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Enthalpic Pairwise Interactions between Some Amino Acids and 2-Butanone in Aqueous Solutions at 298.15 K

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The enthalpies of dilution of aqueous solutions of six kinds of amino acids (glycine, L-α-alanine, L-γ-aminobutyric acid, L-α-valine, L-α-serine, and L-α-threonine) with 2-butanone and enthalpies of mixing were measured at 298.15 K, using a mixing-flow microcalorimeter. The experimental data were treated according to the McMillan−Mayer theory, to obtain the enthalpic interaction coefficients. Combining the enthalpic pairwise interaction coefficients (h_{xy}) of amino acids with cyclohexanone from the literature, the experimental results have been discussed from the point of view of solute−solute and solute−solvent interactions.

Introduction

Free amino acids occurring in all biological cells as a constant stock or so-called “amino acids pool” are indispensable for the proper functioning of living organisms, as are the amino acid segments of polypeptide chains that are physically and chemically affected by the side substituent −R of the amino acid.[1] There is currently a considerable amount of interest in studies on various thermodynamic properties of amino acids in aqueous solutions of organic substances due to their importance in obtaining a better understanding of nature and mechanisms taking place in biological cells.[2−5]

As a part of our extensive research on the interactions of amino acids with alcohols,[6,7] ketones,[8] and heterocyclic compounds,[9−11] the present work reports the enthalpic interaction of amino acids with 2-butanone in aqueous solution at 298.15 K. In addition, the results obtained in the present paper together with those reported in an earlier paper,[8] about the enthalpic interaction of amino acids with cyclohexanone, have been used to investigate the difference between the enthalpic pairwise interaction coefficients of amino acids with cyclic and linear ketones. Linear ketones have a stiff propanone skeleton and are inflexible compared with other linear organic solvents. This characteristic structure of ketones seems to bring an interesting feature in the enthalpic interaction with amino acids in aqueous solutions.

Materials and Methods

Biochemical reagent grade glycine (Gly), L-α-alanine (Ala), L-γ-aminobutyric acid (Aba), L-α-valine (Val), L-α-serine (Ser), and L-α-threonine (Thr) were used after recrystallization from a water−methanol mixture and dried in vacuum desiccators until their weights became constant. Analytical reagent grade 2-butanone was used without further purification. Water was deionized and 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 2-butanone solution were prepared by weight using a Mettler AE 200 balance with a precision of ± 0.0001 g.

The dilution and mixing enthalpies were measured using a mixing-flow microcalorimeter (2277 Thermal Activity Monitor manufactured in Sweden). All the measurements were carried out at 298.15 K. The temperature sensitivity of the measuring system was about 10^{-4} K over 24 h, and the temperature stability of the thermostat was better than 10^{-2} K. The solutions were pumped through the mixing-flow 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 apparatus and procedure used were the same as those described in earlier work.[6−11] The experimental errors in the determinations of the molar enthalpies of dilution and mixing were estimated to be < 1 %. The standard deviation was below 0.96.

Results and Discussion

According to the McMillian−Mayer formalism,[12] all the thermodynamic properties of multicomponent solutions can be expressed by using a virial expansion in m which relates the nonideal contributions of any total thermodynamic function to a series of interaction parameters. The excess enthalpy of the ternary solution per kilogram of water can be expressed as a power series in the molalities

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

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 m_x moles of x and m_y moles of y in 1 kg of water; h_w^{*} is the standard enthalpy of 1 kg of pure water; $H_{x,m}^{\infty}$ and $H_{y,m}^{\infty}$ are the limiting partial molar enthalpies of species x and y, respectively; and the various h_{ij} and h_{iij} are the pairwise and triplet virial coefficients representing interactions between subscripted species. m_x and m_y are the molalities of the solutes x and y, respectively.

