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Enthalpic interactions of some α-amino acids with glycol in aqueous solutions at 298.15 K

Li Yu[a,*], Shuxia Li[a], Yan Zhu[b], Xianhong Pang[b], Fei Geng[a], Xinping Li[a]

[a] Key Lab for Colloid and Interface Chemistry of Shandong University, Ministry of Education, Jinan 250100, PR China
[b] Department of Chemistry and Chemical Engineering, Taishan Medical College, Taian 271000, PR China

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ABSTRACT

The enthalpies of mixing of six kinds of aqueous amino acid solutions (Glycine, L-alanine, L-valine, L-serine, L-threonine and L-proline) and aqueous glycol solution and their respective enthalpies of dilution have been determined at 298.15 K using flow microcalorimetry. The experimental data have been analyzed according to the McMillan–Mayer formalism to obtain the heterotactic enthalpic interaction coefficients (h_{xy}). h_{xy} coefficients have been discussed from the points of view of solute–solute interactions.

1. Introduction

"Non-bonding" interactions play an important role in biological systems. Studies on various thermodynamic properties of amino acids and simple peptides in aqueous solutions of electrolyte [1,2] or organic substances [3–5] are of current interest due to their importance in the better understanding of the nature and mechanisms taking place in biological cells. Many studies have been done on the effects of polyols on the proteins and it was found that polyols help in stabilizing the native conformations of globular proteins [6–8]. Some authors correlate the stabilizing effect of sugars with the number and position of hydroxyl groups. However, our understanding of the stabilization mechanism of proteins is still incomplete.

To understand the nature of interactions between sugars and proteins in aqueous solutions, it is necessary to study biochemical model compounds owing to the complex structure of the biological micromolecules. Amino acids are basic components of protein molecules and are considered to be the model compounds of protein molecules. The native structure of proteins is governed by weak, non-bonding interactions between the amino acid residues and between these residues and the aqueous environment [9].

Although the polyols under investigation are not found in cellular or extracellular fluids of living organisms, they have wide application in pharmacon and the cosmetics industry. When introduced into a living organism as vehicles for pharmaceuticals or cosmetics, they affect the components of cellular fluids. This has been confirmed by numerous biochemical studies devoted to the interactions between polyols and components of biological cells [10].

In our previous studies, the enthalpies of dilution of amino acids in aqueous solutions of DMF, glucose, sucrose, and urea [11–13], and the enthalpies of mixing of amino acids with chloroethanol, methylpyridine, THF and 1,4-dioxane [14–16] in water were measured by the method of mixing flow microcalorimetry. In order to investigate the interactions between amino acids and glycols, calorimetric measurements of the mixing enthalpies of amino acids and glycols aqueous solutions and their respective dilution enthalpies were carried out. It is well known that the enthalpic interaction coefficients derived from McMillan–Mayer's model [17] can be considered as measures of intermolecular interactions in solution, and depend significantly on variation in solvent. This work is aimed at examining the heterotactic enthalpic interaction coefficients between amino acids and glycol molecules.

2. Experimental

Glycine, L-alanine, L-valine, L-serine, L-threonine and L-proline (BR) were purified by means of recrystallization using twice-distilled water. The purified amino acids were used after drying them in a vacuum desiccator until their weights became constant. Glycol (AR grade, from Shanghai Chem. Co.) used in the experiment

* Corresponding author. Fax: +86 531 8856 4750.
E-mail address: ylmlt@sdu.edu.cn (L. Yu).

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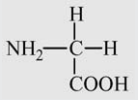
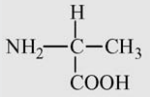
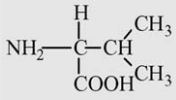
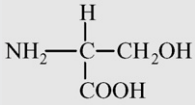
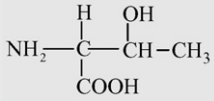
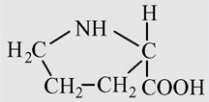
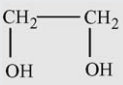
Table 1
Chemical structure of the molecules studied in this work.

Molecule	Chemical structure
Glycine	
L-alanine	
L-valine	
L-serine	
L-threonine	
L-proline	
Glycol	

was purified without further purification. Table 1 gives the chemical structures of glycol and six kinds of amino acid studied in this work.

