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Heterogeneous interaction between zwitterions of amino acids and glycerol in aqueous solutions at 298.15 K

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Abstract The enthalpies of mixing of six kinds of amino acid (glycine, L-alanine, L-valine, L-serine, L-threonine, and L-proline) with glycerol in aqueous solutions and the enthalpies of diluting of amino acid and glycerol aqueous solutions have been determined by flow microcalorimetry at 298.15 K. Employing McMillan–Mayer theory, the enthalpies of mixing and diluting have been used to calculate heterogeneous enthalpic pairwise interaction coefficients (h_{xy}) between amino acids and glycerol in aqueous solutions. Combining h_{xy} values of amino acids with glycol in the previous study, the variations of the h_{xy} values between amino acids and glycerol have been interpreted from the point of view of solute–solute interactions.

Keywords Amino acid · Glycerol · Heterotactic enthalpic pairwise interaction · Solute–solute interactions

Introduction

Interactions between the solvents and various functional groups on the protein, along with the various non-covalent bonding interactions (for example, the hydrophobic interaction) among protein constituent groups, are very important factors that determine the folded conformation of a globular protein [1]. Various added substances affect these interactions and consequently alter the structural stability of proteins. A thorough understanding of this folding process requires knowledge of the interactions that are responsible for stabilizing the native protein structure in aqueous solution. Interactions between the solvent and various functional groups on the protein, along with the various non-covalent bonding interactions among protein constituent groups, are very important factors that determine the folded conformation of a globular protein [2].

As proteins are large complex molecules, small solutes that incorporate some of the structural features found in proteins, such as amino acids [3–15], amides [16–19], and small peptides [20–25], have been used as models for specific aspects of proteins in aqueous solution. The investigation of solute–solute and solute–solvent interactions for these model compounds in aqueous solution can provide information about the various contributions to the interaction between hydrated molecules and help us understand the important interactions that determine protein stability.

As amino acids are the basic building blocks of proteins, it is not surprising that they have been used extensively as model compounds of proteins. A great deal of research articles on the thermodynamic properties of aqueous amino acid solutions have been reported in the past several decades. These include amino acids in pure water [4, 5], in aqueous solutions containing cosolutes or cosolvents such as urea [4, 6], alcohol [3,7], butanol [8], 1, 4-dioxane [9], ketone [10], saccharine [11, 12], electrolytes [13, 15], and so on.

It is well known that polyols help in stabilizing the native conformations of globular proteins [23, 26]. Although some authors correlate the stabilizing effect of sugars with the number and position of hydroxyl groups [11, 18], the understanding of the stabilization mechanism of proteins is still incomplete. In addition to this, glycerol occurs as a primary biomolecule in the intestine as a product of hydrolysis of lipids and also in the liver where it participates in the metabolism of glucose [27].

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As an extension to our previous study [8–10, 28], in the present study, we report a study of the enthalpic behavior of amino acids and glycerol in the aqueous solutions. The enthalpic coefficients derived from McMillan–Mayer's theory [29] can well describe the global effects of the interaction between amino acid and glycerol molecules proceeding with the competitive contribution of water molecules. Moreover, comparison with the previous study concerning the enthalpic characteristics between amino acids and glycol will gain insight into the effect of side chains of amino acid and number of hydroxyl group of polyols on the enthalpic interaction between amino acids and polyols.

Experimental

Materials

Biochemical reagent grade glycine, L-alanine, L-valine, L-serine, L-threonine, and L-proline were used after recrystallization from a water–methanol mixture and dried in vacuum desiccators until their weights became constant. Glycerol (AR grade, from Shanghai Chem. Co., China) was used as received. The water used for the preparation of solutions was deionized, distilled, and degassed. Both the aqueous amino acid solutions and the aqueous glycerol solution were prepared by weight by Mettler AE 200 balance with a precision of ±0.0001 g. All the solutions were degassed with ultrasonic waves and used within 12 h after preparation to minimize decomposition due to bacterial contamination.

Instruments

The calorimetric measurements were performed by a mixing-flow microcalorimeter (Thermometric 2277 thermal activity monitor, Sweden). All the measurements were carried out at (298.15 ± 0.01) K. The pressure under which the experiment has been conducted is (101.325 ± 2.026) kPa. Errors in the determinations of the molar enthalpies of dilution and mixing were estimated to be <1%.

