Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 443–454

ENTHALPIC INTERACTION BETWEEN α-AMINO ACIDS AND PYRIDINE AND METHYLPYRIDINE IN AQUEOUS SOLUTIONS

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(Received June 16, 2003; in revised form November 11, 2003)

Abstract

Enthalpies of dilution of aqueous *L*-serine, pyridine and methylpyridine solutions and their enthalpies of mixing have been determined by a mixing-flow microcalorimeter at 298.15 K. The data have been analyzed in terms of McMillan–Mayer formalism to fit to virial polynomials from which the heterotactic enthalpic pairwise interaction coefficients, h_{xy}, between *L*-serine and pyridine and methylpyridine isomers have been evaluated. The results obtained in the present paper are compared with those reported in the earlier paper about glycine and *L*-alanine in the same organic solvent aqueous solutions, giving a global insight of the interaction mechanism between the α-amino acids and pyridine and methylpyridine from the point of view of solute–solute interactions and substituent effects of methyl groups introduced into the pyridine ring.

Keywords: α-amino acids, aqueous solutions, heterotactic enthalpic pairwise interaction coefficients, methylpyridine, pyridine

Introduction

There is currently a considerable amount of interest in the 'non-bonding' solute–solute interactions which occur in aqueous solutions containing amino acids and other components in cell fluids or compounds with the same functional groups as those existing in biomolecules of living organism [1–6]. The principal reasons for studying such systems are directed towards problems in protein molecular biology, in particular the energetic factors controlling protein folding and assembly and interaction of substrates with the active sites of enzymes.

Until now many studies have been done extensively on aqueous amino acid systems [7–10], but few in binary mixtures of organic solvent and water [11–13]. As an

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

extension to our previous study [14–17], the present work reports the results of calorimetric measurements of the mixing enthalpies of *L*-serine aqueous solutions and aqueous solutions of pyridine and methylpyridine, respectively, and their dilution enthalpies at 298.15 K. These results serve as a basis for calculations the enthalpic coefficients of interactions between *L*-serine and pyridine and methylpyridine isomers in aqueous solutions, according to McMillan–Mayer's model [18]. To gain a further understanding of the interaction mechanism in the aqueous solutions between α-amino acids and pyridine and its methyl derivatives, we have compared the interaction behaviors of *L*-serine with pyridine and methylpyridine obtained in this work with those of glycine and *L*-alanine with pyridine and its methyl derivatives reported previously [17].

L-serine has been chosen as being representative of the α-amino acids with polar side-groups. Pyridine and its derivatives have been chosen because they are an important category of aromatic compound with a six-membered heterocycle. Pyridine is a polar molecule and acts as an electron donor owing to the lone pair of electrons on the nitrogen atom.

Pyridine and its derivatives have caused some attentions because many alkaloids and important natural products contain pyridine ring or hydrogenized pyridine ring structure [19]. Methylpyridine isomers, be generally called as picoline, are a kind of compounds 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.

Experimental

Instrument

The calorimetric system was a 2277-Thermal Activity Monitor produced by Thermometric AB (Thermometric AB is a company in Stockholm, Sweden, working in the field of thermal measurements) [20]. The 2277-Thermal Activity Monitor is an isothermally thermostated 23 L water bath holding up to four independent calorimetric units and operating at working temperatures between 10 to 90°C. With an external water circulator, its stability over 24 h is better than $\pm 10^{-4}$°C. This monitor is very sensitive, the detection limit is 0.15 μW and the baseline stability (over a period of 24 h) is 0.20 μW.

Materials

Biochemical reagent grade *L*-serine was used after recrystallization from methanol–water mixtures and drying in vacuum over P_2O_5 at room temperature for at least 72 h. Analytical reagent grade pyridine and methylpyridine were used without further purification. The water used in the experiments was deionized, twice distilled and degassed. Both the aqueous *L*-serine solutions and the aqueous pyridine and

methylpyridine solutions were prepared by mass by Mettler AE 200 balance with a precision of ±0.0001 g.