Deionized water was distilled using a quartz sub-boiling purifier and stored in a CO_2-free atmosphere before use. Both the aqueous amino acid solutions and the aqueous glycol solution were prepared by weight by Mettler AE 200 balance with a precision of ±0.0001 g. All the solutions were degassed and used within 12 h after preparation to minimize decomposition due to bacterial contamination.

The calorimetric measurements were performed by a mixing flow microcalorimeter (2277 Thermal Activity Monitor manufactured in Sweden). All the measurements were carried out at 298.15 ± 0.01 K. The solutions were pumped through the mixing vessel of the calorimeter at constant rates using a pair of LKB-2132 microperpex peristaltic pumps. 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 experiment. The experimental details have been reported in the earlier publications [14–16].

3. Results and discussion

3.1. Enthalpies of dilution and mixing of aqueous amino acid solutions and aqueous glycol solutions at 298.15 K and the relationship between the enthalpies of dilution and mixing and the heterotactic enthalpic interaction coefficients

The measured enthalpies of mixing of aqueous amino acids solutions and aqueous glycol solutions and their respective dilution enthalpies are given in Table 2 as well as the initial and final molalities of the two solutes.

According to the McMillan–Mayer formalism [17], the excess enthalpy of the ternary solution per 1 kg of water can be expressed as a virial expansion of solute molalities using the following equation

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

where $H^{E}(m_x, m_y)/w_1$ and $H(m_x, m_y)/w_1$ represent the excess and the absolute enthalpy, respectively, of a solution containing 1 kg of water, m_x mol of x and m_y mol of y, 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. m_x and m_y are the molalities of the solutes x and y, respectively. h_{ij} and h_{iij} terms are the enthalpic virial coefficients characterizing the contribution of solute–solute interactions between pair, triplet, etc., in a binary solution.

To facilitate the calculation, an auxiliary function ΔH^* is introduced

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

where ΔH_{mix} denotes the mixing enthalpy of the ternary solution, $\Delta H_{dil}(x)$ and $\Delta H_{dil}(y)$ are the dilution enthalpies of the corresponding binary solutions.

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

$$\Delta H_{mix} = \frac{P^*}{f_x + f_y - m_{x,i}M_x f_x - m_{y,i}M_y f_y} \quad (3)$$

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

The dilution enthalpy ΔH_{dil} (J kg^{-1}) is obtained by measuring thermal power P (μW) and flow rates of solution and solvent (f_A and f_B, mg s^{-1}):

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

where M_x is the molar mass of solute (kg mol^{-1}) and $m_{x,i}$ is initial molality (mol kg^{-1}).

The final molality m_x (mol kg^{-1}) may be calculated by using the equation

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

and combining Eqs. (1)and (2)

$$\frac{\Delta H^*}{w_1} = 2h_{xy}m_x m_y + 3h_{xxy}m_x^2 m_y + 3h_{xyy}m_x m_y^2 + \ldots \quad (6)$$

3.2. The physical meaning of h_{xy} coefficient and classification of the interactions between α-amino acids and glycol in aqueous solutions

The pairwise and triplet enthalpic interaction coefficients for the solutions that are obtained by least-squares analysis with Eq. (6) are reported in Table 3.

Since it is difficult to interpret the higher order coefficients due to the large uncertainty in the values, the analysis in the present paper is restricted to the enthalpic pairwise coefficients h_{xy}. They are regarded as a measure of the heat effects when two solute

Table 2
Enthalpies of dilution and mixing of aqueous amino acid solutions and aqueous glycol solutions at 298.15 K.