Methods

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 liquids passing through pumps A and B were changed in the following sequence:

$A_{water} + B_{water}$ baseline determined
$A_x + B_{water}$ dilution thermal power determined for aqueous x solution
$A_x + B_y$ mixing thermal power determined for aqueous x solution and aqueous y solution
$A_{water} + B_y$ dilution thermal power determined for aqueous y solution
$A_{water} + B_{water}$ baseline re-established

Details of the instrument and experimental procedure have been described earlier [8–10].

The dilution enthalpy $\Delta_{dil}H$(J) is determined by measuring thermal power P (μW) and flow rates of solution and solvent (f_A and f_B, mg s^{-1}):

$$\Delta_{dil}H = P/(f_A + f_B - m_{x,i}M_x f_A) \quad (1)$$

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

The final molality $m_{x,f}$ (mol kg^{-1}) may be calculated by the equation

$$m_{x,f} = m_{x,i}f_A/[f_B(m_{x,i}M_x + 1) + f_A] \quad (2)$$

The mixing enthalpy $\Delta_{mix}H$(J) of aqueous x solution and aqueous y solution can be determined as follows

$$\Delta_{mix}H = P_{mix}/(f_x + f_y - m_{x,i}M_x f_x - m_{y,i}M_y f_y) \quad (3)$$

in which P_{mix} is the mixing thermal power (μW), $m_{x,i}$,$m_{y,i}$ are the initial molalities of solutions x and y before mixing and f_x,f_y are the flow rates of solutions x and y, respectively.

McMillian–Mayer's theory [29] and its application to aqueous solutions of non-electrolytes establish that the excess thermodynamic properties can be expressed as a function of molality using a virial expansion. The coefficients derived from McMillian–Mayer's theory are related to the magnitude and sign of energetic interactions between molecules dissolved in aqueous solutions in the presence of competitive water molecules. In this way, the excess enthalpy of the ternary solution per 1 kg of solvent $H^E(m_x, m_y)/w_1$ can be expressed as a virial expansion of solute molalities using the following equation

$$\begin{aligned} H^E(m_x,m_y)/w_1 &= H(m_x,m_y)/w_1 - h_w^* - m_x H_{x,m}^\infty - m_y H_{y,m}^\infty \\ &= h_{xx}m_x^2 + 2h_{xy}m_x m_y + h_{yy}m_y^2 + h_{xxx}m_x^3 \\ &\quad + 3h_{xxy}m_x^2 m_y + 3h_{xyy}m_x m_y^2 + h_{yyy}m_y^3 + \ldots \end{aligned} \quad (4)$$

in which $H(m_x, m_y)/H(m_x, m_y)w_1.w_1$ represents the absolute enthalpy of a solution. h_w^* is the standard enthalpy of 1 kg pure solvent, 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} denote the enthalpic interaction coefficients of heterogeneous pairwise and triples of the examined molecules, respectively.

The value of the heterogeneous enthalpic pairwise interaction coefficient of x molecule with y molecule in aqueous solution is determined on the basis of measurements of mixing enthalpy of aqueous solutions of these substances and their respective dilution enthalpy in water. To simplify the calculation, an auxiliary function ΔH^* is introduced.

$$\Delta H^* = \Delta_{mix}H - \Delta_{dil}H(x) - \Delta_{dil}H(y) = H^E(m_x, m_y) - H^E(m_x) - H^E(m_y) \quad (5)$$

Thus, Eq. 4 can be rewritten as

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

Results and discussion

Results of the calorimetric experiments at 298.15 K are summarized in Table 1 as well as the initial and final molalities. The heterogeneous enthalpic interaction coefficients determined by the multiparameter linear regression are listed in Table 2. As the triplet enthalpic interaction coefficients contain some contributions from the pairwise interaction terms, they are not discussed in this study.

Heterogeneous enthalpic pairwise interaction of amino acids with glycerol in aqueous solution

The values of the heterogeneous enthalpic pairwise interaction coefficients h_{xy} are a measure of interactions proceeding between the two solute molecules with the competitive co-contribution of water molecules. The global effect is a sum of superimposing processes: partial dehydration of solvation shells of the zwitterions of amino acid and the polar hydroxyl group of glycerol (endothermic process, positive contribution to h_{xy}); direct interaction between amino acid and glycerol molecules. Among these effects, the direct interaction between amino acid and glycerol molecules plays the dominant role during the overall interaction processes.

