Enthalpies of Dilution and Enthalpies of Mixing of α-Amino Acids + Pyridine and α-Amino Acids + Methylpyridine in Aqueous Solutions at 298.15 K

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The enthalpies of mixing of aqueous solutions have been determined for glycine and L-alanine with pyridine and methylpyridine by flow microcalorimetry at 298.15 K. In addition, the enthalpies of dilution at 298.15 K of aqueous solutions containing glycine, L-alanine, pyridine, and methylpyridine have been obtained, respectively. These data have been analyzed using the McMillan−Mayer theory, and heterotactic interaction coefficients are given for the interaction of glycine and L-alanine with pyridine and methylpyridine, among which the enthalpic pairwise interaction coefficients, h_{xy}, are discussed in terms of solute−solute interaction and substituent effects.

Introduction

In recent years there has been considerable interest in the thermodynamic properties of aqueous solutions of low molecular weight solutes. The main objective of these studies is to investigate the solute−solute interactions in such solutions. Much of the current interest in this area arises because the results obtained can be of considerable benefit in increasing our understanding of aqueous solutions of complex biological molecules.[1]

Amino acids are considered to be the model compounds for specific aspects of the complex proteins in aqueous solutions, as these small solutes incorporate some of the structural features found in globular proteins.[2] Organic solvents affect strongly the solubility and denaturalization of proteins, and enzyme activities.[3] Until now many studies have been done extensively on aqueous amino acid systems,[4−7] but few have been done in binary mixtures of organic solvent and water.[8−10] Pyridine and its derivatives are an important category of aromatic compound. They have attracted some attention because many alkaloids and important natural products contain a pyridine ring or hydrogenized pyridine ring structure.[11] Methylpyridine, generally called picoline, is a kind of compound of the most significance among the derivatives of pyridine. They are all very important organic synthesis materials, applied in the fields of medicine, pesticide, and polymer chemistry.

As an extension to our previous study,[2,12−14] we report here the enthalpies of mixing at 298.15 K of aqueous solutions of glycine and L-alanine and aqueous solutions of pyridine and methylpyridine, respectively, and their enthalpies of dilution. Glycine is the simplest amino acid in nature. L-Alanine has been chosen because, according to previous studies, it has a very small effect on water structure, so it can be considered almost "neutral", due to the compensation between hydrophobic hydration effects and charge−water interactions. Thus, it is plausible to expect that changes in solvent structure must be reflected in important changes in the behavior of the solute in the mixed solvent.[15] Besides, L-alanine is considered as the typical representative of the amino acids with nonpolar side groups.

In this paper, the heterotactic enthalpic interaction coefficients of glycine and L-alanine with pyridine and methylpyridine isomers in aqueous solutions have been obtained on the basis of the measurements of enthalpies of dilution and mixing. The major intention of this paper is to study the influence of the changes in the structures of amino acids, pyridine, and methylpyridine isomers on the solute−solute interactions.

Materials and Methods

Glycine and L-alanine (biochemical reagent, >99.0%, from Shanghai Chem. Co.) were purified by the method indicated in the literature.[14] Pyridine and methylpyridine (analytical reagents, >99.0%, from Shanghai Chem. Co.) were used without any pretreatment. The water used in the experiments was deionized, twice distilled, and degassed. The solutions were degassed and used within 12 h after preparation to minimize decomposition due to bacterial contamination. Both the aqueous α-amino acid solutions and the aqueous pyridine and methylpyridine solutions were prepared by mass with a Mettler AE 200 balance with a precision of ±0.0001 g. The enthalpies of dilution and mixing were measured with an LKB-2277 bioactivity monitor. All measurements were carried out at (298.15 ± 0.01) K. Errors in the determinations of the molar enthalpies of dilution and mixing were estimated to be <1%.