$m_{x,i}$ (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 + glycol							
0.1000	0.1000	0.0541	0.0453	0.74	−1.07	1.21	1.54
0.1500	0.1500	0.0811	0.0679	2.62	−2.24	2.45	2.08
0.1800	0.1800	0.0972	0.0814	3.61	−3.06	2.67	2.11
0.2000	0.2000	0.1079	0.0904	4.27	−3.76	3.78	3.27
0.2200	0.2200	0.1186	0.0993	5.54	−5.17	4.01	3.64
0.2500	0.2500	0.1347	0.1128	6.99	−6.47	5.26	4.74
0.2800	0.2800	0.1507	0.1262	8.12	−7.68	7.66	7.23
0.3000	0.3000	0.1613	0.1351	9.35	−8.38	8.10	7.14
0.3200	0.3200	0.1719	0.1440	10.87	−9.41	10.00	8.55
0.3500	0.3500	0.1879	0.1574	12.95	−12.16	10.20	9.41
0.3800	0.3800	0.2038	0.1707	14.82	−14.07	12.13	11.38
0.4000	0.4000	0.2144	0.1795	15.80	−15.42	13.46	13.08
0.4200	0.4200	0.2249	0.1884	17.94	−16.57	14.70	13.32
0.4500	0.4500	0.2407	0.2016	20.05	−18.44	16.84	15.24
0.5000	0.5000	0.2670	0.2237	22.72	−23.23	20.33	20.84
L-alanine + glycol							
0.1000	0.1000	0.0541	0.0453	−0.44	−1.07	0.19	1.70
0.1500	0.1500	0.0810	0.0679	−1.43	−2.24	0.17	3.85
0.1800	0.1800	0.0971	0.0814	−2.08	−3.06	2.67	7.81
0.2000	0.2000	0.1078	0.0904	−2.27	−3.76	1.55	7.59
0.2200	0.2200	0.1185	0.0993	−2.67	−5.17	−0.76	7.09
0.2500	0.2500	0.1344	0.1128	−3.13	−6.47	−1.12	8.48
0.2800	0.2800	0.1504	0.1262	−3.89	−7.68	−0.87	10.71
0.3200	0.3200	0.1716	0.1440	−5.76	−9.41	−0.74	14.43
0.3500	0.3500	0.1875	0.1574	−6.49	−12.16	−1.24	17.41
0.3800	0.3800	0.2033	0.1707	−8.20	−14.07	−0.30	21.98
0.4000	0.4000	0.2138	0.1795	−8.38	−15.42	0.03	23.83
0.4200	0.4200	0.2243	0.1884	−9.55	−16.57	−0.22	25.89
0.4500	0.4500	0.2401	0.2016	−10.93	−18.44	−0.19	29.19
0.5000	0.5000	0.2662	0.2237	−14.28	−23.23	−0.16	37.35
L-valine + glycol							
0.1000	0.1000	0.0540	0.0453	−1.19	−1.07	−0.33	2.04
0.1500	0.1500	0.0808	0.0679	−4.42	−2.24	−1.21	5.45
0.1800	0.1800	0.0968	0.0814	−6.39	−3.06	−1.77	7.67
0.2000	0.2000	0.1075	0.0904	−8.03	−3.76	−2.39	9.39
0.2200	0.2200	0.1181	0.0993	−10.24	−5.17	−3.60	11.80
0.2500	0.2500	0.1340	0.1128	−12.55	−6.47	−4.86	14.16
0.2800	0.2800	0.1499	0.1262	−15.67	−7.68	−5.08	18.27
0.3000	0.3000	0.1604	0.1351	−18.07	−8.38	−5.10	21.36
0.3200	0.3200	0.1709	0.1440	−21.60	−9.41	−5.90	25.11
0.3500	0.3500	0.1866	0.1574	−24.16	−12.16	−7.73	28.60
0.3800	0.3800	0.2023	0.1707	−28.14	−14.07	−9.97	32.24
0.4000	0.4000	0.2127	0.1795	−30.07	−15.42	−10.10	35.39
0.4200	0.4200	0.2231	0.1884	−34.48	−16.57	−10.74	40.30
0.4500	0.4500	0.2387	0.2016	−43.14	−18.44	−12.42	49.17
L-serine + glycol							
0.1000	0.1000	0.0541	0.0453	1.01	−1.07	2.30	2.35
0.1500	0.1500	0.0809	0.0679	4.34	−2.24	4.54	2.44
0.1800	0.1800	0.0969	0.0814	5.81	−3.06	5.73	2.97
0.2000	0.2000	0.1076	0.0904	7.84	−3.76	6.83	2.75
0.2200	0.2200	0.1183	0.0993	8.76	−5.17	8.78	5.19
0.2500	0.2500	0.1342	0.1128	10.73	−6.47	12.02	7.77
0.2800	0.2800	0.1501	0.1262	12.22	−7.68	15.27	10.73
0.3000	0.3000	0.1607	0.1351	15.05	−8.38	15.58	8.92
0.3200	0.3200	0.1712	0.1440	17.21	−9.41	18.70	10.90
0.3500	0.3500	0.1870	0.1574	19.98	−12.16	20.79	12.97
0.3800	0.3800	0.2027	0.1707	24.15	−14.07	24.40	14.33
0.4000	0.4000	0.2132	0.1795	26.00	−15.42	26.73	16.15
0.4200	0.4200	0.2236	0.1884	30.10	−16.57	29.49	15.95
0.4500	0.4500	0.2393	0.2016	33.10	−18.44	33.29	18.63
0.5000	0.5000	0.2653	0.2237	36.37	−23.23	39.33	26.19
L-threonine + glycol							
0.1000	0.1000	0.0540	0.0453	0.25	−1.07	1.33	2.15
0.1500	0.1500	0.0808	0.0679	0.82	−2.24	2.25	3.68
0.1800	0.1800	0.0968	0.0814	1.05	−3.06	2.70	4.71
0.2000	0.2000	0.1075	0.0904	1.65	−3.76	3.40	5.51
0.2200	0.2200	0.1181	0.0993	1.71	−5.17	3.53	6.99
0.2500	0.2500	0.1340	0.1128	1.95	−6.47	4.59	9.12
0.2800	0.2800	0.1498	0.1262	2.13	−7.68	5.75	11.30
0.3000	0.3000	0.1604	0.1351	2.53	−8.38	7.11	12.96
0.3200	0.3200	0.1709	0.1440	3.01	−9.41	8.68	15.09
0.3500	0.3500	0.1866	0.1574	2.35	−12.16	9.04	18.85

