the structural interaction between a pair of glycine molecules is relatively weak. Hence, the values of $h_2$ for glycine in water and aqueous sodium halide solutions are all negative (Fig. 1).

The negative values of $h_2$ generally increase for NaF but decrease for NaI with the increasing molality

Table 3
Homogeneous pair-wise enthalpic interaction coefficients of glycine in aqueous sodium fluoride solution at 298.15 K

| $b$ (mol kg$^{-1}$) | $h_2$ (J kg mol$^{-2}$) | $h_3$ (J kg mol$^{-3}$) | $h_4$ (J kg mol$^{-4}$) | $R^2$ | S.D. |
|---|---|---|---|---|---|
| 0.1003 | −498.8 (3.8) | 148.5 (9.6) | −42.5 (6.7) | 0.9946 | 3.16 |
| 0.1504 | −522.8 (5.3) | 201.3 (13.5) | −56.0 (9.4) | 0.9945 | 4.34 |
| 0.3007 | −593.2 (6.9) | 341.0 (17.6) | −131.3 (12.3) | 0.9946 | 5.60 |
| 0.3508 | −672.6 (7.3) | 506.1 (18.3) | −236.8 (12.7) | 0.9954 | 6.00 |
| 0.4510 | −679.0 (7.4) | 528.0 (18.8) | −238.7 (13.1) | 0.9962 | 5.98 |
| 0.5121 | −706.3 (7.7) | 551.1 (19.6) | −249.4 (13.7) | 0.9961 | 6.33 |
| 0.5521 | −683.7 (7.8) | 528.8 (19.8) | −231.3 (13.8) | 0.9960 | 6.45 |
| 0.6013 | −761.1 (7.6) | 706.4 (19.3) | −338.8 (13.4) | 0.9972 | 6.23 |

Table 4
Homogeneous pair-wise enthalpic interaction coefficients of glycine in aqueous sodium iodide solution at 298.15 K

| $b$ (mol $kg^{-1}$) | $h_2$ (J kg $mol^{-2}$) | $h_3$ (J kg $mol^{-3}$) | $h_4$ (J kg $mol^{-4}$) | $R^2$ | S.D. |
|---|---|---|---|---|---|
| 0.2020 | −423.6 (5.8) | 152.9 (14.9) | −54.1 (10.4) | 0.9838 | 4.77 |
| 0.4071 | −379.2 (4.2) | 136.9 (10.6) | −50.0 (7.4) | 0.9888 | 3.44 |
| 0.5111 | −344.2 (4.1) | 111.0 (10.5) | −33.5 (7.3) | 0.9881 | 3.38 |
| 0.6156 | −334.8 (2.5) | 150.7 (6.3) | −55.6 (4.4) | 0.9967 | 2.04 |
| 0.6679 | −330.4 (3.9) | 154.3 (10.0) | −56.6 (6.9) | 0.9921 | 3.23 |
| 0.7214 | −265.5 (3.2) | 61.2 (8.1) | −10.4 (5.6) | 0.9861 | 2.63 |
| 0.8275 | −283.0 (3.6) | 120.8 (8.9) | −37.0 (6.2) | 0.9922 | 2.94 |
| 1.0429 | −232.7 (2.6) | 115.8 (6.7) | −33.1 (4.7) | 0.9958 | 2.16 |

of salts (Fig. 1), which can be attributed to the influence of salts on the homogeneous enthalpic pair-wise interaction of glycine. Desnoyers et al. [29] have given a general discussion for the structural interaction and suggested that in most cases the net effect of the cosphere overlap on the hydration structure is destructive. Structural interaction makes a fairly large attribution to enthalpic function and sometimes even surpasses the effect of electrostatic interaction and becomes a dominant factor [26,30,31]. We can assume that the interaction of an electrolyte with the polar group of glycine is mainly electrostatic, accompanied by the partial desolvation of the solutes, and that the interaction with the apolar part of glycine is mainly structural [32]. The cation and the anion of electrolyte will undergo electrostatic interactions with the $COO^-$ and $NH_3^+$ groups of glycine, respectively, and make a positive contribution to $h_2$. After the ions of the salts primarily interact with the head groups, it will be hard for other ions to interact with the short extension of hydrocarbon chain of glycine [10]. When considering the variations evident in the sodium halide–glycine systems, we assume that the sodium ion plays an invariant role in each system and that it is the properties of the anions which are responsible for the observed trend. All the anions of halide in the series are structure-breakers except for $F^-$ [33]. As is known, in aqueous solutions, hydration sheaths with defined water molecule order 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 solvent and to assume the order typical for bulk water [13]. The fluoride ion has the smallest radius and the largest surface charging density in the halide ions, therefore, it will exert the largest attractive force on the water molecules which are in the first hydration layer of the fluoride ion. Since the dipole moment of glycine is quite large, the electrostatic interaction between glycine and fluoride ion will be able to destroy the primary hydration structure of fluoride ion and make quite large negative contribution to $h_2$.

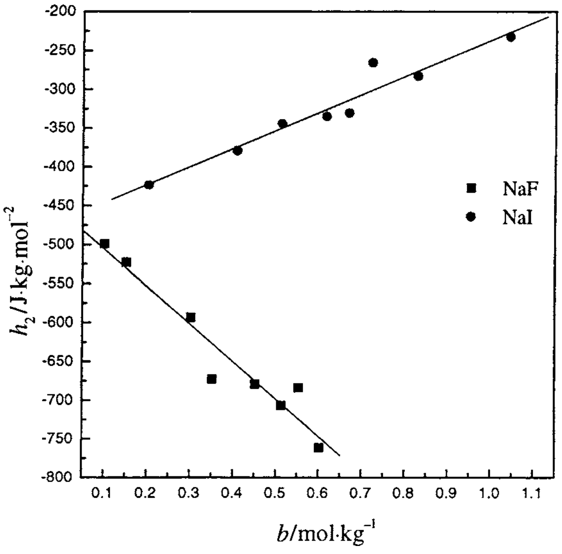

Fig. 1. Variation of homogeneous enthalpic pair-wise interaction coefficients of glycine in aqueous sodium halide solutions at 298.15 K.

The dispersion force of ions upon two amino acid molecules can lead to partial desolvation of solutes, and reorganization of the hydration structure around amino acid. Because this dispersion force is not strong enough to destroy the primary hydration structure of electrolytic ions, the partial desolvation effect can only destroy the secondary hydration layer structure [34] and make a positive contribution to enthalpic interaction parameters. The larger the size of the anion, the more the structure of water will be disrupted and the stronger the dispersion force, the more positive will be the contribution from desolvation [27]. So iodide ion has the strongest dispersion force in halide ions, which results in the more positive contribution to $h_2$ for glycine than that of fluoride ion.

In conclusion, the change of anion ($F^-$ or $I^-$) does exert marked influence on the values of the homogeneous enthalpic pair-wise interaction coefficients of glycine.

## Acknowledgements

The authors are grateful to the National Natural Science Foundation of China and to the National Education Committee of China for support (No. 20073039).

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