The solutions were degassed and used within 12 h after preparation to minimize decomposition due to bacterial contamination.

Methods

The enthalpies of dilution and mixing were measured with the mode of mixing-flow of 2277-Thermal Activity Monitor. All measurements were carried out at 298.15±0.01 K. The solutions were pumped through the mixing-flow vessel of the calorimeter at constant rates by a pair of microperpex peristaltic pumps (LKB-2132). 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 the masses of the liquids passing through pumps within 8 min. Errors in the determinations of the molar enthalpies of dilution and mixing were less than 1%.The liquids passing through pumps A and B were changed in the following sequence:

$A_{water}+B_{water}$	baseline determined
$A_{aqueous\ x\ solution}+B_{water}$	dilution thermal power determined of solute *x*
$A_{aqueous\ x\ solution}+B_{aqueous\ y\ solution}$	mixing thermal power determined
$A_{water}+B_{aqueous\ y\ solution}$	dilution thermal power determined of solute *y*
$A_{water}+B_{water}$	baseline re-established

Results and discussion

The thermodynamics formalism used to treat the enthalpies of dilution is based on the excess enthalpy concept [18]. 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:

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

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 $H_{x,m}^\infty$ and $H_{y,m}^\infty$ 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

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

and combining Eqs (1) and (2), it follows that

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

For the dilution of a solution of initial molality $m_{x,i}$ (kg mol^{-1}) to give a solution of final molality m_x (kg mol^{-1}), the molar enthalpy of dilution ΔH_{dil} (J kg^{-1}) is given by measuring thermal power P (μW) and flow rates of solution and solvent (f_A and f_B, mg s^{-1}):

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

$$m_x = \frac{m_{x,i} f_A}{f_B (m_{x,i} M_x - 1) - f_A} \quad (5)$$

in which M_x is the molar mass of solute (kg mol^{-1}).

The enthalpy of mixing ΔH_{mix} (J kg^{-1}) of aqueous x solution and aqueous y solution is calculated from the equation

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

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

The experimental values of enthalpies of dilution and mixing of aqueous *L*-serine (x) solutions and aqueous pyridine and methylpyridine isomers (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-square procedure. Table 2 shows the heterotactic enthalpic interaction coefficients of the solutions studied in this work and those of the solutions reported previously [17].

The interpretation of the triplet interaction coefficients obscured by the fact that they also contain pairwise interaction terms [21] and for that reason they will not be discussed in this paper. Our attention will be focused on enthalpic pairwise interaction coefficient h_{xy}, which has been verified particularly useful to give information about the interaction mechanism.

The values of heterotactic enthalpic pairwise interaction coefficients reflect the summary process of interaction between the examined molecules in solution proceeding with the participation of water molecules. The process of interaction of two solvated species can be represented as consisting of two successive stages: the partial dehydration of the solutes and the further direct interaction caused by the short-range molecular forces [22, 23]. Thus, in the ternary solutions under investigation (amino acid+pyridine+water and amino acid+methylpyridine+water), the overall effect on h_{xy} reflects the equilibrium among the following superimposed processes.

Table 1 Enthalpies of dilution and enthalpies of mixing for *L*-serine (*x*)+pyridine (*y*) and *L*-serine (*x*)+methylpyridine (*y*) in aqueous solutions at 298.15 K