The direct interaction is possible to include the interaction types as follows: (1) ion–dipolar interaction occurring between the zwitterionic centers of amino acid and –OH groups of glycerol; (2) hydrophilic–hydrophilic interactions between the –OH groups of amino acids and glycerol mediated through hydrogen bonding; (3) hydrophobic–hydrophilic interactions between non-polar group of amino acid and –OH groups of glycerol or non-polar group of glycerol and zwitterionic centers of amino acid; (4) hydrophobic–hydrophobic interactions between non-polar groups of amino acid and glycerol. Among them, interaction types (1) and (2) contribute negatively, whereas the interaction types (3) and (4) contribute positively to h_{xy}.

The resulting sign and magnitude of h_{xy} would be a consequence of the competitive equilibrium between the above effects. The structure of amino acid molecules has a more important effect on the interaction between amino acid and the glycerol molecules. Since the amino acid molecules have the same charged end groups ($–NH_3^+$, $–COO^-$), their contributions to the interaction process with glycerol should be approximately equal. Therefore, it is the side chain and the group on it that is responsible for the observed variation trends of h_{xy} coefficients between amino acids and glycerol.

Analyzing the values of the heterogeneous enthalpic pairwise interaction coefficients and the structures of glycine, L-alanine, and L-valine, one can observe an increase in the value of enthalpic coefficient with substitution of one hydrogen atom of glycine by a methyl and an isopropyl, respectively. The replacement of hydrogen atom with methyl and isopropyl brings about an increased hydrophobicity of the substituent. That is to say, endothermic interaction types (3) and (4) are reinforced with increasing number of carbon atoms in the side amino acid chains. So for glycine, L-alanine, and L-valine, the magnitude of h_{xy} coefficient increases with increasing chain length of them.

The side chain of L-serine can be considered as a substitute for one hydroxyl group of one hydrogen atom of the methyl group of L-alanine. In the case of L-serine, the –OH group leads to additional hydrophilic–hydrophilic (making negative contributions to h_{xy}) and hydrophilic–hydrophobic interaction (making positive contributions to h_{xy}) between it and the –OH and the non-polar groups of glycerol molecule. The more positive h_{xy} for L-serine suggests that the latter interaction is predominant.

The replacement of non-polar group $–CH_3$ with –OH for the side chain of L-valine, resulting in the formation of L-threonine, causes the negative value of heterogeneous enthalpic pairwise interaction coefficient of glycerol with the L-threonine in comparison with L-valine. The experimentally observed negative values of the h_{xy} coefficients testify to the predominance of the exothermic processes over endothermic processes for L-threonine with glycerol. The main differences of the interactions of L-valine and L-threonine with glycerol 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 non-polar group and the –OH groups of the glycerol 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 –OH group of L-threonine and the non-polar group and –OH groups of the glycerol molecule. So the comparative