The solutions were pumped through the mixing-flow vessel of the calorimeter using two LKB-2132 microperpex peristaltic pumps. The variation in flow rates was less than 0.1% both before and after a complete dilution or mixing experiment. The flow rates were determined by weighing

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the masses of the liquids passing through the pumps within 8 min. The liquids passing through pumps A and B were changed in the following sequence:

1. $A_{water} + B_{water}$ baseline determined
2. $A_x + B_{water}$ $\Delta H_{dil}(x)$
3. $A_x + B_y$ ΔH_{mix}
4. $A_{water} + B_y$ $\Delta H_{dil}(y)$
5. $A_{water} + B_{water}$ re-establish baseline.

Each dilution and mixing experiment was repeated three times, and the average of three measured values was given.

The thermodynamics formalism used to treat the enthalpies of dilution is based on the excess enthalpy concept.[16,17] The excess enthalpy $H^E(m_x,m_y)$ of a ternary solution containing the solutes x and y can be expressed in terms of a virial expansion of the molalities:

$$H^E(m_x,m_y)/w_1 = H(m_x,m_y)/w_1 - h^*_w - m_x H^\infty_{x,m} - m_y H^\infty_{y,m} = h_{xx}m_x^2 + 2h_{xy}m_x m_y + h_{yy}m_y^2 + h_{xxx}m_x^3 + 3h_{xxy}m_x^2 m_y + 3h_{xyy}m_x m_y^2 + h_{yyy}m_y^3 + \ldots \quad (1)$$

where $H^E(m_x,m_y)/w_1$ is the excess enthalpy of a solution containing 1 kg of water, m_x mol of x, and m_y mol of y, $H(m_x,m_y)$ is the absolute enthalpy of the solution, h^*_w is the standard enthalpy of 1 kg of pure water, and $H^\infty_{x,m}$ and $H^\infty_{y,m}$ are the limiting partial molar enthalpies of species x and y, respectively. The h_{ij} and h_{ijk} terms are enthalpic virial coefficients representing interactions between the subscripted species. To evaluate these coefficients, the excess enthalpies of the binary solutions must be known. Introducing an auxiliary function ΔH^*, defined as

$$\Delta H^* = \Delta H_{mix} - \Delta H_{dil}(x) - \Delta H_{dil}(y) = H^E(m_x,m_y) - H^E(m_x) - H^E(m_y) \quad (2)$$

and combining eq 1 and 2, it follows that

$$\Delta H^*/w_1 = 2h_{xy}m_x m_y + 3h_{xxy}m_x{}^2 m_y + 3h_{xyy}m_x m_y{}^2 + \ldots \quad (3)$$

For the dilution of a solution of initial molality $m_{x,i}$ to give a solution of final molality m_x, the molar enthalpy of dilution ΔH_{dil} is given by measuring the thermal power P and the flow rates of the solution and solvent (f_A and f_B):

$$\Delta H_{dil} = P/(f_A + f_B - m_{x,i}M_x f_A) \quad (4)$$

$$m_x = m_{x,i}f_A/[f_B(m_{x,i}M_x + 1) + f_A] \quad (5)$$

in which M_x is the molar mass of solute.

The enthalpy of mixing ΔH_{mix} of aqueous x solution and aqueous y solution is calculated from the equation

$$\Delta H_{mix} = P^*/(f_x + f_y - m_{x,i}M_x f_x - m_{y,i}M_y f_y) \quad (6)$$

where P^* is the mixing thermal power; f_x and f_y are the flow rates of solutions x and y, respectively; and $m_{x,i}$ and $m_{y,i}$ are the initial molalities of the two kinds of aqueous solutions before mixing.

Experimental Results and Discussion

The experimental values of enthalpies of dilution and mixing of aqueous α-amino acid solutions (x) and pyridine and methylpyridine isomer (y) solutions together with the initial and final molalities are given in Table 1. The values of the auxiliary function ΔH^* introduced can be obtained according to eq 2. The results have been fitted to eq 3 using the least-squares procedure.

Table 2 shows the heterotactic enthalpic interaction coefficients obtained. Since the interpretation of a triplet interaction coefficient is complicated by the fact that it also contains pairwise interaction contributions,[18,19] our attention will be focused on the enthalpic pairwise interaction coefficient h_{xy}.

