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# Enthalpies of dilution of L-cystine in aqueous solutions of sodium hydroxide, potassium hydroxide and hydrochloric acid

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## Abstract

The enthalpies of dilution of L-cystine in solutions of two strong alkalis and one strong acid have been determined by isothermal flow-mix calorimetry at the temperatures 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K. Equations of apparent enthalpies of dilution have been obtained from the experimental data in terms of the improved McMillan–Mayer theory. Enthalpic interaction coefficients, $h_2$, $h_3$, and $h_4$, are obtained and the values of pair-wise enthalpic interaction coefficient, $h_2$, discussed in the light of solute–solute and solute–solvent interactions.

*Keywords:* L-Cystine; Enthalpies of dilution; Microcalorimetry; Enthalpic interaction coefficients

## 1. Introduction

The enthalpy of dilution of amino acids is arguably the most important thermodynamic quantity [1–8], for it includes solute–solute interaction, solute–solvent interaction and all other interactions with other components of the solution. As solubility of L-cystine is low in neutral aqueous media, the enthalpies of dilution of L-cystine in aqueous solutions of hydrochloric acid, sodium hydroxide and potassium hydroxide have been studied. Enthalpic interaction coefficients of L-cystine in the two types of solvents are discussed according to the solute–solute and solute–solvent interactions.

## 2. Experimental

L-Cystine (product of Aldrich, purity, 99%) was dried in an infrared drier until there was no significant change in mass; hydrochloric acid, sodium hydroxide and potassium hydroxide were analytical pure reagents supplied by Shanghai Chemical Reagent Company. All the solid 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 preparation of solutions.

Acid and alkali aqueous solutions, used as solvents and the cystine solutions in them were prepared by mass using a Mettler AE 200 balance precise to ±0.0001 g. The molality of acid or alkali aqueous solution is 1.00 mol kg$^{-1}$. The molality ranges of L-cystine are (0.04–0.15) mol kg$^{-1}$. All the solutions were degassed and used within 12 h.

Solutions of L-cystine and solvent were pumped through the flow-mix vessel of a Thermometric 2277 TAM using LKB VS2–10R MIDI dual channel pumps [9]. The performance of the apparatus was checked by measuring the relative apparent molar enthalpy of glycine in water. The results are in good agreement (±1%) with those reported in literature (Fig. 1) [10].

Thermal effects of the dilute process have been obtained with the method described following:

The liquids passing through tubes A and B of the pump were changed in the following sequence:

1. A, aqueous acid or alkaline solution; B, aqueous acid or alkaline solution—baseline determined.

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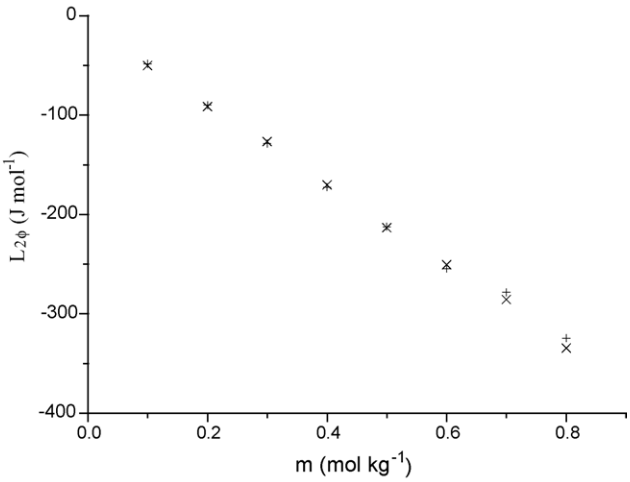


Fig. 1. Relative apparent molar enthalpy of glycine with water at 298.15 K: (+) this work; (×) from literature 20.

2. A, aqueous acid or alkaline solution; B, aqueous L-cystine solution—dilution thermal power determined.
3. A, aqueous acid or alkaline solution; B, aqueous acid or alkaline solution—baseline re-established.