$m_{x,i}$	$m_{y,i}$	$m_{x,f}$	$m_{y,f}$	$\Delta H_{dil(x)}/w_i$	$\Delta H_{dil(y)}/w_i$	$\Delta H_{mix}/w_i$	$\Delta H^*/w_i$
mol kg^{-1}				J kg^{-1}			
				L-serine+pyridine			
0.1000	0.1000	0.0504	0.0493	1.34 (0.01)	–3.54 (0.04)	10.08 (0,10)	11.78
0.1500	0.1500	0.0754	0.0737	4.34 (0.04)	–7.32 (0.07)	16.23 (0.16)	19.42
0.1800	0.1800	0.0903	0.0884	5.81 (0.06)	–10.61 (0.10)	19.66 (0.20)	24.48
0.2000	0.2000	0.1002	0.0981	7.84 (0.08)	–12.70 (0.13)	22.40 (0.22)	27.67
0.2200	0.2200	0.1101	0.1078	8.76 (0.09)	–15.77 (0.16)	24.24 (0.24)	31.76
0.2500	0.2500	0.1250	0.1224	10.73 (0.11)	–19.73 (0.20)	28.03 (0.28)	36.81
0.2800	0.2800	0.1397	0.1369	12.22 (0.12)	–25.43 (0.25)	30.61 (0.31)	42.87
0.3000	0.3000	0.1496	0.1466	15.05 (0.15)	–28.93 (0.29)	32.75 (0.33)	46.47
0.3200	0.3200	0.1594	0.1562	17.21 (0.17)	–33.13 (0.33)	35.59 (0.36)	52.43
0.3500	0.3500	0.1740	0.1707	19.98 (0.20)	–39.62 (0.40)	38.83 (0.39)	58.93
0.3800	0.3800	0.1887	0.1851	24.15 (0.24)	–46.18 (0.46)	41.95 (0.42)	65.14
0.4000	0.4000	0.1984	0.1947	26.00 (0.26)	–51.78 (0.52)	43.71 (0.44)	69.93
0.4200	0.4200	0.2081	0.2043	30.10 (0.30)	–55.12 (0.55)	46.25 (0.46)	72.75
0.4500	0.4500	0.2226	0.2186	33.10 (0.33)	–64.75 (0.65)	51.38 (0.51)	83.11
0.5000	0.5000	0.2468	0.2424	38.28 (0.38)	–81.50 (0.82)	54.45 (0.54)	97.72

Table 1 Continued

$m_{x,i}$	$m_{y,i}$	$m_{x,f}$	$m_{y,f}$	$\Delta H_{dil(x)}/w_i$	$\Delta H_{dil(y)}/w_i$	$\Delta H_{mix}/w_i$	$\Delta H^*/w_i$
mol kg^{-1}				J kg^{-1}			
L-serine+2-methylpyridine							
0.1000	0.1000	0.0541	0.0453	1.34 (0.01)	–0.47 (0.01)	21.69 (0.22)	20.83
0.1500	0.1500	0.0809	0.0677	4.34 (0.04)	–1.92 (0.02)	34.80 (0.35)	32.37
0.1800	0.1800	0.0969	0.0811	5.81 (0.06)	–3.32 (0.03)	43.32 (0.43)	40.83
0.2000	0.2000	0.1076	0.0901	7.84 (0.08)	–4.83 (0.05)	50.64 (0.51)	47.63
0.2200	0.2200	0.1183	0.0990	8.76 (0.09)	–5.72 (0.06)	56.23 (0.56)	53.19
0.2500	0.2500	0.1342	0.1123	10.73 (0.11)	–8.30 (0.08)	64.66 (0.65)	62.23
0.2800	0.2800	0.1501	0.1256	12.22 (0.12)	–11.80 (0.12)	75.69 (0.76)	75.28
0.3000	0.3000	0.1607	0.1344	15.05 (0.15)	–13.04 (0.13)	80.53 (0.81)	78.53
0.3200	0.3200	0.1712	0.1432	17.21 (0.17)	–15.17 (0.15)	85.68 (0.86)	83.64
0.3500	0.3500	0.1870	0.1564	19.98 (0.20)	–19.69 (0.20)	94.71 (0.95)	94.42
0.3800	0.3800	0.2027	0.1696	24.15 (0.24)	–23.91 (0.24)	104.17 (0.10)	103.92
0.4000	0.4000	0.2132	0.1783	26.00 (0.26)	–27.30 (0.27)	111.26 (0.11)	112.56
0.4200	0.4200	0.2236	0.1871	30.10 (0.30)	–31.04 (0.30)	116.67 (0.12)	117.61