The enthalpic pairwise interaction coefficients, h_{xy}, being a measure of interactions between two molecules, depend to a considerable extent on the interactions between the molecules under investigation and solvent water. The overall effect reflects three superimposed processes:

The first is the direct interaction of the molecules of α-amino acids with pyridine and methylpyridine isomers. The direct interaction comprises three kinds of interactions: the hydrophilic−hydrophilic interaction between the zwitterion part of the α-amino acid molecule and the nitrogen atom (containing two pairs of lone pair electrons, hydrophilic group) of the pyridine ring; the hydrophobic−hydrophilic interaction between the apolar side group of α-amino acids and the nitrogen atom of the pyridine ring and that between the pyridine ring of pyridine and methylpyridine and the zwitterion part of the amino acid molecule; and the hydrophobic−hydrophobic interaction between the apolar side group of α-amino acids and the nonpolar ring of pyridine and its methyl derivatives.

The second is the partial dehydration of the hydration shell of the α-amino acid zwitterion (an endothermic process). The dehydration is caused by mutual penetration of the hydration shells of interacting molecules in the aqueous medium.

The third is the partial dehydration of hydration shells of pyridine and methylpyridine isomer molecules (an endothermic process).

The resulting sign of h_{xy} would be a consequence of the balance between the above effects. The experimentally observed positive values of h_{xy} testify to the predominance of endothermic processes over the effect of direct interaction of the α-amino acid molecules with pyridine and methylpyridine isomer molecules. The discrepancies of h_{xy} are mainly dependent on the differences in the structures of the two interaction molecules.

1. Heterotactic Enthalpic Interaction of the Same Kind of α-Amino Acid with Pyridine and Methylpyridine Isomers in the Aqueous Solutions. Compared to the case of pyridine, one methyl group is inducted for methylpyridine isomers, which leads to stronger hydrophobic−hydrophobic and hydrophobic−hydrophilic interactions (making positive contributions to h_{xy}) between α-amino acids and the isomers than those of α-amino acids and pyridine. Thus, the enthalpic interaction coefficients between α-amino acids and methylpyridine isomers are larger than those of pyridine.

In the case of methylpyridine isomers, the direct interactions between them and α-amino acid molecules are approximately identical with each other in intensity, but there are some differences present in the processes of partial dehydration. A donor inductive effect and superconjugative effect exist (here they are consensus) because of the introduction of a methyl group.[20] When the methyl group is in the o-position, the two effects as above are present simultaneously, and in the m-position, only the former effect exists. While for *p*-methylpyridine, in addition

Table 1. Enthalpies of Dilution and Enthalpies of Mixing for α-Amino Acids (*x*) + Pyridine (*y*) and α-Amino Acids (*x*) + Methylpyridine (*y*) in Aqueous Solutions at 298.15 K