The enthalpies of dilution ($\Delta_{\text{dil}}H_{\text{m}}$) can be obtained from the equation:

$$\Delta_{\text{dil}}H_m = -\frac{P(1+m_{\text{i}}M)}{m_{\text{i}}f_2} \tag{1}$$

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

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

in which $f_1$ is the flow rate of diluents (aqueous acid or alkali solutions).

## 3. Results and discussion

The molar excess enthalpy of a solution with molality $m$ can be written as a power series of $m$ with coefficients $h_n$ by [11,12]:

$$H_m^E = \frac{H^E}{m} = h_2m + h_3m^2 + h_4m^3 + \cdots \tag{3}$$

where $H_m^E$ is the relative apparent molar enthalpy. The enthalpic interaction coefficients $h_n$, which are related to the McMillan–Mayer coefficients, measure the enthalpic interactions, mediated by the solvent, occurring between pairs, triplets, and higher order multiplets of solute species. The molar enthalpy of dilution $\Delta_{\text{dil}}H_m$ in terms of the excess enthalpy at initial molality $m_{\text{i}}$ and final molality $m_{\text{f}}$ is

$$\Delta_{\text{dil}}H_m = H_m^{\text{exp}}(m_{\text{f}}) - H_m^{\text{exp}}(m_{\text{i}}) = h_2(m_{\text{f}}-m_{\text{i}}) + h_3(m_{\text{f}}^2-m_{\text{i}}^2) + h_4(m_{\text{f}}^3-m_{\text{i}}^3) + \cdots \tag{4}$$

where $H_m^{\text{exp}}$ ($m_{\text{f}}$) and $H_m^{\text{exp}}$ ($m_{\text{i}}$) are the molar excess (relative apparent molar) enthalpies of the solute in the solutions before and after dilution.

The pair-wise $h_2$, triplet $h_3$, and higher terms are the enthalpic contributions to the corresponding virial coefficients of the excess Gibbs energy $g_2, g_3, \ldots$ [13]. For the pair-wise coefficient $h_{2:}$

$$h_2 = \left(\frac{\partial(g_2/T)}{\partial(1/T)}\right)_P \tag{5}$$

and

$$h_2 = g_2 + Ts_2 \tag{6}$$

where $s_2$, the entropic pair-wise interaction coefficient, is in the series of virial coefficients of the excess entropy $s_2$, $s_3$, .... Generally, $h_2$, $g_2$ and $s_2$ are all functions of temperature.

In this paper, the aqueous acid and alkali solutions are regarded wholly as “solvents”. Table 1 lists the enthalpic interaction coefficients for each system. Fig. 2 shows the variation of homogeneous enthalpic pair-wise interaction coefficients with temperature for L-cystine in aqueous solutions of sodium hydroxide, potassium hydroxide and hydrochloric acid (Tables 2 and 3).

### 3.1. *Isothermal dilution enthalpies and enthalpic pair-wise coefficients ($h_2$)*

In strong acid or strong alkali solutions, L-cystine exists as a bivalent cation or bivalent anion (Scheme 1).

Only the enthalpic pair-wise interaction coefficient $h_2$ is discussed here. $h_2$ is a measure of the solvent-mediated solute–solute interactions, and, therefore, should be treated