Table 1 Continued

$m_{x,i}$	$m_{y,i}$	$m_{x,f}$	$m_{y,f}$	$\Delta H_{dil(x)}/w_i$	$\Delta H_{dil(y)}/w_i$	$\Delta H_{mix}/w_i$	$\Delta H^*/w_i$
mol kg^{-1}				J kg^{-1}			
			L-serine+3-methylpyridine				
0.1000	0.1000	0.0541	0.0453	1.34 (0.01)	–3.22 (0.03)	14.05 (0.14)	15.94
0.1500	0.1500	0.0809	0.0677	4.34 (0.04)	–7.50 (0.08)	21.38 (0.21)	24.54
0.1800	0.1800	0.0969	0.0811	5.81 (0.06)	–13.09 (0.13)	25.23 (0.25)	32.51
0.2000	0.2000	0.1076	0.0901	7.84 (0.08)	–16.66 (0.17)	28.58 (0.29)	37.40
0.2200	0.2200	0.1183	0.0990	8.76 (0.09)	–19.57 (0.20)	31.11 (0.31)	41.91
0.2500	0.2500	0.1342	0.1123	10.73 (0.11)	–25.38 (0.25)	34.66 (0.35)	49.31
0.2800	0.2800	0.1501	0.1256	12.22 (0.12)	–32.18 (0.32)	39.23 (0.39)	59.19
0.3000	0.3000	0.1607	0.1344	15.05 (0.15)	–36.82 (0.37)	41.37 (0.42)	63.14
0.3200	0.3200	0.1712	0.1432	17.21 (0.17)	–41.40 (0.41)	44.01 (0.44)	68.20
0.3500	0.3500	0.1870	0.1564	19.98 (0.20)	–49.78 (0.50)	46.93 (0.47)	76.73
0.3800	0.3800	0.2027	0.1696	24.15 (0.24)	–57.91 (0.58)	50.01 (0.50)	83.77
0.4000	0.4000	0.2132	0.1783	26.00 (0.26)	–61.89 (0.62)	52.62 (0.53)	88.51
0.4200	0.4200	0.2236	0.1871	30.10 (0.30)	–68.19 (0.68)	55.32 (0.55)	93.41
0.4500	0.4500	0.2393	0.2001	33.10 (0.33)	–78.90 (0.79)	61.04 (0.61)	106.83
0.5000	0.5000	0.2653	0.2218	38.28 (0.38)	–96.26 (0.96)	69.18 (0.69)	127.17

Table 1 Continued

$m_{x,i}$	$m_{y,i}$	$m_{x,f}$	$m_{y,f}$	$\Delta H_{dil(x)}/w_i$	$\Delta H_{dil(y)}/w_i$	$\Delta H_{mix}/w_i$	$\Delta H^*/w_i$
mol kg^{-1}				J kg^{-1}			
L-serine+4-methylpyridine							
0.1000	0.1000	0.0541	0.0453	1.34 (0.01)	–3.96 (0.04)	18.26 (0.18)	20.88
0.1500	0.1500	0.0809	0.0677	4.34 (0.04)	–8.75 (0.09)	27.11 (0.27)	31.51
0.1800	0.1800	0.0969	0.0811	5.81 (0.06)	–16.18 (0.16)	32.03 (0.32)	42.40
0.2000	0.2000	0.1076	0.0901	7.84 (0.08)	–20.56 (0.21)	36.59 (0.37)	49.31
0.2200	0.2200	0.1183	0.0990	8.76 (0.09)	–24.02 (0.24)	38.99 (0.39)	54.25
0.2500	0.2500	0.1342	0.1123	10.73 (0.11)	–31.09 (0.31)	42.85 (0.43)	63.22
0.2800	0.2800	0.1501	0.1256	12.22 (0.12)	–39.02 (0.39)	48.29 (0.48)	75.09
0.3000	0.3000	0.1607	0.1344	15.05 (0.15)	–44.30 (0.44)	49.95 (0.50)	79.20
0.3200	0.3200	0.1712	0.1432	17.21 (0.17)	–50.63 (0.51)	52.90 (0.53)	86.32
0.3500	0.3500	0.1870	0.1564	19.98 (0.20)	–59.65 (0.60)	56.20 (0.56)	95.87
0.3800	0.3800	0.2027	0.1696	24.15 (0.24)	–70.60 (0.71)	59.31 (0.59)	105.76
0.4000	0.4000	0.2132	0.1783	26.00 (0.26)	–73.54 (0.74)	62.01 (0.62)	109.55
0.4200	0.4200	0.2236	0.1871	30.10 (0.30)	–82.10 (0.82)	65.95 (0.66)	117.95
0.4500	0.4500	0.2393	0.2001	33.10 (0.33)	–93.88 (0.94)	71.99 (0.72)	132.76
0.5000	0.5000	0.2653	0.2218	38.28 (0.38)	–114.02 (0.11)	77.66 (0.78)	153.40