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Table 1. Enthalpies of Dilution and Mixing of Amino Acid (x) and 2-Butanone (y) in Aqueous Solutions at 298.15 K

$m_{x,i}{}^{a}$ / $mol \cdot kg^{-1}$	$m_{y,i}$ / $mol \cdot kg^{-1}$	$m_{x,f}$ / $mol \cdot kg^{-1}$	$m_{y,i}$ / $mol \cdot kg^{-1}$	$\Delta H_{dil(x)}/w_1$ / $J \cdot kg^{-1}$	$\Delta H_{dil(y)}/w_1$ / $J \cdot kg^{-1}$	$\Delta H_{mix}/w_1$ / $J \cdot kg^{-1}$	$\Delta H^{*}/w_1$ / $J \cdot kg^{-1}$
Glycine + 2-Butanone							
0.1000	0.1000	0.0541	0.0453	0.74	−2.53	0.22	2.01
0.1500	0.1500	0.0811	0.0678	2.62	−7.87	0.47	5.73
0.1800	0.1800	0.0972	0.0813	3.61	−10.14	0.71	7.23
0.2000	0.2000	0.1079	0.0903	4.27	−13.14	1.08	9.95
0.2200	0.2200	0.1186	0.0992	5.54	−15.87	1.18	11.50
0.2500	0.2500	0.1347	0.1126	6.99	−20.09	1.09	14.19
0.2800	0.2800	0.1507	0.1260	8.12	−26.52	1.19	19.60
0.3000	0.3000	0.1613	0.1349	9.35	−29.75	1.10	21.50
0.3201	0.3200	0.1719	0.1438	10.87	−34.44	1.15	24.72
0.3500	0.3500	0.1879	0.1571	12.95	−39.43	−0.34	26.14
0.3800	0.3800	0.2038	0.1703	14.82	−47.36	0.23	32.77
0.4000	0.4000	0.2144	0.1791	15.80	−51.02	−0.80	34.42
0.4200	0.4200	0.2249	0.1880	17.94	−57.56	−0.28	39.35
0.4500	0.4500	0.2407	0.2012	20.05	−66.58	−1.33	45.20
0.5000	0.5000	0.2670	0.2231	24.33	−85.56	−2.75	58.48
L-α-Alanine + 2-Butanone							
0.1000	0.1000	0.0541	0.0453	−0.44	−2.53	−0.99	1.99
0.1490	0.1490	0.0810	0.0678	−1.43	−7.87	−1.37	7.94
0.1800	0.1800	0.0971	0.0813	−2.08	−10.14	−2.35	9.87
0.2000	0.2000	0.1078	0.0903	−2.27	−13.14	−2.69	12.72
0.2200	0.2200	0.1185	0.0992	−2.67	−15.87	−2.98	15.56
0.2500	0.2500	0.1344	0.1126	−3.13	−20.09	−3.96	19.26
0.2800	0.2801	0.1504	0.1260	−3.89	−26.52	−5.41	25.01
0.3000	0.3000	0.1610	0.1349	−5.35	−29.75	−5.73	29.37
0.3200	0.3199	0.1716	0.1438	−5.76	−34.44	−7.12	33.08
0.3500	0.3499	0.1875	0.1571	−6.49	−39.43	−8.99	36.92
0.3799	0.3800	0.2033	0.1703	−8.20	−47.36	−10.75	44.81
0.4000	0.4000	0.2138	0.1791	−8.38	−51.02	−11.48	47.92
0.4200	0.4200	0.2243	0.1880	−9.55	−57.56	−13.21	53.90
0.4500	0.4500	0.2401	0.2012	−10.93	−66.58	−14.58	62.93
0.5000	0.5000	0.2662	0.2231	−13.36	−85.56	−18.99	79.93
L-γ-Aminobutyric Acid + 2-Butanone							
0.1000	0.1000	0.0541	0.0453	−1.09	−2.53	−1.91	1.72
0.1500	0.1500	0.0809	0.0678	−2.96	−7.87	−3.99	6.85
0.1800	0.1800	0.0970	0.0813	−4.70	−10.14	−5.95	8.90
0.2000	0.2000	0.1076	0.0903	−5.44	−13.14	−7.60	10.97
0.2200	0.2200	0.1183	0.0992	−7.27	−15.87	−9.30	13.84
0.2500	0.2500	0.1342	0.1126	−8.48	−20.09	−12.26	16.32
0.2800	0.2800	0.1501	0.1260	−10.49	−26.52	−15.12	21.89
0.3000	0.3000	0.1607	0.1349	−11.62	−29.75	−17.15	24.22
0.3200	0.3200	0.1713	0.1438	−13.32	−34.44	−18.53	29.22
0.3800	0.3800	0.2028	0.1703	−19.00	−47.36	−23.30	43.06
0.4000	0.4000	0.2133	0.1791	−20.24	−51.02	−28.91	42.36
0.4200	0.4200	0.2237	0.1880	−22.02	−57.56	−32.96	46.62
0.4500	0.4500	0.2394	0.2012	−27.05	−66.58	−39.15	54.48
0.5000	0.5000	0.2654	0.2231	−31.56	−85.56	−47.11	70.00
L-α-Valine + 2-Butanone							
0.1000	0.1000	0.0540	0.0453	−1.49	−2.53	−0.15	3.87
0.1500	0.1500	0.0808	0.0678	−4.42	−7.87	−0.34	11.96
0.1800	0.1800	0.0968	0.0813	−6.39	−10.14	−0.99	15.53
0.2000	0.2000	0.1075	0.0903	−8.03	−13.14	−0.94	20.22
0.2200	0.2200	0.1181	0.0992	−10.24	−15.87	−0.93	25.18
0.2500	0.2500	0.1340	0.1126	−12.55	−20.09	−1.34	31.30
0.2800	0.2800	0.1499	0.1260	−15.67	−26.52	−1.83	40.36
0.3000	0.3000	0.1604	0.1349	−18.07	−29.75	−2.09	45.73
0.3200	0.3200	0.1709	0.1438	−21.60	−34.44	−2.19	53.85
0.3500	0.3500	0.1866	0.1571	−24.16	−39.43	−3.53	60.05
0.3800	0.3800	0.2023	0.1703	−28.14	−47.36	−3.74	71.76
0.4000	0.4000	0.2127	0.1791	−30.07	−51.02	−4.81	76.29
0.4200	0.4200	0.2231	0.1880	−34.48	−57.56	−4.79	87.25
0.4500	0.4500	0.2387	0.2012	−43.14	−66.58	−5.33	104.40
L-α-Serine + 2-Butanone							
0.1000	0.1000	0.0541	0.0453	1.34	−2.53	1.57	2.77
0.1500	0.1500	0.0809	0.0678	4.34	−7.87	3.71	7.24
0.1800	0.1800	0.0969	0.0813	5.81	−10.14	5.58	9.90
0.2000	0.2000	0.1076	0.0903	7.84	−13.14	7.03	12.33
0.2200	0.2200	0.1183	0.0992	8.76	−15.87	7.98	15.09
0.2500	0.2500	0.1342	0.1126	10.73	−20.09	9.26	18.63
0.2800	0.2800	0.1501	0.1260	12.22	−26.52	10.30	24.61
0.3000	0.3000	0.1607	0.1349	15.05	−29.75	13.36	28.05
0.3200	0.3200	0.1712	0.1438	17.21	−34.44	15.02	32.25
0.3500	0.3500	0.1870	0.1571	19.98	−39.43	15.78	35.22