$m_{x,i}$[a] / mol·kg^{-1}	$m_{y,i}$ / mol·kg^{-1}	$m_{x,f}$ / mol·kg^{-1}	$m_{y,f}$ / mol·kg^{-1}	$\Delta H_{dil(x)}/w_1$ / J·kg^{-1}	$\Delta H_{dil(y)}/w_1$ / J·kg^{-1}	$\Delta H_{mix}/w_1$ / J·kg^{-1}	$\Delta H^*/w_1$ / J·kg^{-1}
				Glycine + Pyridine			
0.1000	0.1000	0.0504	0.0493	1.07 (0.01)[b]	−3.54 (0.03)	4.99 (0.05)	7.46
0.1500	0.1500	0.0755	0.0737	2.50 (0.02)	−7.32 (0.07)	7.33 (0.07)	12.15
0.1800	0.1800	0.0905	0.0884	3.58 (0.03)	−10.61 (0.10)	8.66 (0.87)	15.70
0.2000	0.2000	0.1005	0.0981	4.32 (0.04)	−12.70 (0.13)	8.36 (0.84)	16.75
0.2200	0.2200	0.1104	0.1078	5.13 (0.05)	−15.77 (0.16)	9.04 (0.90)	19.68
0.2500	0.2500	0.1254	0.1224	6.65 (0.07)	−19.73 (0.20)	11.13 (0.11)	24.22
0.2800	0.2800	0.1403	0.1369	8.05 (0.08)	−25.43 (0.25)	11.57 (0.12)	28.95
0.3000	0.3000	0.1502	0.1466	9.21 (0.09)	−28.93 (0.29)	12.21 (0.12)	31.93
0.3200	0.3200	0.1601	0.1562	10.24 (0.10)	−33.13 (0.33)	11.54 (0.12)	34.43
0.3500	0.3500	0.1749	0.1707	12.37 (0.12)	−39.62 (0.40)	12.94 (0.13)	40.19
0.3800	0.3800	0.1897	0.1851	14.32 (0.14)	−46.18 (0.46)	12.89 (0.13)	44.75
0.4000	0.4000	0.1995	0.1947	15.80 (0.16)	−51.78 (0.52)	12.88 (0.13)	48.87
0.4200	0.4200	0.2093	0.2043	17.26 (0.17)	−55.12 (0.55)	13.00 (0.13)	50.86
0.4500	0.4500	0.2240	0.2186	20.07 (0.20)	−64.75 (0.65)	12.95 (0.13)	57.63
0.5000	0.5000	0.2485	0.2424	23.93 (0.24)	−81.50 (0.82)	13.11 (0.13)	70.68
				Glycine + 2-Methylpyridine			
0.1000	0.1000	0.0541	0.0453	0.74 (0.01)	−0.47 (0.01)	12.95 (0.13)	12.68
0.1500	0.1500	0.0811	0.0677	2.62 (0.03)	−1.92 (0.02)	20.88 (0.21)	20.17
0.1800	0.1800	0.0972	0.0811	3.61 (0.04)	−3.32 (0.03)	25.86 (0.26)	25.56
0.2000	0.2000	0.1079	0.0901	4.27 (0.04)	−4.83 (0.05)	30.17 (0.30)	30.74
0.2200	0.2200	0.1186	0.0990	5.54 (0.06)	−5.72 (0.06)	33.45 (0.33)	33.62
0.2500	0.2500	0.1347	0.1123	6.99 (0.07)	−8.30 (0.08)	38.59 (0.39)	39.89
0.2800	0.2800	0.1507	0.1256	8.12 (0.08)	−11.80 (0.12)	43.62 (0.44)	47.31
0.3000	0.3000	0.1613	0.1344	9.35 (0.09)	−13.04 (0.13)	47.16 (0.47)	50.86
0.3200	0.3200	0.1719	0.1432	10.87 (0.11)	−15.17 (0.15)	50.63 (0.51)	54.94
0.3500	0.3500	0.1879	0.1564	12.95 (0.13)	−19.69 (0.20)	55.51 (0.56)	62.25
0.3800	0.3800	0.2038	0.1696	14.82 (0.15)	−23.91 (0.24)	60.35 (0.60)	69.43
0.4000	0.4000	0.2144	0.1783	15.80 (0.16)	−27.30 (0.27)	63.87 (0.64)	75.36
0.4200	0.4200	0.2249	0.1871	17.94 (0.18)	−31.04 (0.31)	67.62 (0.68)	80.72
				Glycine + 3-Methylpyridine			
0.1000	0.1000	0.0541	0.0453	0.74 (0.01)	−3.22 (0.03)	5.53 (0.06)	8.00
0.1500	0.1500	0.0811	0.0677	2.62 (0.03)	−7.50 (0.08)	8.25 (0.08)	13.13
0.1800	0.1800	0.0972	0.0811	3.61 (0.04)	−13.09 (0.13)	11.20 (0.11)	20.68
0.2000	0.2000	0.1079	0.0901	4.27 (0.04)	−16.66 (0.17)	11.45 (0.11)	23.85