Table 1 Enthalpies of dilution and mixing of aqueous amino acid solutions and aqueous glycerol 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}	$\Delta_{dil}H_{(x)}/w_1$/ J kg^{-1}	$\Delta_{dil}H_{(y)}$/w$_1$/ J kg^{-1}	$\Delta_{mix}H$/w$_1$/ J kg^{-1}	ΔH^*/w$_1$/ J kg^{-1}
Glycine + glycerol							
0.1000	0.1000	0.0541	0.0453	0.74	−1.03	0.53	0.82
0.1500	0.1500	0.0811	0.0677	2.62	−2.21	0.91	0.51
0.1800	0.1800	0.0972	0.0812	3.61	−2.95	0.99	0.32
0.2000	0.2000	0.1079	0.0901	4.27	−3.79	1.18	0.70
0.2200	0.2200	0.1186	0.0990	5.54	−5.19	0.73	0.37
0.2500	0.2500	0.1347	0.1123	6.99	−6.11	1.10	0.21
0.2800	0.2800	0.1507	0.1256	8.12	−7.80	1.44	1.13
0.3000	0.3000	0.1613	0.1344	9.35	−8.04	2.25	0.95
0.3200	0.3200	0.1719	0.1433	10.87	−9.45	2.22	0.81
0.3500	0.3500	0.1879	0.1565	12.95	−12.09	2.09	1.23
0.3800	0.3800	0.2038	0.1696	14.82	−13.58	3.32	2.08
0.4000	0.4000	0.2144	0.1784	15.80	−15.21	3.70	3.11
0.4200	0.4200	0.2249	0.1871	17.94	−16.15	3.67	1.87
0.4500	0.4500	0.2407	0.2002	20.05	−17.58	4.33	1.85
0.5000	0.5000	0.2670	0.2219	24.33	−22.40	4.96	3.04
L-alanine + glycerol							
0.1000	0.1000	0.0541	0.0453	−0.44	−1.03	−0.24	1.22
0.1500	0.1500	0.0810	0.0677	−1.43	−2.21	−0.57	3.08
0.1800	0.1800	0.0971	0.0812	−2.08	−2.95	−1.20	3.82
0.2000	0.2000	0.1078	0.0901	−2.27	−3.79	−1.49	4.58
0.2200	0.2200	0.1185	0.0990	−2.67	−5.19	−2.42	5.44
0.2500	0.2500	0.1344	0.1123	−3.13	−6.11	−3.39	5.84
0.2800	0.2800	0.1504	0.1256	−3.89	−7.80	−3.56	8.14
0.3000	0.3000	0.1610	0.1344	−5.35	−8.04	−3.36	10.03
0.3200	0.3200	0.1716	0.1433	−5.76	−9.45	−4.50	10.71
0.3500	0.3500	0.1875	0.1565	−6.49	−12.09	−5.42	13.16
0.3800	0.3800	0.2033	0.1696	−8.20	−13.58	−5.13	16.66
0.4000	0.4000	0.2138	0.1784	−8.38	−15.21	−5.47	18.12
0.4200	0.4200	0.2243	0.1871	−9.55	−16.15	−6.24	19.46
0.4500	0.4500	0.2401	0.2002	−10.93	−17.58	−7.05	21.46
0.5000	0.5000	0.2662	0.2219	−14.28	−22.40	−8.43	28.26
L-valine + glycerol							
0.1000	0.1000	0.0540	0.0453	−1.70	−1.03	−0.40	2.32
0.1500	0.1500	0.0808	0.0677	−4.42	−2.21	−1.41	5.23
0.1800	0.1800	0.0968	0.0812	−6.39	−2.95	−2.01	7.32
0.2000	0.2000	0.1075	0.0901	−8.03	−3.79	−2.70	9.12
0.2200	0.2200	0.1181	0.0990	−10.24	−5.19	−3.80	11.63
0.2500	0.2500	0.1340	0.1123	−12.55	−6.11	−5.31	13.34
0.2800	0.2800	0.1499	0.1256	−15.67	−7.80	−5.80	17.67
0.3000	0.3000	0.1604	0.1344	−18.07	−8.04	−5.90	20.21
0.3200	0.3200	0.1709	0.1433	−21.60	−9.45	−6.86	24.19
0.3500	0.3500	0.1866	0.1565	−24.16	−12.09	−9.02	27.23
0.3800	0.3800	0.2023	0.1696	−28.14	−13.58	−10.21	31.52
0.4000	0.4000	0.2127	0.1784	−30.07	−15.21	−13.23	32.05
0.4200	0.4200	0.2231	0.1871	−34.48	−16.15	−12.70	37.93
0.4500	0.4500	0.2387	0.2002	−43.14	−17.58	−14.45	46.27

