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Enthalpy of transfer of amino acids from water to aqueous glucose solutions at 298.15 K

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Abstract

The enthalpies of solution of amino acids, glycine, *L*-alanine, *L*-serine and *L*-proline were measured in water and in aqueous glucose solutions at 298.15 K with a microcalorimeter. Enthalpies of transfer of amino acids from water to aqueous glucose solutions were derived. The processes of solution of glycine, *L*-alanine and *L*-serine are endothermic, while that of *L*-proline is exothermic. Enthalpies of transfer of glycine and *L*-serine are negative, while those of *L*-alanine and *L*-proline are positive. The transfer enthalpies suggest that the highly polar zwitterion group and OH group of the molecule of amino acids cause a breakdown of structure in the aqueous glucose solutions. The non-polar side chains produce order in proportion to the size of the side chain. The breakdown and ordering effects are greater in water than in glucose solutions. *L*-Serine is quite special; there are a minimum and a maximum in the plot of transfer enthalpies vs. glucose concentrations. All results are discussed using hydrophobic interactions and structure-breaking–structure-making theory. © 1998 Elsevier Science B.V.

Keywords: Amino acids; Enthalpies of solution; Glucose; Microcalorimeter

1. Introduction

It was found that sugars and polyols help in stabilizing the native conformation of globular proteins [1–8]. Many studies [9–11] have been done on the alteration of water structure using the hypothesis of polyol-induced stabilization of proteins. But the interpretation about water-structure modifications by polyhydroxy compounds are not identical [12]. This may be because most of polyhydroxy compounds have both hydrophobic and hydrophilic parts, hence the promotion of water structure by hydrophobic hydration [13] tends to cancel the effect of structure breakdown by hydrophilic sites. The highly ordered structure of water owing to the hydrogen bonds and the resemblance of polyhydroxy compound structure to water structure make the whole situation complex.

Of the thermodynamic functions describing solvation or solution processes, entropy is significantly connected with the solvent structure perturbations brought about by the introduction of solute. Unfortunately, only limited entropy data in mixed solvents are available. Enthalpy values are more widely available and are more frequently used. As is well known, plots of entropy changes vs. mixed solvent compositions are analogous to corresponding enthalpy plots. Since amino acids are the basic components of proteins and are considered to be the model compounds of proteins, it is necessary to study model compounds

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owing to the complex structure of the biological macromolecules. Therefore, in this paper we report the enthalpy of transfer of glycine, *L*-alanine, *L*-serine and *L*-proline from water to aqueous solutions of glucose to understand the structure features and solute-solvent interactions in the protein-stabilizing media.

2. Experimental

Biochemical reagent glycine, *L*-alanine, *L*-serine and *L*-proline were used without further purification. Analytical grade KCl was recrystallized from water. The crystals were then ground in an agate mortar and sieved through a No. 300 mesh sieve, which guaranteed all solute particles were in the same size range (<48 μm in diameter). Afterward, they were dried in an infrared drier until there were no significant changes in mass. Analytical grade D-glucose was dried in a vacuum desiccator for 48 h at room temperature. Water was deionized and distilled using a quartz sub-boiling purifier.

The enthalpies of solution were obtained using a twin heat flux microcalorimeter model RD496-II (manufactured by the 2905 factory of the Nuclear Industry Department of China). Its heat-flux detectors of sample and reference are composed of 496 pairs of thermocouples, respectively. The calorimeter has a high temperature-control accuracy (±0.001°C), a high stability (±0.1 μV for base line) and a high sensitivity (62.13 mV W^{-1} at 298.15 K). The mixing vessel of the microcalorimeter is divided into two parts by a drop partition, the lower part is ca. 4 ml and the upper part ca. 6 ml. The partition was first placed into the vessel with a special device, then the solid was introduced into the lower part and the solvent into the upper part. The lower part of the reference vessel is empty, the upper part is the same solvent as the sample vessel. The partition is released through a pole, then the solid and solvent become mixed, and the enthalpies of solution recorded automatically by a computer. The calorimeter was calibrated by the solution enthalpy of KCl in water with the mole ratio of 1 : 500. All the substances were weighed on a Metter (AE200) balance with a sensitivity of 0.1 mg. The final molality of amino acids was 0.1100 mol kg^{-1}; the weight percentage range of glucose was from 0 to 50. All experiments were performed at least twice and were reproducible within 1%.

3. Results and discussion

The enthalpies of solution of glycine, *L*-alanine, *L*-serine and *L*-proline in glucose solutions are presented in Table 1. Our result of the molar enthalpy of solution of glycine in water (14 120 J mol^{-1}) agrees well with the value obtained by Lu and Xie [14] (14 110 J mol^{-1}).

The enthalpies of solution of glycine, *L*-alanine and *L*-serine are endothermic in water and aqueous glucose solutions, while those of *L*-proline are exothermic. Enthalpies of solution of glycine and *L*-proline decrease monotonically with increasing glucose concentration, while those of *L*-alanine increase a little. Enthalpies of solution of *L*-serine are quite complex: they decrease first, then increase and reach a maximum between 15–20 wt% glucose solution, before they decrease again.