0.2200	0.2200	0.1186	0.0990	5.54 (0.06)	−19.57 (0.20)	12.00 (0.12)	26.02
0.2500	0.2500	0.1347	0.1123	6.99 (0.07)	−25.38 (0.25)	12.82 (0.13)	31.20
0.2800	0.2800	0.1507	0.1256	8.12 (0.08)	−32.18 (0.32)	12.73 (0.13)	36.80
0.3000	0.3000	0.1613	0.1344	9.35 (0.09)	−36.82 (0.37)	13.16 (0.13)	40.63
0.3200	0.3200	0.1719	0.1432	10.87 (0.11)	−41.40 (0.41)	13.48 (0.13)	44.01
0.3500	0.3500	0.1879	0.1564	12.95 (0.13)	−49.78 (0.50)	13.38 (0.13)	50.21
0.3800	0.3800	0.2038	0.1696	14.82 (0.15)	−57.91 (0.58)	13.66 (0.14)	56.75
0.4000	0.4000	0.2144	0.1783	15.80 (0.16)	−61.89 (0.62)	13.55 (0.14)	59.64
0.4200	0.4200	0.2249	0.1871	17.94 (0.18)	−68.19 (0.68)	14.66 (0.15)	64.91
0.4500	0.4500	0.2407	0.2001	20.05 (0.20)	−78.90 (0.79)	14.97 (0.15)	73.82
0.5000	0.5000	0.2670	0.2218	24.33 (0.24)	−96.26 (0.96)	15.20 (0.15)	87.14
				Glycine + 4-Methylpyridine			
0.1000	0.1000	0.0541	0.0453	0.74 (0.01)	−3.96 (0.04)	8.92 (0.09)	12.13
0.1500	0.1500	0.0811	0.0677	2.62 (0.03)	−8.75 (0.09)	10.29 (0.10)	16.42
0.1800	0.1800	0.0972	0.0811	3.61 (0.04)	−16.18 (0.16)	14.02 (0.14)	26.59
0.2000	0.2000	0.1079	0.0901	4.27 (0.04)	−20.56 (0.21)	14.62 (0.15)	30.92
0.2200	0.2200	0.1186	0.0990	5.54 (0.06)	−24.02 (0.24)	14.99 (0.15)	33.47
0.2500	0.2500	0.1347	0.1123	6.99 (0.07)	−31.09 (0.31)	15.60 (0.16)	39.70
0.2800	0.2800	0.1507	0.1256	8.12 (0.08)	−39.02 (0.39)	15.11 (0.15)	46.01
0.3000	0.3000	0.1613	0.1344	9.35 (0.09)	−44.30 (0.44)	15.38 (0.15)	50.33
0.3200	0.3200	0.1719	0.1432	10.87 (0.11)	−50.63 (0.51)	16.00 (0.16)	55.76
0.3500	0.3500	0.1879	0.1564	12.95 (0.13)	−59.65 (0.60)	15.19 (0.15)	61.90
0.3800	0.3800	0.2038	0.1696	14.82 (0.15)	−70.60 (0.71)	15.25 (0.15)	71.03
0.4000	0.4000	0.2144	0.1783	15.80 (0.16)	−73.54 (0.74)	14.14 (0.14)	71.87
0.4200	0.4200	0.2249	0.1871	17.94 (0.18)	−82.10 (0.82)	14.81 (0.15)	78.96
0.4500	0.4500	0.2407	0.2001	20.05 (0.20)	−93.88 (0.94)	16.67 (0.17)	90.50
0.5000	0.5000	0.2670	0.2218	24.33 (0.24)	−114.02 (1.10).	15.51 (0.16)	105.21
				L-Alanine + Pyridine			
0.1000	0.1000	0.0504	0.0493	−0.73 (0.01)	−3.54 (0.04)	3.34 (0.03)	7.62
0.1500	0.1500	0.0754	0.0737	−1.22 (0.01)	−7.32 (0.07)	5.44 (0.05)	13.97
0.1800	0.1800	0.0903	0.0884	−1.69 (0.02)	−10.61 (0.11)	5.22 (0.05)	17.53
0.2000	0.2000	0.1003	0.0981	−2.17 (0.02)	−12.70 (0.13)	5.41 (0.05)	20.28
0.2200	0.2200	0.1102	0.1078	−2.54 (0.03)	−15.77 (0.16)	5.24 (0.05)	23.55
0.2500	0.2500	0.1251	0.1224	−3.24 (0.03)	−19.73 (0.20)	5.49 (0.05)	28.46
0.2800	0.2800	0.1399	0.1369	−3.99 (0.04)	−25.43 (0.25)	5.25 (0.05)	34.67
0.3000	0.3000	0.1498	0.1466	−4.65 (0.05)	−28.93 (0.29)	5.17 (0.05)	38.75
0.3200	0.3200	0.1596	0.1562	−5.33 (0.05)	−33.13 (0.33)	4.77 (0.05)	43.24