Table 1 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}	$\Delta_{dil}H_{(x)}/w_1$/ J kg^{-1}	$\Delta_{dil}H_{(y)}$/w$_1$/ J kg^{-1}	$\Delta_{mix}H$/w$_1$/ J kg^{-1}	ΔH^*/w$_1$/ J kg^{-1}
L-serine + glycerol							
0.1000	0.1000	0.0541	0.0453	1.34	−1.03	1.72	1.41
0.1500	0.1500	0.0809	0.0677	4.34	−2.21	2.93	0.80
0.1800	0.1800	0.0969	0.0812	5.81	−2.95	3.44	0.58
0.2000	0.2000	0.1076	0.0901	7.84	−3.79	4.93	0.88
0.2200	0.2200	0.1183	0.0990	8.76	−5.19	4.86	1.29
0.2500	0.2500	0.1342	0.1123	10.73	−6.11	6.51	1.89
0.2800	0.2800	0.1501	0.1256	12.22	−7.80	9.49	5.08
0.3000	0.3000	0.1607	0.1344	15.05	−8.04	9.57	2.56
0.3200	0.3200	0.1712	0.1433	17.21	−9.45	11.74	3.98
0.3500	0.3500	0.1870	0.1565	19.98	−12.09	12.45	4.56
0.3800	0.3800	0.2027	0.1696	24.15	−13.58	15.01	4.44
0.4000	0.4000	0.2132	0.1784	26.00	−15.21	16.70	5.91
0.4200	0.4200	0.2236	0.1871	30.10	−16.15	18.46	4.51
0.4500	0.4500	0.2393	0.2002	33.10	−17.58	20.75	5.22
0.5000	0.5000	0.2653	0.2219	38.28	−22.40	23.97	8.10
L-threonine + glycerol							
0.1000	0.1000	0.0540	0.0453	0.25	−1.03	0.92	1.70
0.1500	0.1500	0.0808	0.0677	0.82	−2.21	1.15	2.55
0.1800	0.1800	0.0968	0.0812	1.05	−2.95	1.14	3.04
0.2000	0.2000	0.1075	0.0901	1.65	−3.79	1.40	3.54
0.2200	0.2200	0.1181	0.0990	1.71	−5.19	1.00	4.48
0.2500	0.2500	0.1340	0.1123	1.95	−6.11	1.41	5.56
0.2800	0.2800	0.1498	0.1256	2.13	−7.80	2.21	7.88
0.3000	0.3000	0.1604	0.1344	2.53	−8.04	2.78	8.29
0.3200	0.3200	0.1709	0.1433	3.01	−9.45	2.81	9.25
0.3500	0.3500	0.1866	0.1565	2.35	−12.09	2.81	12.55
0.3800	0.3800	0.2022	0.1696	3.19	−13.58	4.49	14.89
0.4000	0.4000	0.2127	0.1784	3.35	−15.21	5.27	17.13
0.4200	0.4200	0.2231	0.1871	3.62	−16.15	5.31	17.84
0.4500	0.4500	0.2386	0.2002	3.09	−17.58	6.02	20.51
0.5000	0.5000	0.2644	0.2219	4.71	−22.40	7.00	24.70
L-proline + glycerol							
0.1000	0.1000	0.0540	0.0453	−0.73	−1.03	0.24	1.99
0.1500	0.1500	0.0808	0.0677	−1.87	−2.21	0.13	4.21
0.1800	0.1800	0.0969	0.0812	−2.61	−2.95	−0.32	5.24
0.2000	0.2000	0.1181	0.0990	−3.88	−5.19	−0.82	8.25
0.2200	0.2200	0.1340	0.1123	−5.08	−6.11	−0.84	10.34
0.2500	0.2500	0.1499	0.1256	−6.07	−7.80	−0.63	13.24
0.2800	0.2800	0.1710	0.1433	−7.78	−9.45	−0.38	16.85
0.3000	0.3000	0.1867	0.1565	−8.37	−12.09	−0.91	19.55
0.3200	0.3200	0.2024	0.1696	−13.94	−13.58	−0.14	27.39
0.3500	0.3500	0.2128	0.1784	−15.03	−15.21	−0.13	30.11
0.3800	0.3800	0.2232	0.1871	−17.98	−16.15	−0.33	33.80
0.4000	0.4000	0.2388	0.2002	−18.92	−17.58	−0.35	36.14
0.4200	0.4200	0.2647	0.2219	−23.54	−22.40	−0.42	45.52

Table 2 Heterogeneous enthalpic interaction coefficients between amino acids and glycerol 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}	SD[a]	R^{2b}
Glycine + glycerol	−42.0	−2.2	2.8	0.57	0.9926
L-alanine + glycerol	132.1	−33.3	40.2	0.58	0.9959
L-valine + glycerol	990.2	−1290	1532	1.19	0.9939
L-serine + glycerol	244.4	610.1	−729.8	0.84	0.9935
L-threonine + glycerol	−167.8	532.4	−633.3	0.40	0.9976
L-proline + glycerol	−99.3	1100.0	−1310.7	1.17	0.9947

[a] Standard deviation

[b] Square of correlation coefficient

magnitude of h_{xy} for L-valine and L-threonine with glycerol molecule would be a consequence of the competitive equilibrium of the above-varied interactions. For L-threonine, the negative h_{xy} value is associated with effects of intensified hydrophilic effect, which is caused by the cooperation of hydrogen bonds between the –OH groups of it and glycerol.