Table 1. (Continued)

$m_{x,i}$[a] mol·kg^{-1}	$m_{y,i}$ mol·kg^{-1}	$m_{x,f}$ mol·kg^{-1}	$m_{y,i}$ 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-α-Serine + 2-Butanone				
0.3800	0.3800	0.2027	0.1703	24.15	−47.36	18.77	41.98
0.4000	0.4000	0.2132	0.1791	26.00	−51.02	20.64	45.66
0.4200	0.4200	0.2236	0.1880	30.10	−57.56	22.18	49.64
0.4500	0.4500	0.2393	0.2012	33.10	−66.58	24.46	57.94
0.5000	0.5000	0.2653	0.2231	38.28	−85.56	27.53	74.82
			L-α-Threonine + 2-Butanone				
0.1000	0.1000	0.0540	0.0453	0.25	−2.53	0.65	2.93
0.1500	0.1500	0.0808	0.0678	0.82	−7.87	1.73	8.78
0.1800	0.1800	0.0968	0.0813	1.05	−10.14	2.00	11.10
0.2000	0.2000	0.1075	0.0903	1.65	−13.14	2.85	14.34
0.2200	0.2200	0.1181	0.0992	1.71	−15.87	3.77	17.93
0.2500	0.2500	0.1340	0.1126	1.95	−20.09	4.50	22.65
0.2800	0.2800	0.1498	0.1260	2.13	−26.52	5.11	29.50
0.3000	0.3000	0.1604	0.1349	2.53	−29.75	6.18	33.40
0.3200	0.3200	0.1709	0.1438	3.01	−34.44	6.94	38.37
0.3500	0.3500	0.1866	0.1571	2.35	−39.43	6.81	43.88
0.3800	0.3800	0.2022	0.1703	3.19	−47.36	8.55	52.72
0.4000	0.4000	0.2127	0.1791	3.35	−51.02	7.94	55.61
0.42000	0.42000	0.2231	0.1880	3.62	−57.56	9.30	63.25
0.4500	0.4500	0.2386	0.2012	4.50	−66.58	10.74	72.82
0.5000	0.5000	0.2644	0.2231	4.70	−85.56	10.76	91.62

[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.

