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ENTHALPIES OF SOLUTION OF SOME *L*-α-AMINO ACIDS IN AQUEOUS SOLUTIONS OF UREA AT 298.15 K

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Abstract

The standard molar enthalpies of solution of glycine, *L*-α-alanine, *L*-α-valine and *L*-α-leucine in aqueous solutions of urea at 298.15 K were determined by calorimetry. The results obtained were used to calculate the heterogeneous enthalpic interaction coefficients between the zwitterions of the *L*-α-amino acids and a molecule of urea in water. The values of the resultant enthalpic interaction coefficients are interpreted in terms of the effects of the hydrophobic alkyl groups on the interactions between the zwitterions of the *L*-α-amino acids and a polar molecule of urea in aqueous solutions.

Keywords: aqueous solutions of urea, enthalpies of solution, *L*-α-amino acids

Introduction

Thermodynamic studies on the interactions in aqueous solution between *L*-α-amino acids and organic molecules present in living organisms or possessing functional groups identical to those in protein polypeptide chains have been performed in many research centres [1–5]. In our laboratory, previous studies were devoted to the examination of interactions between the simplest amino acid, glycine, and amides, ureas [6, 7], alcohols and diols [8, 9].

The aim of the present study was to determine the enthalpic interaction coefficients [10, 11] in the system amino acid–urea in aqueous solution. Urea is present in living organisms as a product of the degradation of nitrogen compounds. It contains a peptide group (–CONH–) and its aqueous solutions are used for protein denaturation in biochemical laboratories.

Experimental

Glycine (G) (99.5% from Merck), *L*-α-alanine (A), *L*-α-valine (V), *L*-α-leucine (L) and urea (U) (all 99% from Merck) were crystallized from water–methanol mixtures and dried under reduced pressure at 323 K. The water used in the experiments was deionized and distilled twice.

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The enthalpies of solution were determined with a calorimeter of isoperibol type [6, 7]. The temperature sensitivity was about $4\cdot 10^{-5}$ K, and the temperature stability of the thermostat was better than 10^{-3} K. The standard enthalpies of solution, ΔH_s^0, of amino acids were calculated as the mean of the results of 8 to 12 independent measurements within the concentration range 0.001–0.015 mol kg^{-1} water. The ampoules containing the examined amino acid and aqueous urea solutions were weighed with Sartorius RC 210D balance.

Results and discussion

The solution enthalpies of the *L*-α-amino acids in aqueous solutions of urea containing 0.5–4.0 mol urea kg^{-1} water, in the amino acid concentration range 0.001–0.015 mol kg^{-1} solvent, were measured at 298.15 K. The calculated standard solution enthalpies of the *L*-α-amino acids, $\Delta H^0_{S(W+U)}$, in aqueous solutions of urea, together with their standard deviations, are presented in Table 1. The solution enthalpies of these *L*-α-amino acids in aqueous solutions of urea display a decrease in the endothermic effect of the solutions with increasing urea concentration (Table 1).

Table 1 Standard enthalpies of solution of *L*-α-amino acids in aqueous urea solutions at 298.15 K

m/ mol urea kg^{-1} H_2O	$\Delta H^0_{S(W+U)}$/kJ mol^{-1}			
	Gly	Ala	Val	Leu
0.0	14.20±0.06[a]	7.67±0.05[b]	3.12±0.07[b]	3.41±0.07
0.5	13.83±0.06[a]	7.41±0.06		
1.0	13.47±0.06[a]	7.24±0.07	2.89±0.08	3.25±0.08
1.5	13.15±0.07[a]	7.02±0.06		
2.0	12.86±0.05[a]	6.86±0.06	2.73±0.07	3.08±0.07
2.5	12.65±0.06	6.69±0.07		
3.0	12.35±0.07	6.53±0.07	2.55±0.08	2.97±0.08
4.0	12.00±0.07	6.29±0.07	2.43±0.08	2.91±0.08

[a] Ref. [12], [b] Ref. [13]

From the standard solution enthalpies of the amino acids in water, $\Delta H^0_{S(W)}$ [12, 13], and the aqueous solution of urea, $\Delta H^0_{S(W+U)}$, the enthalpic heterogeneous coefficients of the *L*-α-amino acid molecule–urea molecule interactions in water were estimated [11, 14]. The standard solution enthalpies of the amino acids in water–urea mixtures are presented as

$$\Delta H^0_{S(W+U)} = \Delta H^0_{S(W)} + bm_U + cm_U^2 + \ldots \qquad (1)$$

where m_U is the molal concentration of urea (mol kg^{-1} water), while b and c are coefficients that can be determined by a least-squares procedure.

The parameter b, which represents the limiting slope of the function $\Delta H^{o}_{S(W+U)}$ *vs.* m_U, is simply related to the McMillan-Mayer [15] heterogeneous pair interaction coefficient $h_{XU}=b/2$ [7] (Table 2). The parameter c is related to a triplet interaction coefficient $h_{XUU}=c/3$. The interpretation of the triplet interaction coefficients (Table 2) is obscured by the fact that they also contain pairwise interaction terms [15, 16] and for this reason they will not be discussed in the present paper.