Table 1. (Continued)

$m_{x,i}$[a] / mol·kg^{-1}	$m_{y,i}$ / mol·kg^{-1}	$m_{x,f}$ / mol·kg^{-1}	$m_{y,f}$ / mol·kg^{-1}	$\Delta H_{dil(x)}/w_1$ / J·kg^{-1}	$\Delta H_{dil(y)}/w_1$ / J·kg^{-1}	$\Delta H_{mix}/w_1$ / J·kg^{-1}	$\Delta H^*/w_1$ / J·kg^{-1}
			L-Alanine + Pyridine (Continued)				
0.3500	0.3500	0.1743	0.1707	−6.50 (0.07)	−39.62 (0.40)	3.54 (0.04)	49.66
0.3800	0.3800	0.1890	0.1851	−7.54 (0.08)	−46.18 (0.46)	2.67 (0.03)	56.39
0.4000	0.4000	0.1988	0.1947	−8.42 (0.08)	−51.78 (0.52)	2.96 (0.03)	63.16
0.4200	0.4200	0.2086	0.2043	−9.61 (0.10)	−55.12 (0.55)	2.04 (0.02)	66.77
0.4500	0.4500	0.2232	0.2186	−11.04 (0.11)	−64.75 (0.65)	0.98 (0.01)	76.77
0.5000	0.5000	0.2475	0.2424	−13.36 (0.13)	−81.50 (0.82)	−0.42 (0.01)	94.44
			L-Alanine + 2-Methylpyridine				
0.1000	0.1000	0.0541	0.0453	−0.44 (0.01)	−0.47 (0.01)	10.97 (0.11)	11.88
0.1500	0.1500	0.0810	0.0677	−1.43 (0.01)	−1.92 (0.02)	13.03 (0.13)	16.38
0.1800	0.1800	0.0971	0.0811	−2.08 (0.02)	−3.32 (0.03)	20.99 (0.21)	26.40
0.2000	0.2000	0.1078	0.0901	−2.27 (0.02)	−4.83 (0.05)	24.61 (0.25)	31.72
0.2200	0.2200	0.1185	0.0990	−2.67 (0.03)	−5.72 (0.06)	27.67 (0.28)	36.06
0.2500	0.2500	0.1344	0.1123	−3.13 (0.03)	−8.30 (0.08)	31.20 (0.31)	42.62
0.2800	0.2800	0.1504	0.1256	−3.89 (0.04)	−11.80 (0.12)	35.60 (0.36)	51.30
0.3000	0.3000	0.1610	0.1344	−5.35 (0.05)	−13.04 (0.13)	37.86 (0.38)	56.25
0.3200	0.3200	0.1716	0.1432	−5.76 (0.06)	−15.17 (0.15)	40.55 (0.41)	61.49
0.3500	0.3500	0.1875	0.1564	−6.49 (0.06)	−19.69 (0.20)	43.79 (0.44)	69.97
0.3800	0.3800	0.2033	0.1696	−8.20 (0.08)	−23.91 (0.24)	47.41 (0.47)	79.52
0.4000	0.4000	0.2138	0.1783	−8.38 (0.08)	−27.30 (0.27)	50.57 (0.51)	86.25
0.4200	0.4200	0.2243	0.1871	−9.55 (0.10)	−31.04 (0.31)	52.03 (0.52)	92.62
			L-Alanine + 3-Methylpyridine				
0.1000	0.1000	0.0541	0.0453	−0.44 (0.01)	−3.22 (0.03)	4.08 (0.04)	7.75
0.1500	0.1500	0.0810	0.0677	−1.43 (0.01)	−7.50 (0.08)	5.95 (0.06)	14.88
0.1800	0.1800	0.0971	0.0811	−2.08 (0.02)	−13.09 (0.13)	7.58 (0.08)	22.75