Table 2 (*Continued*)

$m_{x,i}$ (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})
0.3800	0.3800	0.2022	0.1707	3.19	−14.07	10.77	21.65
0.4000	0.4000	0.2127	0.1795	3.35	−15.42	12.05	24.12
0.4200	0.4200	0.2231	0.1884	3.62	−16.57	12.91	25.86
0.4500	0.4500	0.2386	0.2016	3.09	−18.44	15.15	30.50
0.5000	0.5000	0.2644	0.2237	4.71	−23.23	17.88	36.41
L-proline + glycol							
0.1000	0.1000	0.0540	0.0453	−0.93	−1.07	0.53	2.52
0.1500	0.1500	0.0808	0.0679	−2.02	−2.24	0.79	5.05
0.1800	0.1800	0.0969	0.0814	−2.59	−3.06	0.84	6.49
0.2000	0.2000	0.1075	0.0904	−3.16	−3.76	1.25	8.16
0.2200	0.2200	0.1181	0.0993	−3.87	−5.17	0.79	9.83
0.2500	0.2500	0.1340	0.1128	−5.09	−6.47	1.23	12.79
0.2800	0.2800	0.1499	0.1262	−5.96	−7.68	1.96	15.60
0.3000	0.3000	0.1604	0.1351	−6.69	−8.38	2.47	17.55
0.3200	0.3200	0.1710	0.1440	−7.27	−9.41	2.23	18.92
0.3500	0.3500	0.1867	0.1574	−8.37	−12.16	2.71	23.25
0.3800	0.3800	0.2024	0.1707	−13.94	−14.07	4.19	32.19
0.4000	0.4000	0.2128	0.1795	−15.03	−15.42	4.35	34.80
0.4200	0.4200	0.2232	0.1884	−17.98	−16.57	4.62	39.17
0.4500	0.4500	0.2388	0.2016	−18.92	−18.44	5.51	42.87
0.5000	0.5000	0.2647	0.2237	−23.54	−23.23	6.97	53.73

[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.

species approach each other. This process is accompanied by overlapping of the salvation cospheres of the solute molecules, resulting in a partial reorganization of the salvation cospheres and a change of the solute–solvent interactions.