Table 2. Enthalpic Interaction Coefficients between Amino Acids and 2-Butanone in Aqueous Solutions at 298.15 K

solutes x + y	h_{xy} J·kg·mol^{-2}	$h_{xxy}\cdot 10^{-4}$ J·kg^2·mol^{-3}	$h_{xyy}\cdot 10^{-4}$ J·kg^2·mol^{-3}	R^2[a]	SD[b]
Gly + 2-butanone	1019 ± 201[c]	75.0 ± 24.2	−89.9 ± 29.0	0.9975	0.91
L-α-Ala + 2- butanone	1216 ± 179	−283.8 ± 78.3	338.5 ± 93.4	0.9990	0.81
L-γ-Aba + 2-butanone	891 ± 332	−26.2 ± 26.1	31.2 ± 30.9	0.9958	1.49
L-α-Val + 2-butanone	2084 ± 491	−57.2 ± 25.7	67.7 ± 30.3	0.9979	1.60
L-α-Ser + 2-butanone	1286 ± 201	−51.7 ± 14.2	61.3 ± 16.8	0.9985	0.90
L-α-Thr + 2-butanone	1190 ± 193	−19.3 ± 7.8	22.7 ± 9.2	0.9991	0.86

[a] Square of correlation coefficient. [b] Standard deviation. [c] The estimated deviation.

To make the calculations easier, an auxiliary function ΔH^* has been 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 and $\Delta H_{dil}(x)$ and $\Delta H_{dil}(y)$ are the dilution enthalpies of the corresponding binary solutions.

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

$$m_x = m_{x,i} f_A/[f_B(m_{x,i}M_x + 1) + f_A] \quad (3)$$

where f_A and f_B are the flow rate of the aqueous solution and the solvent, respectively.

Combining eqs 1 to 3, we can obtain the following equation

$$\Delta H^*/w_1 = 2h_{xy}m_xm_y + 3h_{xxy}m_x^2m_y + 3h_{xyy}m_xm_y^2 + \cdots \quad (4)$$

Experimentally determined enthalpies of dilution and mixing together with ΔH^* are presented in Table 1. The heterotactic enthalpic interaction coefficients calculated from eq 4 using the least-squares method are given in Table 2.

The interpretation of the triplet interaction coefficients is obscured by the fact that they also contain pairwise interaction terms,[13] and for that reason, they are not discussed in this paper. Only the enthalpic pairwise interaction coefficient h_{xy} is discussed here. h_{xy} represents enthalpic contributions due to the corresponding coefficients of free energy and includes the change of energy in the system originating from two types of interactions: solute−solute and solute−solvent.[2] Table 3 gives the chemical structures of five amino acids studied in this paper and in the literature[8] and of 2-butanone and cyclohexanone.

The enthalpic interaction coefficients h_{xy} between amino acid and ketone molecules are the sum of the contributions from the following possible processes:

I. Partial dehydration of the amino acid molecule (endothermic effect). The dehydration is caused by mutual penetration of the hydration shells of interacting molecules in the aqueous medium.

II. Partial dehydration of the ketone molecule (endothermic effect).

III. Direct interaction between amino acid and ketone molecules. It includes the following two kinds of interactions: (i) hydrophobic interactions (endothermic effect) and (ii) intermolecular interactions between solutes due to specific forces (H-bonding, dipole−dipole interactions, etc.) (exothermic effect).[8]

The value of h_{xy} between amino acid and ketone molecules results from the competition between the above various complex interactions. Among the above effects, the direct interaction between amino acid and ketone molecules plays the dominant role in the overall interaction process. The enthalpic interaction coefficients between amino acids and 2-butanone in the aqueous solutions at 298.15 K are reported in Table 3. With the aim to conveniently compare data with previous work[8] for cyclohex-