The enthalpies of transfer, ΔH_{trs} can be obtained from the differences between $\Delta H_{sol,ws}$, the enthalpies of solution of amino acids in glucose solutions, and $\Delta H_{sol,w}$, the enthalpies of amino acids in pure water:

$$\Delta H_{trs} = \Delta H_{sol,ws} - \Delta H_{sol,w} \quad (1)$$

Fig. 1 explicitly shows the behavior of the enthalpy of transfer of amino acids from water to the aqueous

Table 1
Enthalpies of solution ΔH_{sol} (in J mol^{-1}) of amino acids in aqueous glucose solutions at 298.15 K

D-glucose		ΔH_{sol}/(J mol^{-1})			
wt%	(m/mol kg^{-1})	glycine	*L*-alanine	*L*-serine	*L*-proline
0	0	14 120	7600	10 860	−3130
5.0	0.292	13 930	7800	10 310	−2847
10.0	0.617	13 710	7920	9960	−2642
14.9	0.972	13 620			
15.0	0.980			10 260	
20.0	1.388	13 450	8090	10 240	−2168
25.0	1.850	13 220		9980	
30.0	2.379	12 910	8080	9870	−1985
35.0	2.989	12 740			
40.0	3.700	12 440	8060	9480	−1825
45.0	4.541	11 910			
50.0	5.5506	11 460		9110	−1730

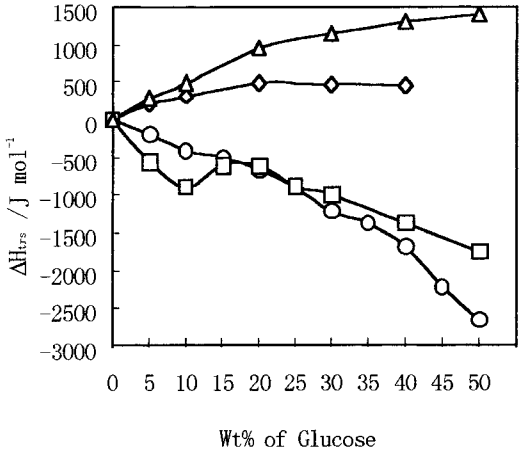

Fig. 1. Enthalpy of transfer of amino acids from water to aqueous glucose solutions at 298.15 K. (○), Glycine; (◇), *L*-alanine; (□), *L*-serine; (△), *L*-proline.

glucose solutions. Transfer enthalpies of glycine and *L*-serine are negative, while those of *L*-alanine and *L*-proline are positive.

The types of interactions occurring between glucose molecules and the amino acid molecules can be classified as follows:

1. Hydrophilic–ionic group interacts between the OH groups of glucose and the zwitterionic centers of the amino acids [15].
2. Hydrophilic–hydrophilic group interacts between the OH group of glucose and the OH group of the *L*-serine through hydrogen bonding.
3. Hydrophilic–hydrophobic group interacts between the OH group of glucose and non-polar groups of the amino acids [15].
4. Hydrophobic–hydrophobic group interacts of non-polar groups between glucose and amino acids.

There are a number of studies in the literature [5,16,17] which support the idea that glycine is a net structure breaker due to its highly polar zwitterion portion, while the higher aliphatic homologs are structure makers in water. Some authors concluded [18–20] that polyhydroxy compounds have a structure-breaking effect in water. Taylor and Rowlinson [21] found that a strong hydrogen bonding exists between glucose and surrounding water molecules, which is stronger than the hydrogen bonding within the water molecule itself. Using the foregoing descriptions, it is more difficult to make or break the solvent structure in glucose solution than in water. Thus, we can assert that glycine is less effective as a structure breaker and *L*-alanine is less effective as a structure maker in glucose than in water.

The structure of *L*-proline and *L*-serine are quite different from those of glycine and *L*-alanine. *L*-proline is the only native amino acid which has an azole. The cyclic structure diminishes the interactions between the *L*-proline molecules due to the steric effect, which makes solvation easy. So, its enthalpies of solution are exothermic. Its relatively large non-polar group makes hydrophobic interactions predominant. Therefore, the enthalpies of transfer increase with increasing glucose concentrations and are more positive than that of *L*-alanine. The side chain of *L*-serine has a hydroxyl which makes the enthalpies of transfer complex. It was said that two interacting molecules would prefer a configuration where favorable interactions between like groups are maximized – the hydrophobic group interacts with hydrophobic group and the hydrophilic group interacts with hydrophilic group [22–24]. Interactions between *L*-serine and glucose include all the four types. In addition, it is possible for a molecule of *L*-serine to interact with a glucose molecule side by side. That means the ionic group and OH group of an *L*-serine molecule interact with the different OH groups of the same glucose molecule. In this situation, the non-polar groups of *L*-serine and glucose become closer and the hydrophobic interactions are enhanced. In the region of 0–10 wt%, the side-by-side interactions are quite poor because of the relatively few glucose molecules in the solvent. So, hydrophilic interactions are predominant and the enthalpies of transfer decrease sharply. In the region of 10–20 wt%, with increasing glucose concentrations, hydrophobic interactions increase, so that the enthalpies of transfer increase as well. When the glucose concentrations are >20%, interactions between glucose molecules are strong and the hydrophobic interactions are inhibited, so the enthalpies of transfer decrease again, but much slower than in low glucose concentration solutions.

At present, many studies focus on the thermodynamic property of amino acids with non-polar side chains [14,25–28] in different solvents. Amino acids with polar side chains and some special amino acids such as *L*-proline need draw more attention in order

to deepen the understanding of solute–solvent interactions.

Acknowledgements

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