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Enthalpic interactions between some amino acids and cyclohexanone in aqueous solutions at 298.15 K

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Abstract

The enthalpies of mixing of glycine, L-α-alanine, L-γ-aminobutyric acid, L-α-valine, L-α-serine and L-α-threonine with cyclohexanone in aqueous solutions and their respective enthalpies of dilution have been measured by calorimetry at 298.15 K. Experimental enthalpies of dilution and mixing have been correlated with the virial expansion equation that was obtained with the McMillan–Mayer theory. The enthalpic interaction parameters h_{xy}, h_{xxy} and h_{xyy} of the amino acids studied with cyclohexanone in aqueous solutions have been evaluated, and the heterotactic enthalpic pair interaction coefficients (h_{xy}) are discussed in terms of solute–solute interactions.

Keywords: Amino acid; Cyclohexanone; Heterotactic enthalpic pair-wise interaction coefficient; Solute–solute interactions

1. Introduction

This work is a continuation of our studies on thermodynamic properties of amino acids with electrolytes [1] or nonelectrolytes [2–6] in aqueous solutions. In the present work, we expand the investigations of the enthalpic interaction to amino acids with cyclohexanone in aqueous solutions at 298.15 K.

2. Experimental

Glycine, L-α-alanine, L-γ-aminobutyric acid, L-α-valine, L-α-serine and L-α-threonine (BR) were recrystallized from water-methanol mixture and dried in a vacuum desiccators until their weights became constant. Cyclohexanone (AR grade, from Shanghai Chem. Co.) in this experiment was used without further purification. The water used in the experiments 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 cyclohexanone solution were prepared by weight using a 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.

Enthalpies of dilution and mixing were determined with a ThermoMetric (TAM 2277) flow microcalorimeter operating at (298.15 ± 0.01 K). Details of this apparatus, associated equipment, and the experimental procedure adopted have been reported in previous papers [3–6]. The baseline stability (over a period of 24 h) of the calorimetric equipment is 0.2 μW. Experimental errors in the determinations of the molar enthalpies of dilution and mixing were estimated to be <1%. Every dilution and mixing experiments were repeated three times and the average of three measured values was given. 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 the masses of the liquids through each pump within 8 min. The variation in flow rates was less than 0.1% both before and after a complete experiment.

3. Results and discussion

The enthalpies of mixing of aqueous amino acids solutions and aqueous cyclohexanone solutions and their respective

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dilution enthalpies are given in Supplementary data together with the initial and final molalities of the two solutes.

According to the McMillian–Mayer formalism [7], the excess enthalpy of the ternary solution per kg of water can be expressed in terms of a virial expansion of the molalities:

$$\begin{aligned}\frac{H^{\mathrm{E}}(m_x, m_y)}{\mathrm{w}_1} &= \frac{H(m_x, m_y)}{\mathrm{w}_1} - h_{\mathrm{w}}^{*} - m_x H_{x,\mathrm{m}}^{\infty} - m_y H_{y,\mathrm{m}}^{\infty} \\ &= h_{xx}m_x^2 + 2h_{xy}m_x m_y + h_{yy}m_y^2 + h_{xxx}m_x^3 \\ &\quad + 3h_{xxy}m_x^2 m_y + 3h_{xyy}m_x m_y^2 + h_{yyy}m_y^3 + \cdots \end{aligned} \tag{1}$$

where $H^{\mathrm{E}}(m_x, m_y)/\mathrm{w}_1$ and $H(m_x, m_y)/\mathrm{w}_1$ 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}^{*} the standard enthalpy of 1 kg of pure water; $H_{x,\mathrm{m}}^{\infty}$ and $H_{y,\mathrm{m}}^{\infty}$ are the limiting partial molar enthalpies of species x and y, respectively. The h_{ij} and h_{iij} terms are the enthalpic virial coefficients representing interactions between the subscripted species. m_x and m_y are the molalities of the solutes x and y, respectively.

To make the calculations easier, an auxiliary function ΔH has been introduced:

$$\begin{aligned}\Delta H^{*} &= \Delta H_{\mathrm{mix}} - \Delta H_{\mathrm{dil}}(x) - \Delta H_{\mathrm{dil}}(y) \\ &= H^{\mathrm{E}}(m_x, m_y) - H^{\mathrm{E}}(m_x) - H^{\mathrm{E}}(m_y)\end{aligned} \tag{2}$$

where ΔH_{mix} denotes the mixing enthalpy of the ternary solution, $\Delta H_{\mathrm{dil}}(x)$ and $\Delta H_{\mathrm{dil}}(y)$ are the dilution enthalpies of the corresponding binary solutions.The mixing enthalpy ΔH_{mix} ($\mathrm{J\,kg^{-1}}$) of aqueous x solution and aqueous y solution is calculated from the equation:

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

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

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

$$\Delta H_{\mathrm{dil}} = \frac{P}{(f_{\mathrm{A}} + f_{\mathrm{B}} - m_{x,i}M_x f_{\mathrm{A}})} \tag{4}$$

where M_x is the molar mass of solute ($\mathrm{kg\,mol^{-1}}$) and $m_{x,i}$ is initial molality ($\mathrm{mol\,kg^{-1}}$).The final molality m_x ($\mathrm{mol\,kg^{-1}}$) may be calculated by using the equation:

$$m_x = \frac{m_{x,i}f_{\mathrm{A}}}{[f_{\mathrm{B}}(m_{x,i}M_x + 1) + f_{\mathrm{A}}]} \tag{5}$$

and combining Eqs. (1) and (2):

$$\frac{\Delta H^{*}}{\mathrm{w}_1} = 2h_{xy}m_x m_y + 3h_{xxy}m_x^2 m_y + 3h_{xyy}m_x m_y^2 + \cdots \tag{6}$$

In the studied systems, amino acid is identified as species “x” and cyclohexanone is considered as species “y”. In Table 1 the results of fitting the enthalpies of mixing and dilution to Eq. (6) by an analysis of nonlinear least-squares regressions are given. Because it is difficult to interpret the higher-order h coefficients, only the heterotactic enthalpic pair-wise coefficient h_{xy} is discussed here.

Enthalpic pair interaction coefficients represent the thermochemical result when two solvated solutes interact in solution. The enthalpic pair interaction coefficients are the sum of the processes occurring in the systems discussed here: (i) partial dehydration of two solute particles (endothermic effect); (ii) hydrophobic interactions (endothermic effect); (iii) intermolecular interactions between solutes due to specific forces (H-bonding, dipole–dipole interactions, etc.) (exothermic effect) [8].

The h_{xy} coefficients for the interactions between cyclohexanone and amino acid molecules in aqueous solutions are the results of competition of the above complex interactions between the two kinds of solute molecules. The h_{xy} values between cyclohexanone and L-α-alanine, L-α-valine, L-α-serine and L-α-threonine are all positive. This suggests that the interaction of cyclohexanone with these amino acid molecules in aqueous solutions is an endothermic process and the partial dehydration effect and, perhaps, the hydrophobic interactions dominate over specific forces during the interaction process. While the negative values of h_{xy} between cyclohexanone and glycine, L-γ-aminobutyric acid indicate that the interaction process is an exothermic process and can be ascribed to the predominance of specific forces of solutes (exothermic effect, negative contribution to h_{xy}) against hydrophobic interactions and partial dehydration of solutes, which contribute positively to the value of h_{xy}.

Comparing to glycine, L-α-alanine and L-α-valine have one hydrogen atom on the α-carbon replaced by a methyl and by an isopropyl, respectively, which results in the hydrophobic interaction (making positive contributions to h_{xy}) strengthen notably with the prolongation of non-polar side chains.

Table 1
Heterotactic enthalpic interaction coefficients between amino acids and cyclohexanone in aqueous solutions at 298.15 K

Solutes $x+y$	h_{xy} ($\mathrm{J\,kg\,mol^{-2}}$)	h_{xxy} ($\times 10^{-4}\,\mathrm{J\,kg^2\,mol^{-3}}$)	h_{xyy} ($\times 10^{-4}\,\mathrm{J\,kg^2\,mol^{-3}}$)	R^2
Glycine + cyclohexanone	−49.45	−10.22	10.68	0.9973
L-α-Alanine + cyclohexanone	437.1	−13.47	13.78	0.9991
L-γ-Aminobutyric acid + cyclohexanone	−527.6	412.0	−420.7	0.9953
L-α-Valine + cyclohexanone	851.1	2.315	−2.303	0.9998
L-α-Serine + cyclohexanone	411.7	−26.68	27.27	0.9947
L-α-Threonine + cyclohexanone	568.9	−10.12	10.30	0.9956

Therefore the h_{xy} coefficients are in the following sequence: h_{xy}(L-α-valine) > h_{xy}(L-α-alanine) > h_{xy}(glycine). There exists one more methyl for L-γ-aminobutyric acid than L-α-alanine. It seems that the h_{xy} coefficients should increase in the order h_{xy}(L-γ-aminobutyric acid) > h_{xy}(L-α-alanine). But the experimental result is contrary to expectation. The cause can be boiled down to the structural discrepancy between γ-amino acid and α-amino acid. Since there does not exist steric effect resulting from the carboxyl group which has a relative large volume, the former has a proton donor group, the NH group, are capable of association through formation of NH···OC hydrogen bonds. The negative contribution bringing by the hydrogen bonds is predominant over the positive contributions resulting from the hydrophobic interaction and dehydration.

The hydroxyl group, which can participate in hydrogen bonding on pair-wise interaction, of α-amino acid can make great influence on the h_{xy} values. L-α-Serine is similar to L-α-alanine except that it has an OH group replacing a hydrogen atom of the methyl group, which strengthens its hydrophobic interaction (making positive contributions to h_{xy}) and hydrogen bond interaction (making negative contributions to h_{xy}) between it and cyclohexanone molecule. Since the former dominates over the interaction process, the h_{xy} coefficients decrease as follows h_{xy}(L-α-serine) > h_{xy}(L-α-alanine). There is one methyl on the side chain of L-α-threonine as compared to L-α-serine. As a general rule, the hydrophobic interaction between L-α-threonine and cyclohexanone is stronger than that of L-α-serine. So there exists the following rule: h_{xy}(L-α-threonine) > h_{xy}(L-α-serine). As can be seen from Table 1, the experimental result is consistent with the expectation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.07.009.

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