0.2000	0.2000	0.1078	0.0901	−2.27 (0.02)	−16.66 (0.17)	7.90 (0.08)	26.84
0.2200	0.2200	0.1185	0.0990	−2.67 (0.03)	−19.57 (0.20)	7.69 (0.08)	29.93
0.2500	0.2500	0.1344	0.1123	−3.13 (0.03)	−25.38 (0.25)	7.98 (0.08)	36.48
0.2800	0.2800	0.1504	0.1256	−3.89 (0.04)	−32.18 (0.32)	7.20 (0.07)	43.27
0.3000	0.3000	0.1610	0.1344	−5.35 (0.05)	−36.82 (0.37)	6.78 (0.07)	48.95
0.3200	0.3200	0.1716	0.1432	−5.76 (0.06)	−41.40 (0.41)	7.64 (0.08)	54.80
0.3500	0.3500	0.1875	0.1564	−6.49 (0.06)	−49.78 (0.50)	5.96 (0.06)	62.23
0.3800	0.3800	0.2033	0.1696	−8.20 (0.08)	−57.91 (0.58)	5.46 (0.05)	71.57
0.4000	0.4000	0.2138	0.1783	−8.38 (0.08)	−61.89 (0.62)	4.56 (0.05)	74.82
0.4200	0.4200	0.2243	0.1871	−9.55 (0.10)	−68.19 (0.68)	6.39 (0.06)	84.13
0.4500	0.4500	0.2401	0.2001	−10.93 (0.11)	−78.90 (0.79)	4.40 (0.04)	94.23
0.5000	0.5000	0.2662	0.2218	−13.36 (0.13)	−96.26 (0.96)	2.78 (0.03)	112.40
			L-Alanine + 4-Methylpyridine				
0.1000	0.1000	0.0541	0.0453	−0.44 (0.01)	−3.96 (0.04)	6.80 (0.07)	11.20
0.1500	0.1500	0.0810	0.0677	−1.43 (0.01)	−8.75 (0.08)	8.15 (0.08)	18.33
0.1800	0.1800	0.0971	0.0811	−2.08 (0.02)	−16.18 (0.16)	10.34 (0.10)	28.60
0.2000	0.2000	0.1078	0.0901	−2.27 (0.02)	−20.56 (0.21)	10.66 (0.11)	33.50
0.2200	0.2200	0.1185	0.0990	−2.67 (0.03)	−24.02 (0.24)	10.18 (0.10)	36.87
0.2500	0.2500	0.1344	0.1123	−3.13 (0.03)	−31.09 (0.31)	10.16 (0.10)	44.38
0.2800	0.2800	0.1504	0.1256	−3.89 (0.04)	−39.02 (0.39)	9.78 (0.10)	52.70
0.3000	0.3000	0.1610	0.1344	−5.35 (0.05)	−44.30 (0.44)	9.15 (0.09)	58.80
0.3200	0.3200	0.1716	0.1432	−5.76 (0.06)	−50.63 (0.51)	9.27 (0.09)	65.66
0.3500	0.3500	0.1875	0.1564	−6.49 (0.06)	−59.65 (0.60)	7.76 (0.08)	73.90
0.3800	0.3800	0.2033	0.1696	−8.20 (0.08)	−70.60 (0.71)	7.17 (0.07)	85.97
0.4000	0.4000	0.2138	0.1783	−8.38 (0.08)	−73.54 (0.74)	5.70 (0.06)	87.62
0.4200	0.4200	0.2243	0.1871	−9.55 (0.10)	−82.10 (0.82)	5.52 (0.06)	97.17
0.4500	0.4500	0.2401	0.2001	−10.93 (0.11)	−93.88 (0.94)	5.86 (0.06)	110.67
0.5000	0.5000	0.2662	0.2218	−13.36 (0.13)	−114.02 (1.14)	3.33 (0.03)	130.72