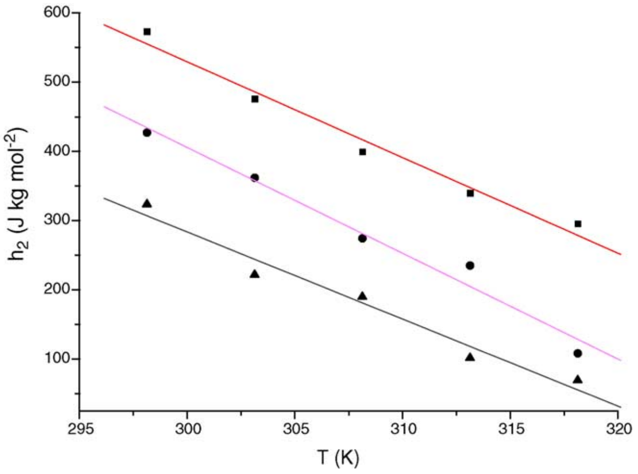


Fig. 2. Variation of homogeneous enthalpic pair-wise interaction coefficients with temperature of L-cystine in aqueous solutions of sodium hydroxide (●), potassium hydroxide (▲) and hydrochloric acid (■).

Table 1
Enthalpic interaction coefficients for L-cystine in aqueous solutions of sodium hydroxide, potassium hydroxide and hydrochloric acid

| Solvent | $h_2$ (J kg mol$^{-2}$) | $h_3$ (J kg$^2$ mol$^{-3}$) | $h_4$ (J kg$^3$ mol$^{-4}$) | $R^2$ | S.D. |
|---|---|---|---|---|---|
| $T$ = 298.15 K | | | | | |
| NaOH | 426.9 (±5.5) | −263.8 (±8.7) | 759.1 (±17.8) | 0.9978 | 0.27 |
| KOH | 323.4 (±4.3) | 388.6 (±5.9) | −515.2 (±6.4) | 0.9967 | 0.35 |
| HCl | 572.9 (±3.5) | −852.7 (±9.8) | 5241.1(±20.9) | 0.9988 | 0.65 |
| $T$ = 303.15 K | | | | | |
| NaOH | 361.6 (±3.5) | −311.5 (±5.5) | 977.6 (±14.5) | 0.9987 | 0.45 |
| KOH | 221.3 (±5.9) | 599.2 (±17.9) | −918.1 (±20.5) | 0.9979 | 0.13 |
| HCl | 475.7 (±8.5) | −147.7 (±5.4) | −926.0 (±18.5) | 0.9960 | 0.68 |
| $T$ = 308.15 K | | | | | |
| NaOH | 273.9 (±3.3) | 180.1 (±4.5) | −296.8 (±9.5) | 0.9992 | 0.28 |
| KOH | 189.6 (±5.9) | 148.9 (±3.8) | 119.8 (±4.9) | 0.9987 | 0.11 |
| HCl | 399.3 (±9.5) | −576.3 (±9.2) | 3756.4 (±20.5) | 0.9984 | 0.36 |
| $T$ = 313.15 K | | | | | |
| NaOH | 234.9 (±6.3) | −112.3 (±4.3) | 358.4 (±8.5) | 0.9982 | 0.22 |
| KOH | 101.4 (±3.5) | 529.1 (±6.5) | −678.4 (±9.5) | 0.9988 | 0.29 |
| HCl | 339.6 (±4.8) | −766.1(±15.1) | 4421.7 (±15.5) | 0.9974 | 0.47 |
| $T$ = 318.15 K | | | | | |
| NaOH | 107.8 (±2.9) | 241.1 (±3.7) | −408.6 (±17.9) | 0.9958 | 0.48 |
| KOH | 68.9 (±1.8) | 661.0 (±15.9) | −1215.5(±19.5) | 0.9987 | 0.25 |
| HCl | 262.8 (±4.5) | −635.1 (±9.8) | 2875.0 (±24.5) | 0.9964 | 0.43 |