The differences of h_{xy} coefficients between L-proline and L-valine, and glycerol are dramatically contingent on the discrepancies of the structures of amino acids. L-proline has the same carbon number as L-valine but it has a pyrrole ring structure, which has distinct steric effect. The cyclic structure can diminish the interactions between L-proline molecules, so the partial dehydration process of L-proline molecules makes a less positive contribution to h_{xy}. Moreover, the cyclic structure of L-proline can weaken the interaction between it and glycol molecule. The experimentally observed values of h_{xy} testify to the predominance of the exothermic processes over endothermic processes for L-proline with glycerol, while for L-valine with glycerol the endothermic processes play a dominant role.

Comparison between the heterogeneous enthalpic pairwise interaction of amino acids with glycerol and glycol in aqueous solution

In the continuing series of investigation, Table 3 shows the heterogenous enthalpic pairwise interaction coefficients of amino acids with glycol at 298.15 K, which has been reported in our previous study [28]. It can be clearly seen from Tables 2 and Table 3 that the rules for the interactions of the same kind of amino acids with glycerol in aqueous solutions are analogous to those of glycol. In the meantime, there exist some distinctions in their interaction behavior. These can be attributed primarily to the similarities and discrepancies in the structures of glycerol and glycol.

The glycerol molecule contains one more OH group and carbon atom in the alkyl chain than the glycol molecule. On the one hand, the partial dehydration process of

Table 3 Heterogeneous enthalpic interaction coefficients between amino acids and glycol in aqueous solutions at 298.15 K 31

Solutes x + y	H_{xy}/J kg mol^{-2}
Glycine + glycol	221.3
L-alanine + glycol	271.7
L-valine + glycol	992.0
L-serine + glycol	544.0
L-threonine + glycol	637.4
L-proline + glycol	−45.7

hydration shells of polyol hydroxyl groups is accompanied by the effect brought about by the influence of polyol alkyl groups resulting in reinforcing hydrogen bonds between water molecules surrounding these non-polar groups [27, 30]. The cooperativity of hydrogen bonds reinforces the interaction between water molecules in hydration layers of hydroxyl groups (directly combined with alkyl groups) as well as the amino acid zwitterion interacting with them. This enhances the endothermic dehydration effects of interacting molecules which increase with increasing alkyl group size [27]. So an increase in the alkyl group size in the polyol molecule brings about an increase in h_{xy}. On the other hand, glycerol bears more –OH groups, which result in the hydrophilic effect (making negative contribution to h_{xy}) larger than that of glycol in the process of interaction with amino acids. As a result, the h_{xy} values decrease as the number of the –OH groups on the alkyl chain of polyol molecule increases. For the same kind of amino acid, the experimental result is h_{xy} (glycerol) < h_{xy} (glycol), which indicates that the latter effect is predominant over the former.

Conclusions

The heterogeneous enthalpic pairwise interaction coefficients (h_{xy}) between amino acids and glycerol in the aqueous solutions were determined with a Thermometric 2277 Thermal Activity Monitor at 298.15 K. The experimental values of h_{xy} for glycine, L-threonine, and

L-proline with glycerol are negative while those of L-alanine, L-valine, and L-serine with glycerol are positive. This testifies to the predominance of exothermic processes over endothermic processes for glycine, L-threonine, and L-proline with glycerol, while for L-alanine, L-valine, and L-serine with glycerol, the endothermic processes play the dominant role. By comparison, the interaction behavior of the same kind of amino acid with glycerol is similar to that of glycol, which was reported in the previous study and with the following sequence observed: h_{xy} (glycerol) $< h_{xy}$ (glycol). This can be ascribed to the predominant role played by the hydrophilic effect. The different structures of amino acids and polyol molecules make a contribution to the different values of h_{xy} coefficients.

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