Table 2 Heterogeneous enthalpic interaction coefficients for *L*-α-amino acids with urea in water at 298.15 K

L-α-amino acid	CH_2	h_{XU}/J kg mol^{-2}	h_{XUU}/J kg^2 mol^{-3}
Glycine	0.5	–390.2	19.1
Alanine	1.5	–238.2	11.0
Valine	3.5	–116.0	4.7
Leucine	4.5	–98.0	5.8

For the four aqueous urea solvent systems studied, the experiment data yield explicit expressions for Eq. (1):

$$\text{(G)}\ \Delta H^{o}_{S(W+U)} = 14.20 - 0.7805 m_U + 0.0575 m_U^2 + \ldots\ (R^2=0.9993)$$

$$\text{(A)}\ \Delta H^{o}_{S(W+U)} = 7.67 - 0.4765 m_U + 0.0329 m_U^2 + \ldots\ (R^2=0.9991)$$

$$\text{(V)}\ \Delta H^{o}_{S(W+U)} = 3.12 - 0.2321 m_U + 0.0148 m_U^2 + \ldots\ (R^2=0.9985)$$

$$\text{(L)}\ \Delta H^{o}_{S(W+U)} = 3.41 - 0.1961 m_U + 0.0174 m_U^2 + \ldots\ (R^2=0.9970)$$

The enthalpic heterogeneous pair interaction coefficients constitute a measure of the interactions between a hydrated amino acid zwitterion and a hydrated urea molecule in water. This effect may be assumed to be a sum of three contributions.

The essential process involves a direct interaction between a zwitterion ($-CHCOO^-NH_3^+$) and a polar urea molecule, which is exothermic. However, for the direct interaction to occur a number of water molecules have to be removed from the hydration shells of both molecules, and it is therefore necessary to consider partial dehydration of the urea molecule hydration shells, this being an endothermic process, and also the endothermic effect resulting from the removal of a number of water molecules from the hydration zone of the amino acid zwitterion. For amino acids with alkyl side-chains, this process is accompanied by an additional effect generated by the non-polar groups. The water molecules surrounding these groups do not interact with them, which makes the hydrogen-bonds between them stronger. The cooperation of the hydrogen-bonds leads to this effect being transferred on to the water molecules in the zwitterion hydration layer, which reinforces the interaction between the water molecules and the polar moiety of the amino acid molecule. Consequently, the removal of a number of water molecules from the reinforced hydration layer of the zwitterion requires the supply of more energy, and hence its endothermic character increases.

The enthalpic pair interaction coefficients between a molecule of glycine and a molecule of urea have negative values. This is indicative of the strongly exothermic effect of a direct interaction between a zwitterion of glycine and a polar molecule of urea predominating over the endothermic effect of partial dehydration of the solvation layers of the glycine and urea molecules in water. Replacement of a hydrogen atom in a molecule of glycine by an alkyl group causes an increase in the enthalpic pair interaction coefficients h_{XU}, this increase depending on the number and size of the alkyl groups (Table 2). This can be explained by the reinforcement of the hydrogen-bonds of the water molecules in the hydrating layer zwitterion of the amino acid (directly combined with an alkyl group) and the urea molecule interacting with it. This brings about an increase in the endothermic dehydrating effect of the interacting molecules, which increases with increasing alkyl group size. The dependence of h_{XU} on the number of CH_2 groups in the *L*-α-amino acid molecule is linear (Fig. 1) (with the CH_3 group corresponding to $1.5CH_2$ and the CH group corresponding to $0.5CH_2$ [17, 18]), as described by the equation $h_{XU}=-387.25+70.66n_{CH_2}$ ($R^2=0.9137$).

The constant term in this equation describes the contribution of the interaction of the zwitterion of the amino acid and a molecule of urea, $h_{(\pm U)}$, to the het-

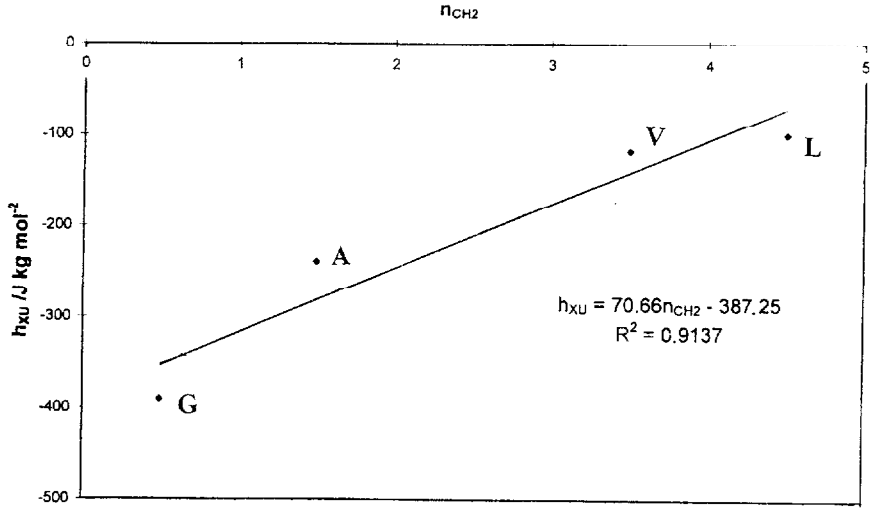

Fig. 1 Dependence of enthalpic pair interaction coefficients for interactions of *L*-α-amino acids and urea on the number of CH_2 groups in the amino acids

erogeneous enthalpic pair interaction coefficient. A negative value of $h_{(\pm U)}$ testifies to a stronger exothermic effect of the direct zwitterion–polar molecule interaction than the effect of dehydration of the hydrating shells of the interacting polar groups. The slope of this function measures the contribution of the CH_2 group to the value of the enthalpic pair interaction coefficient h_{XU}; the presence of this group brings about a higher reinforcement of the hydrogen-bonds in the shells of the interacting zwitterions of this amino acid.

The enthalpic pair interaction coefficient h_{XU}, which is a measure of the interaction between two molecules, depends to a considerable extent on the interaction between the molecules (ions) under investigation and solvent water. All the processes that stabilize the hydrogen-bonds of water (e.g. hydrophobic hydration) weaken the direct interactions between the polar groups of the interacting solute molecules (ions).

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