Table 2
Enthalpies of dilution for L-cystine in aqueous potassium hydroxide solutions

| $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil}H^{exp}$ (J mol$^{-1}$) | $\Delta_{dil}H^{cal}$ (J mol$^{-1}$) | $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg) | $\Delta_{dil}H^{exp}$ (J mol$^{-1}$) | $\Delta_{dil}H^{cal}$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $T$ = 298.15 K | | | | | | | |
| 0.0760 | 0.0365 | −23.6 | −22.9 | 0.1782 | 0.0844 | −45.4 | −45.4 |
| 0.0918 | 0.0439 | −24.3 | −24.1 | 0.1804 | 0.0853 | −45.9 | −46.0 |
| 0.1093 | 0.0523 | −29.4 | −29.6 | 0.2061 | 0.0976 | −51.9 | −52.0 |
| 0.1269 | 0.0606 | −33.6 | −33.5 | 0.2396 | 0.1130 | −59.8 | −60.1 |
| 0.1455 | 0.0692 | −37.9 | −37.8 | 0.2451 | 0.1158 | −61.4 | −61.3 |
| 0.1611 | 0.0766 | −41.5 | −41.4 | 0.2701 | 0.1274 | −66.8 | −67.2 |
| $T$ = 303.15 K | | | | | | | |
| 0.0561 | 0.0268 | −17.2 | −16.9 | 0.2036 | 0.0967 | −45.1 | −44.9 |
| 0.0789 | 0.0379 | −20.4 | −20.5 | 0.2284 | 0.1079 | −50.1 | −50.1 |
| 0.1073 | 0.05138 | −22.9 | −22.6 | 0.2563 | 0.1215 | −55.5 | −55.5 |
| 0.1171 | 0.0559 | −27.6 | −27.5 | 0.2904 | 0.1367 | −62.1 | −62.1 |
| 0.1389 | 0.0664 | −30.8 | −31.1 | 0.3011 | 0.1419 | −62.6 | −63.1 |
| 0.1746 | 0.0834 | −38.7 | −38.9 | 0.3808 | 0.1551 | −81.9 | −82.5 |
| $T$ = 308.15 K | | | | | | | |
| 0.0540 | 0.0278 | −16.3 | −16.2 | 0.1627 | 0.0835 | −30.1 | −29.8 |
| 0.0829 | 0.0428 | −18.04 | −18.3 | 0.1802 | 0.0922 | −31.8 | −31.8 |
| 0.0914 | 0.0470 | −20.3 | −20.4 | 0.1975 | 0.1011 | −34.2 | −34.3 |
| 0.1131 | 0.0580 | −22.8 | −22.9 | 0.2205 | 0.1127 | −38.9 | −37.8 |
| 0.1294 | 0.0662 | −25.0 | −24.9 | 0.2426 | 0.1233 | −41.6 | −41.5 |
| 0.1447 | 0.0739 | −27.1 | −26.9 | 0.2683 | 0.1369 | −45.7 | −45.8 |
| $T$ = 313.15 K | | | | | | | |
| 0.0633 | 0.0343 | −8.1 | −8.2 | 0.1628 | 0.0873 | −19.0 | −19.1 |
| 0.0790 | 0.0427 | −10.6 | −10.7 | 0.1798 | 0.0963 | −21.4 | −21.2 |
| 0.0966 | 0.0520 | −11.5 | −11.4 | 0.1979 | 0.1057 | −23.8 | −23.6 |
| 0.1144 | 0.0617 | −13.5 | −13.3 | 0.2226 | 0.1193 | −26.6 | −26.7 |
| 0.1302 | 0.0701 | −15.2 | −15.1 | 0.2504 | 0.1337 | −30.4 | −30.4 |
| 0.1467 | 0.0788 | −16.5 | −16.9 | 0.2635 | 0.1406 | −33.7 | −32.9 |
| $T$ = 318.15 K | | | | | | | |
| 0.0694 | 0.0358 | −2.6 | −2.6 | 0.1637 | 0.0839 | −12.2 | −12.2 |
| 0.0840 | 0.0434 | −3.8 | −3.8 | 0.1846 | 0.0945 | −14.4 | −14.5 |
| 0.1017 | 0.0524 | −5.6 | −5.6 | 0.2049 | 0.1046 | −16.4 | −16.6 |
| 0.1154 | 0.0593 | −7.9 | −7.5 | 0.2241 | 0.1142 | −18.5 | −18.5 |
| 0.1313 | 0.0674 | −9.2 | −9.3 | 0.2473 | 0.1256 | −20.9 | −20.7 |
| 0.1480 | 0.0760 | −10.5 | −10.4 | 0.2598 | 0.1319 | −22.3 | −21.6 |