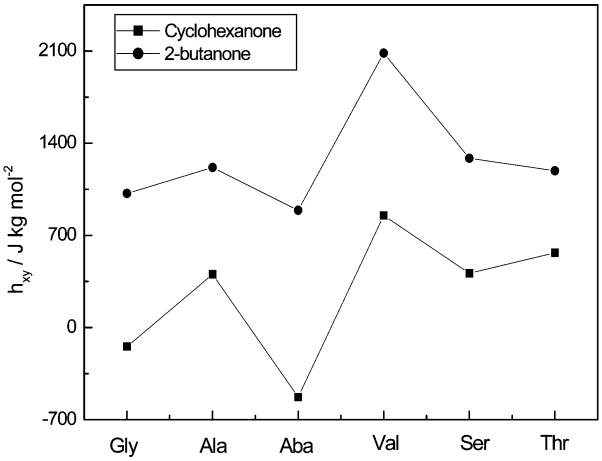
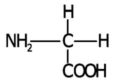
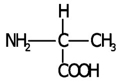
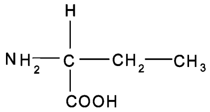
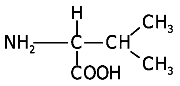
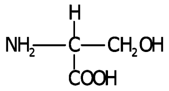
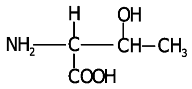
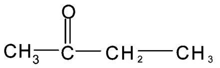
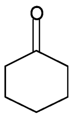


Figure 1. Comparisons between the values of the heterotactic enthalpic pairwise interaction coefficients of amino acids with cyclohexanone and 2-butanone in aqueous solutions at 298.15 K.

Table 3. Chemical Structure of the Molecules Studied in This Paper and in the Literature[8]

molecule	Chemical structure
Glycine	 $NH_2-\overset{H}{\underset{COOH}{C}}-H$
L-α-alanine	 $NH_2-\overset{H}{\underset{COOH}{C}}-CH_3$
L-γ-aminobutyric acid	 $NH_2-\overset{H}{\underset{COOH}{C}}-CH_2-CH_3$
L-α-valine	 $NH_2-\overset{H}{\underset{COOH}{C}}-CH(CH_3)_2$
L-α-serine	 $NH_2-\overset{H}{\underset{COOH}{C}}-CH_2OH$
L-α-threonine	 $NH_2-\overset{H}{\underset{COOH}{C}}-\overset{OH}{C}H-CH_3$
2-Butanone	 $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_3$
Cyclohexanone	

anone, the tendency of h_{xy} values of the two systems is gathered in Figure 1.

As can be seen from Figure 1, in addition to the negative h_{xy} coefficients between cyclohexanone and glycine and L-γ-aminobutyric acid, the experimentally observed positive values of h_{xy} testify to the predominance of endothermic processes over the effect of direct interaction of amino acid with ketone molecules studied in our work.

Heterotactic Enthalpic Pairwise Interaction between Amino Acids and 2-Butanone in Aqueous Solutions. The discrepancy of h_{xy} between 2-butanone and amino acids exhibits the obvious dependence on the side chain structures of the amino acids studied.

It is well-known that glycine is the simplest amino acid in nature. As can be seen, the introduction of methyl groups and isopropyl groups to the hydrocarbon chain of the glycine molecule causes a considerable increase in the value of the enthalpic pairwise interaction coefficient for the pairs of amino acid with 2-butanone. A positive shift in the h_{xy} values can result from the enhanced hydrophobicity of the amino acid molecule in the following sequence: $h_{xy}(Gly) < h_{xy}(Ala) < h_{xy}(Val)$.

It is evident from the h_{xy} values that the position of the amino group has a significant effect on the pairwise interactions. Compared to L-α-alanine, L-γ-aminobutyric acid has one more methyl. It seems that the h_{xy} coefficients should increase in the sequence: $h_{xy}(Ala) < h_{xy}(Aba)$. But that is not the case. The orientation of the amino group at the $C_{(3)}$ carbon atom brings about an increase in direct exothermic interactions between the L-γ-aminobutyric acid and 2-butanone molecules, which seems to be caused by the greater ability of the −NH group of L-γ-aminobutyric acid to form a donor−acceptor hydrogen bond in comparison with that of L-α-alanine which has steric hindrance resulting from the carboxyl group.

The replacement of the hydrogen atom in the alkyl side chain of L-α-alanine with the strongly polar group −OH (L-α-serine) brings about a slight increase in the value of the enthalpic interaction coefficient of 2-butanone with the L-α-serine molecule in comparison with the L-α-alanine molecule. This can be boiled down to the hydrophobic interaction between the −OH group of L-α-serine and the nonpolar group of 2-butanone (making positive contributions to h_{xy}) that predominates over the hydrogen bond interaction (making negative contributions to h_{xy}) between it and the carbonyl group of the 2-butanone molecule.