By and large, the interactions between α-amino acids and glycol in the aqueous solutions reflect three superimposed processes: the first is the partial dehydration of hydration shell of the α-amino acid zwitterions (making positive contributions to h_{xy}); the second is the partial dehydration of hydration shell of glycol (making positive contributions to h_{xy}); and the third is the direct interaction, which plays the dominant role in the processes of interaction between α-amino acid and glycol molecules.

The relative magnitude of h_{xy} coefficients studied in this work mainly depends on the direct interactions between α-amino acids and glycol. Since both the amino acid and glycol molecules have hydrophobic and hydrophilic groups, the direct interaction between the two kinds of molecules can be interpreted as the result of different contributions: (a) the hydrophobic–hydrophobic interaction (characterized by a positive contribution to h_{xy}); (b) the hydrophobic–hydrophilic interaction (characterized by a positive contribution to h_{xy}); (c) the hydrophilic–hydrophilic interaction (characterized by a negative contribution to h_{xy}).

The resulting sign and magnitude of h_{xy} would be a consequence of the competitive equilibrium between the above effects.

3.3. Enthalpic pairwise interactions between different kinds of amino acid and glycol in aqueous solutions

With the aim to show the variational tendency of h_{xy} coefficients for different amino acids and glycol, the data in Table 2 are presented in Fig. 1.

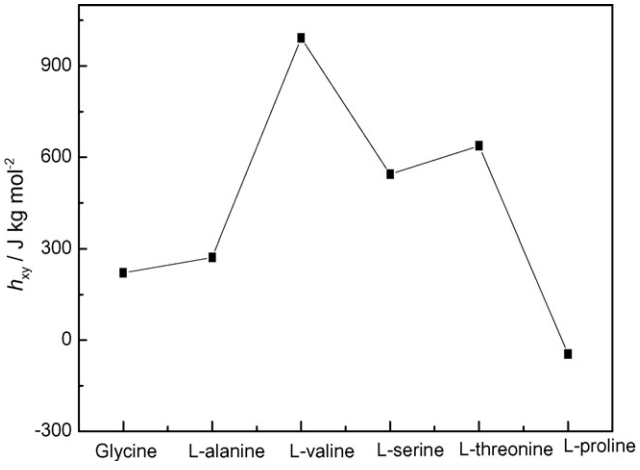


Fig. 1. Heterotactic enthalpic pairwise interaction coefficients between amino acids and glycol in aqueous solutions at 298 K.

As can be seen from Fig. 1, in addition to the negative h_{xy} coefficients between L-proline, a kind of cyclic amino acid, and glycol, all the other h_{xy} coefficients between straight-chain amino acids and glycol are positive. For chain amino acids studied, the experimentally observed positive values of h_{xy} testify to the predominance of endothermic processes over the effect of exothermic direct interaction of amino acid with glycol. While for cyclic L-proline, the negative value of h_{xy} indicates that the exothermic effect plays a significant role during the process of the interaction between it and glycol.

The differences of h_{xy} coefficients between different kinds of α-amino acids and glycol are dramatically contingent on the

Table 3
Heterotactic enthalpic interaction coefficients between amino acids and glycol in aqueous solutions at 298.15 K.

Solutes $x + y$	h_{xy} (J kg mol^{-2})	$h_{xxy} \times 10^{-3}$ (J kg^2 mol^{-3})	$h_{xyy} \times 10^{-3}$ (J kg^2 mol^{-3})	R^2
Glycine + glycol	221.3 (129)	−1306.6 (1176)	1559.7 (1048)	0.9916
L-alanine + glycol	271.7 (144)	−52.0 (214)	62.0 (254)	0.9921
L-valine + glycol	992.0 (280)	218.6 (105)	257.2 (124)	0.9968
L-serine + glycol	544.0 (276)	153.2 (119)	180.7 (140)	0.9952
L-threonine + glycol	637.4 (66)	80.8 (19)	−94.8 (23)	0.9994
L-proline + glycol	−45.7 (68)	126.5 (88)	−148.3 (103)	0.9953

[a] R = correlation coefficient.

discrepancies in the structure of the studied amino acids. Glycine, which has no side-chain, is the simplest amino acid in nature. Compared to Glycine, L-alanine and L-valine have one hydrogen atom on the α-carbon replaced by a methyl and by an isopropyl, respectively. For the above three kinds of amino acid, there are marked discriminations in the interaction (a) and (b) concerning the non-polar groups of α-amino acid, which make positive contributions to h_{xy}. As the alkyl side-chain of amino acid is lengthened, the positive contributions made to the h_{xy} coefficients of the interaction between amino acids and glycol in aqueous solutions become larger. Therefore, the h_{xy} coefficients are in the following sequence: h_{xy} (L-valine) > h_{xy} (L-alanine) > h_{xy} (Glycine).