Table 3
Enthalpies of dilution for L-cystine in aqueous hydrochloric acid solutions

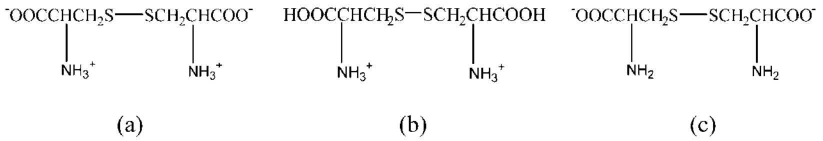
| $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil}H^{exp}$ (J mol$^{-1}$) | $\Delta_{dil}H^{cal}$ (J mol$^{-1}$) | $m_i$ (mol kg$^{-1}$) | $m_f$ (mol kg$^{-1}$) | $\Delta_{dil}H^{exp}$ (J mol$^{-1}$) | $\Delta_{dil}H^{cal}$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $T$ = 298.15 K | | | | | | | |
| 0.0748 | 0.0359 | −11.8 | −11.7 | 0.1887 | 0.0901 | −55.5 | −55.6 |
| 0.0945 | 0.0456 | −17.9 | −17.6 | 0.2072 | 0.0987 | −67.6 | −66.7 |
| 0.1134 | 0.0546 | −22.6 | −22.9 | 0.2172 | 0.1040 | −70.4 | −72.1 |
| 0.1311 | 0.0632 | −29.4 | −29.3 | 0.2354 | 0.1113 | −89.4 | −88.7 |
| 0.1521 | 0.0729 | −38.4 | −37.8 | 0.2579 | 0.1227 | −102.3 | −104.1 |
| 0.1752 | 0.0843 | −46.3 | −46.2 | 0.2726 | 0.1295 | −118.7 | −118.9 |
| $T$ = 303.15 K | | | | | | | |
| 0.0457 | 0.0219 | −0.57 | −0.59 | 0.1804 | 0.0862 | −61.5 | −61.6 |
| 0.0626 | 0.0300 | −8.4 | −8.6 | 0.1847 | 0.0882 | −64.1 | −63.9 |
| 0.0819 | 0.0393 | −12.7 | −12.9 | 0.2026 | 0.0968 | −74.5 | −73.9 |
| 0.1010 | 0.0484 | −22.1 | −22.3 | 0.2390 | 0.1135 | −92.2 | −96.0 |
| 0.1441 | 0.0690 | −39.8 | −42.5 | 0.2561 | 0.1217 | −108.9 | −106.5 |
| 0.1599 | 0.0766 | −54.3 | −50.5 | 0.2920 | 0.1410 | −136.7 | −132.8 |
| $T$ = 308.15 K | | | | | | | |
| 0.0787 | 0.0409 | −6.7 | −6.6 | 0.1820 | 0.0945 | −32.5 | −32.4 |
| 0.0948 | 0.0493 | −9.1 | −9.1 | 0.2015 | 0.1045 | −39.9 | −40.0 |
| 0.1133 | 0.0588 | −12.8 | −13.0 | 0.2227 | 0.1153 | −50.7 | −49.6 |
| 0.1306 | 0.0678 | −17.5 | −17.0 | 0.2458 | 0.1271 | −61.1 | −61.9 |
| 0.1476 | 0.0769 | −21.2 | −21.4 | 0.2615 | 0.1352 | −66.8 | −71.4 |
| 0.1666 | 0.0867 | −26.7 | −27.1 | 0.2693 | 0.1392 | −76.7 | −76.5 |
| $T$ = 313.15 K | | | | | | | |
| 0.0586 | 0.0324 | −5.8 | −5.7 | 0.1519 | 0.0836 | −22.1 | −21.7 |
| 0.0741 | 0.0409 | −7.7 | −7.7 | 0.1691 | 0.0927 | −26.6 | −26.3 |
| 0.0887 | 0.0490 | −9.2364 | −9.7 | 0.1889 | 0.1034 | −33.0 | −32.7 |
| 0.1032 | 0.0570 | −11.5 | −11.9 | 0.2078 | 0.1138 | −38.8 | −39.1 |
| 0.1207 | 0.0665 | −14.8 | −14.9 | 0.2275 | 0.1246 | −48.6 | −48.6 |
| 0.1356 | 0.0747 | −18.5 | −17.9 | 0.2596 | 0.1418 | −66.6 | −66.4 |
| $T$ = 318.15 K | | | | | | | |
| 0.0596 | 0.0324 | −5.2 | −5.1 | 0.1713 | 0.0924 | −17.4 | −17.6 |
| 0.0778 | 0.0422 | −5.6 | −5.7 | 0.1895 | 0.1021 | −21.0 | −21.2 |
| 0.0947 | 0.0513 | −7.3 | −7.3 | 0.2064 | 0.1110 | −25.2 | −25.1 |
| 0.1127 | 0.0610 | −9.5 | −9.2 | 0.2296 | 0.1235 | −31.2 | −31.4 |
| 0.1320 | 0.0714 | −10.9 | −11.5 | 0.2479 | 0.1333 | −37.6 | −37.3 |
| 0.1516 | 0.0818 | −14.9 | −14.3 | 0.2638 | 0.1415 | −43.0 | −43.2 |