[a] $m_{x,i}$ and $m_{y,i}$ are the initial molalities of solutes x and y; $m_{x,f}$ and $m_{y,f}$ are the final molalities of solutes x and y. [b] The values in parentheses are the experimental errors.

Table 2. Heterotactic Enthalpic Interaction Coefficients for α-Amino Acids with Pyridine and Methylpyridine in Aqueous Solutions at 298.15 K[a]

solutes $x + y$	S	h_{xy} / J·kg·mol^{-2}	$10^{-4}h_{xxy}$ / J·kg^2·mol^{-3}	$10^{-4}h_{xyy}$ / /J·kg^2·mol^{-3}	SD	cr / mol·kg^{-1}
glycine + pyridine	2.49	1147.4 (151.7)	105.7 (33.9)	−105.6 (34.7)	0.69	0.10−0.50
glycine + 2-methylpyridine	4.15	2149.5 (192.7)	−39.7 (9.6)	47.6 (11.7)	0.50	0.10−0.42
glycine + 3-methylpyridine	0.57	1869.1 (188.1)	33.5 (6.9)	−40.7 (8.4)	0.85	0.10−0.50
glycine + 4-methylpyridine	2.38	2270.0 (365.4)	39.9 (13.4)	−48.5 (16.2)	1.64	0.10−0.50
L-alanine + pyridine	2.42	1268.2 (151.7)	−80.3 (19.3)	81.7 (19.6)	0.54	0.10−0.42
L-alanine + 2-methylpyridine	1.72	2176.2 (495.9)	−46.5 (40.8)	56.2 (49.1)	1.29	0.10−0.50
L-alanine + 3-methylpyridine	−0.07	1956.3 (221.6)	45.8 (13.4)	−55.3 (16.1)	0.99	0.10−0.50
L-alanine + 4-methylpyridine	1.12	2412.9 (344.3)	59.7 (20.8)	−72.0 (25.0)	1.54	0.10−0.50

[a] S = intercept of regression; SD = standard deviation; cr = concentration range.

to the above two effects, there also exists a steric effect, which can weaken the conjugative effect of the substituent. So, the charge densities on the pyridine rings are in the sequence as follows: 4-methylpyridine > 2-methylpyridine

>3-methylpyridine. Because the desolvation of methylpyridine isomers will become increasingly easy as the charge density decreases, its positive contributions made to h_{xy} will decrease in the same sequence as above. So, values of h_{xy} for α-amino acid and methylpyridine decrease in the following order: h_{xy}(4-methylpyridine) > h_{xy}(2-methylpyridine)> h_{xy}(3-methylpyridine).

2. Heterotactic Enthalpic Interactions of Different Kinds of α-Amino Acids with Pyridine and Methylpyridine in the Aqueous Solutions. Similarly, if we consider the amino acid series, then the discrepancies of h_{xy} are mainly ascribed to the differences in the structures of amino acids.

Glycine is the simplest amino acid with the smallest hydrocarbon backbone. The hydrocarbon backbone of L-alanine has one $-CH_2$ group more than glycine. Thus, for L-alanine there are two more interaction terms (both make positive contributions to h_{xy}) than there are for glycine: the hydrophobic−hydrophobic interaction and the hydrophobic−hydrophilic interaction between the methylene group of L-alanine and the hydrophobic part and the hydrophilic part of the pyridine ring, respectively. Therefore, the magnitudes of h_{xy} of the two kinds of amino acids studied with pyridine and methylpyridine are in the following order: h_{xy}(L-alanine) > h_{xy}(glycine).

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