L-Serine is similar to L-alanine except that it has a hydroxyl group replacing a hydrogen atom of the methyl group, which strengthens its hydrophilic properties and enhances interactions (b) and (c). The relative magnitudes of the values of h_{xy} for L-serine can be treated as a result of competition between interactions (b) and (c). The dominant role played by interaction (b) causes h_{xy} (L-serine) > h_{xy} (L-alanine).

Since there is one methyl on the side-chain of L-threonine as compared to L-serine, interactions (a) and (b) (both of them making positive contribution to h_{xy}) are reinforced. In consequence, the h_{xy} values decrease in the following order: h_{xy} (L-threonine) > h_{xy} (L-serine).

Thus, for the unbranched long-chain amino acids, there exists the following rule: h_{xy} (L-valine) > h_{xy} (L-threonine) > h_{xy} (L-serine) > h_{xy} (L-alanine) > h_{xy} (Glycine).

As to L-valine and L-threonine, the side-chain of L-threonine can be considered as a substitute for one hydroxyl group of one of the methyl groups of L-valine. The main differences of the interactions of L-valine and L-threonine with glycol lie in the following: there exist hydrophobic–hydrophobic and hydrophobic–hydrophilic interactions (both of them making positive contributions to h_{xy}) between the methyl group of L-valine with the glycol molecule, and there also exist hydrophilic–hydrophobic (making positive contributions to h_{xy}) and hydrophilic–hydrophilic interactions (making negative contributions to h_{xy}) between the hydroxyl group on the side-chain of L-threonine with the glycol molecule. The comparative magnitude of the heterotactic enthalpic pairwise interaction coefficients of L-valine and L-threonine with glycol molecule depends on the competitive balance of the above-varied interactions. In aqueous glycol solutions, there exists h_{xy} (L-valine) > h_{xy} (L-threonine), which shows that the former yields very strong interaction effects.

L-proline is a natural amino acid that has one pyrrole ring. Its special structure makes it important to the properties of polypeptide. On one hand, the cyclic structure diminishes the interactions between L-proline molecules due to the steric effect, which makes solvation easy. This indicates that the absorbing heat of the dehydration process and the positive contribution to the enthalpic pairwise interaction coefficient are relatively little. On the other hand, although both of L-proline and L-valine contain four carbon atoms, the cyclic structure of the former can weaken the interaction between it and glycol molecule. As a result of the above two effects, the exothermic process dominates over the overall interaction process. And consequently, the value of h_{xy} of L-proline with glycol is negative.

4. Conclusions

The experimental values of h_{xy} coefficient for five kinds of straight-chain α-amino acids studied (Glycine, L-alanine, L-valine, L-serine and L-threonine) with glycol in aqueous solutions are all positive. However, the h_{xy} coefficient between L-proline, a kind of cyclic natural amino acid, and glycol in aqueous solution is negative. This indicates that the predominance of endothermic effect for the former and dominance of exothermic effect for the latter, respectively, during the process of interactions between amino acids and glycol.

For the straight-chain amino acids studied, the h_{xy} coefficients between them and glycol decrease in the following sequence: h_{xy} (L-valine) > h_{xy} (L-threonine) > h_{xy} (L-serine) > h_{xy} (L-alanine) > h_{xy} (Glycine). The variations of the h_{xy} coefficients have been interpreted in terms of the chemical structures of the molecules studied and solute–solute interactions. The extension of the non-polar side-chain and the existence of the hydroxyl group of amino acids can increase to an extent the hydrophobic and hydrophilic quality, respectively. Pyrrole ring structure of L-proline can weaken the interactions due to the steric effect.

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