as a competition between solute hydration and solute–solute interaction [14–16]. The interaction between two hydrated solute molecules/ions is supposed to occur by the overlap of their hydration cospheres with consequent release of water molecules from these cospheres to the bulk medium [17–19]. The overall effect thus reflects the following three superimposed processes:

1. Direct static repulsion between two bivalent L-cystine ions, which makes the process of the two ions approaching each other an endoergic process.
2. Partial dehydration of the hydration shell of the amino acid ions, which is another endoergic process [20].
3. Interaction between the amino acid and the coexisting ions in the solvents. This interaction weakens the above-mentioned effects for two reasons. Hydration of the coexisting ions makes dehydration of the amino acid ions easier, and coexisting ions directly weaken the electrostatic repulsion between the divalent cystine ions.

The direct interaction between two amino acid ions dominates the overall interaction.

Table 1 shows that, at comparable temperatures, the values of $h_2$ in acid solution are higher than those in alkaline solutions. The hydration of cations is generally stronger than that of anions, the carboxyl group (–COOH) and the protonated amino group (–$NH_3^+$) of L-cystine cation can form more hydrogen bonds with water molecules than the carboxylate group (–$COO^-$) and the amino group (–$NH_2$) of L-cystine anion. Therefore, when two L-cystine ions approach each



(a) (b) (c)

Scheme 1. Ionic forms of L-cystine (a) zwitterion in neutral solution (b) dipositive ion in strong acid solution; (c) dinegative ion in strong alkali solution.

other, the energy absorbed by dehydration of the bivalent L-cystine cation is larger than that absorbed by dehydration of the bivalent anion.

Table 1 also shows that the values of $h_2$ in sodium hydroxide solutions are larger than those in potassium hydroxide. The hydration of $K^+$ is weaker than that of $Na^+$. According to Huang [21], the first order hydration number of $K^+$ and $Na^+$ are about 3 and 4, respectively, and the difference between the second order hydration numbers is larger. So it is understandable that $K^+$ ion can approach L-cystine anion and weaken repulsive force between each pair of such anions more easily than $Na^+$ ion can. Thus, when two L-cystine ions approach each other, the energy absorbed by L-cystine ions in sodium hydroxide solutions to overcome static repulsion is larger than that absorbed by L-cystine ions in potassium hydroxide solutions.