* $m_{x,i}$ 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*;
** The values in parentheses are the experimental errors.

Table 2 Heterotactic enthalpic interaction coefficients for various α-amino acids with pyridine and methylpyridine in aqueous solutions at 298.15 K

Solutes, *x*+*y*	h_{xy}/ J kg mol^{-2}	h_{xxy} 10^{-4}/ J kg^2 mol^{-3}	h_{xyy} 10^{-4}/ J kg^2 mol^{-3}	*SD*	*c.r.*/ mol kg^{-1}
Glycine+pyridine[a]	1147	105	–106	0.69	0.10–0.50
L-alanine+pyridine[a]	1268	–80	82	0.54	0.10–0.50
L-serine+pyridine[b]	1769	73	82	0.98	0.10–0.50
Glycine+2-methylpyridine[a]	2150	–40	48	0.50	0.10–0.42
L-alanine+2-methylpyridine[a]	2176	–47	56	1.39	0.10–0.42
L-serine+2-methylpyridine[b]	3192	264	317	1.27	0.10–0.42
Glycine+3-methylpyridine[a]	1869	34	–41	0.85	0.10–0.50
L-alanine+3-methylpyridine[a]	1956	46	–55	0.99	0.10–0.50
L-serine+3-methylpyridine[b]	3128	383	–458	1.19	0.10–0.50
Glycine+4-methylpyridine[a]	2270	40	–49	1.64	0.10–0.50
L-alanine+4-methylpyridine[a]	2413	60	–72	1.54	0.10–0.50
L-serine+4-methylpyridine[b]	3771	418	–501	1.38	0.10–0.50

[a][17]. [b]this work
**SD*: standard derivation; *c.r.*: concentration range

The values of heterotactic enthalpic pairwise interaction coefficients reflect the summary process of interaction between the examined molecules in solution proceeding with the participation of water molecules. The process of interaction of two solvated species can be represented as consisting of two successive stages: the partial dehydration of the solutes and the further direct interaction caused by the short-range molecular forces [22, 23]. Thus, in the ternary solutions under investigation (amino acid+pyridine+water and amino acid+methylpyridine+water), the overall effect on h_{xy} reflects the equilibrium among the following superimposed processes.

- A 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.
- A partial dehydration of hydration shells of pyridine or methylpyridine isomers molecules (an endothermic process).
- Hydrophilic–hydrophilic interaction between the zwitterion center of α-amino acid molecule and the nitrogen atom (hydrophilic group, containing two pairs of lone pair electrons) of pyridine ring (an exothermic process).
- Hydrophobic–hydrophilic interaction of the apolar side-group of α-amino acid with the nitrogen atom of pyridine and methylpyridine and that of the hydroxyl group of α-amino acid with the non-polar group of pyridine and methylpyridine (endothermic processes).
- Hydrophobic–hydrophobic interaction between the apolar side-group of α-amino acid and the non-polar group of pyridine and methylpyridine (an endothermic process).