The addition of a nonpolar $-CH_2$ group to the side chain of L-α-serine, resulting in the formation of L-α-threonine, brings about an increase in the value of the enthalpic pairwise interaction coefficient between the ketone and L-α-threonine in comparison with L-α-serine. However, the steric effect, which can weaken the interaction between L-α-threonine and 2-butanone, becomes more extensive because of the existence of the methyl group. So as a result of the balance between the above effects, the h_{xy} values change in the following order: $h_{xy}(Thr) < h_{xy}(Ser)$.

Comparison between the Heterotactic Enthalpic Pairwise Interaction Coefficients of Amino Acids and 2-Butanone Molecules and Those of Amino Acids and Cyclohexanone Molecules. The results in Figure 1 indicate that the changes of the h_{xy} values for amino acids with 2-butanone and cylcohexanone show a similar trend which results from the similarities of the ketone molecules. However, there are also certain differences in the interaction behavior between 2-butanone, cyclohexanone, and amino acid molecules in aqueous solutions. The discrepancy of h_{xy} between the same kind of amino acid and 2-butanone and cyclohexanone in aqueous solutions mainly depends on the differences in the structure of the ketone molecules studied.

On one hand, molecules of cyclohexanone and 2-butanone differ structurally from one another by two or more $-CH_2$ groups in the former. It seems that hydrophobic interactions in the amino acid + cyclohexanone system are stronger than in the amino acid + 2-butanone system during the direct interaction processes of amino acid and ketone molecules. On the other hand, the dipole moment of 2-butanone ($9.20 \cdot 10^{-30}$ C·m) is less than that of cylcohexanone ($10.27 \cdot 10^{-30}$ C·m).[14] The 2-butanone molecule is, however, able to orient itself in a better arrangement than the cyclohexanone molecule because of the bulkiness of the latter. Cyclohexanone is a solid globular molecule and shows a stable armchair conformation, whereas 2-butanone is hardly flexible because of the nonflexible acetone skeleton and exhibits a plane zigzag conformation. This makes the 2-butanone molecule able to match the tetrahedron structure of water molecules better. Also, it is easier for 2-butanone to form CO···HO hydrogen bonds, which makes the probability of interaction between the polar carbonyl group of the 2-butanone molecule and the amino acid molecule decrease. The hydrophobic−hydrophobic and hydrophobic−hydrophilic interactions are notable in the direct interaction process between amino acid and 2-butanone molecules. Therefore, the net result is that the h_{xy} values are larger for the amino acid + 2-butanone system compared to the amino acid + cyclohexanone system which indicates that the hydrophobic interaction is dominant in the mixing processes of amino acids and 2-butanone aqueous solutions.

To summarize, the structure and the solvation state of considered solutes define the character of their interactions that is reflected in the thermodynamic parameters of intermolecular interactions. The enthalpic pairwise interaction coefficients between the amino acid and the 2-butanone in water can be interpreted in terms of the hydrophobic or hydrophilic effects of the side chain. Compared with the results of the previous work on cyclohexanone, on one hand, the interaction behavior of the same kind of amino acid with 2-butanone is similar to that of cyclohexanone. On the other hand, there also exists the enhanced enthalpic pairwise interaction coefficient in the following sequence: h_{xy}(cyclohexanone) < h_{xy}(2-butanone). These are dramatically contingent on the discrepancies of the structure of amino acids. These can be attributed primarily to the similarities and discrepancies in the structures of the cyclic and linear ketone.

Conclusions

On the basis of the obtained results on mixing and dilution enthalpies, the enthalpic pairwise interaction coefficients, h_{xy}, between amino acids and 2-butanone are calculated. According to the discrepancy in the molecular structure of amino acids, the relative magnitude order of h_{xy} coefficients is interpreted from the point of view of solute−solute and solute−solvent interactions. In addition, compared with the results of previous work for cyclohexanone, the interaction behavior of the same kind of amino acid with 2-butanone is similar to that of cyclohexanone, with the following sequence observed: h_{xy}(cyclohexanone) < h_{xy}(2-butanone). This can be ascribed to the difference in molecular structure and conformation of cyclohexanone and 2-butanone. This work gives a better understanding of the nature of interactions between cyclic and linear ketones and peptides and proteins in aqueous solutions.

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