### 3.2. Temperature effect on pair-wise coefficient and entropic pair-wise coefficients ($s_2$)

In both acid and alkaline solutions, the pair-wise enthalpic interaction coefficients $h_2$ decrease when the temperature increases (Fig. 2). According to the first two factors affecting $h_2$, the value of $h_2$ should decline as temperature increases. The reason is that the hydration ability of ions or molecules will decrease when their temperature increases. Therefore, along with the increase of temperature, the hydration ability of L-cystine ions is weakened, the quantity of water molecules in its hydration shell is lessened, and the number of hydrogen bonds between L-cystine ion and water molecules decreased. Thus, when two L-cystine ions approach each other, the energy absorbed to overcome hydrogen bonds in partial dehydration is reduced along with the increase of temperature. On the other hand, along with temperature increases, the quantity of hydrogen bonds in solvent molecules also decreases, which provides more opportunities for the interaction between L-cystine and water molecule and results in reorganization of the hydration structure around the solute molecule. Thereby when two L-cystine ions approach each other, the energy absorbed to overcome interaction between L-cystine and water molecule increases, which results in more positive contribution to $h_2$. Nevertheless, the hydration ability of L-cystine ions plays a dominant role during all the interactions, so the trend of $h_2$ in Fig. 2 is decided by it. In the experimental range of temperature, values of $h_2$ show a linear dependence on temperature, Eq. (6) (Fig. 2). For each system:

$$h_2 = (939.6 \pm 25.8) - (15.10 \pm 0.72)T \quad \left(\text{in } \frac{\text{HCl}}{1\,\text{mol kg}^{-1}},\ R = -0.99\right) \tag{7}$$

$$h_2 = (816.5 \pm 32.2) - (15.29 \pm 0.85)T \quad \left(\text{in } \frac{\text{NaOH}}{1\,\text{mol kg}^{-1}},\ R = -0.98\right) \tag{8}$$

$$h_2 = (621.3 \pm 27.5) - (12.58 \pm 0.93)T \quad \left(\text{in } \frac{\text{KOH}}{1\,\text{mol kg}^{-1}},\ R = -0.98\right) \tag{9}$$

The intercept and the slope of each line denote the pair-wise Gibbs energy interaction coefficient $g_2$ and the pair-wise entropy interaction coefficient $s_2$, respectively. The uncertainties of $g_2$ and $s_2$ were estimated according to three repeated experiments. Eqs. (7)–(9) indicate that the values of pair-wise entropy interaction coefficient are negative, that is to say, pair-wise interaction of L-cystine ions causes an entropy decrease when the ions approach each other. Eqs. (8) and (9) also clearly show the different influences of $Na^+$ and $K^+$ on the pair-wise interaction coefficients.

## 4. Conclusions

The enthalpies of dilution of L-cystine in solutions of two strong alkalis and one strong acid have been determined by isothermal flow–mix microcalerimetry at five temperatures from 298.15 K to 318.15 K. Experimental equations of enthalpies of dilution have been obtained from the experimental data in terms of the McMillan–Mayer theory. Enthalpic interaction coefficients, $h_2$, $h_3$, and $h_4$, are obtained and the values of the pair-wise enthalpic interaction coefficient, $h_2$, are discussed in terms of solute–solute and solute–solvent interactions. Corresponding pair-wise Gibbs free energy interaction coefficients ($g_2$) and entropic coefficients ($s_2$) have been estimated from values of $h_2$ at different temperatures. The data show that pair-wise interaction causes an enthalpy increase and an entropy decrease as distance between two L-cystine ions becomes shorter in aqueous media. The changes of enthalpy and entropy are affected by co-existent ions.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2004.11.026.

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