The positive values of h_{xy} for the ternary solutions under investigation (amino acid+pyridine+water and amino acid+methylpyridine+water) testify to the predominance of endothermic processes over the effect of direct interaction of α-amino acid molecule with pyridine and methylpyridine molecules. A concrete analysis of the tendency showed by Table 2 has been conducted as follows.

1. The heterotactic enthalpic interaction between the same amino acid and pyridine and methylpyridine isomers in the aqueous solutions

In the case of the same amino acid, the discrepancies of h_{xy} are mainly dependent on the differences in the structures of pyridine and methylpyridine. As for glycine and *L*-alanine, we have interpreted in the previous works [17]. The tendency of relative magnitude for h_{xy} between *L*-serine and pyridine and methylpyridine isomers is similar to those of glycine and *L*-alanine. So the interpretation is analogous.

The structure of the isomers of methylpyridine has one methyl group more than pyridine. For methylpyridine there are two more interaction terms (both making positive contributions to h_{xy}) than that for pyridine: hydrophobic–hydrophobic and hydrophobic–hydrophilic interactions between the methyl group of methylpyridine and the hydrophobic part and the hydrophilic part of *L*-serine, respectively. Therefore, the magnitudes of h_{xy} of *L*-serine with pyridine and methylpyridine are in the following order: h_{xy} (methylpyridine)>h_{xy} (pyridine).

In the case of methylpyridine isomers, the direct interactions between them and *L*-serine molecule are approximately identical with each other in intensity, but there are some differences present in the processes of partial dehydration. Donor inductive effect and super-conjugative effect exist (here they are consensus) because of the introduction of methyl group [24]. 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 to the above two effects, there also exists 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 change density decreases, its positive contributions made to h_{xy} will decrease in the same sequence as above. So the values of h_{xy} for *L*-serine and methylpyridine isomers decrease in the order: h_{xy} (4-methylpyridine)>h_{xy} (2-methylpyridine)>h_{xy} (3-methylpyridine).

2. The heterotactic enthalpic interactions between different α-amino acids and pyridine or the same methylpyridine isomer 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 making positive contributions to h_{xy}) than 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 pyridine ring, respectively. The hydrocarbon

backbone of *L*-serine has the same number of $–CH_2$ group as *L*-alanine. However, it has an –OH group in its hydrocarbon backbone. So there increase the two types interactions: the hydrophilic–hydrophobic interaction (make positive contributions to h_{xy}) and the hydrophilic–hydrophilic interaction (make negative contributions to h_{xy}) between the –OH group of serine and the non-polar part and polar one of pyridine ring, respectively, among which the former predominates in the interaction process. Therefore, the magnitudes of h_{xy} between the three amino acids studied and pyridine or methylpyridine are in the following order:

$$h_{xy}\ (L\text{-serine}) > h_{xy}\ (L\text{-alanine}) > h_{xy}\ (\text{glycine}).$$

Conclusions

- The heterotactic enthalpic pairwise interaction coefficients illustrate the differences in the total energetic effects of interactions between the examined α-amino acid molecules with pyridine and methylpyridine isomers molecules, with the participation of water molecules.
- The values of h_{xy} between the three amino acids studied and pyridine and methylpyridine isomers decrease in the order: h_{xy} (*L*-serine)>h_{xy} (*L*-alanine)>h_{xy} (glycine), which can be attributed to the differences in the structures of the three amino acids.
- The relative magnitudes of h_{xy} values between the same amino acids studied and pyridine and methylpyridine isomers are in the following order: h_{xy} (methylpyridine)>h_{xy} (pyridine); h_{xy} (4-methylpyridine)>h_{xy} (2-methylpyridine)>h_{xy} (3-methylpyridine). The results have been interpreted according to solute–solute interactions and substituent effects.

The comparison between the results obtained in the present paper and those reported in the earlier paper may play the role of a parameter that differentiates the hydrophobic/hydrophilic properties of amino acid side chains, and may help in a better understanding of the protein folding process.

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The authors are grateful to the National Natural Science Foundation of China (No.20073039) and to the Natural Science Foundation of Shandong Province of China (No.Q2003B01) for financial support.

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