Transfer Enthalpies of Amino Acids and Glycine Peptides from Water to Aqueous Solutions of Sugar Alcohol at 298.15 K†

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Enthalpies of solution of glycine, L-alanine, L-serine, L-threonine, diglycine, and triglycine in aqueous solutions of D-sorbitol, D-mannitol, and xylitol have been measured by calorimetry at 298.15 K. These data have been used to calculate the transfer enthalpies of the amino acids and glycine peptides from water to aqueous solutions of sugar alcohol. It has been observed that all the values of the transfer enthalpies are negative and decrease with an increase of the concentration of sugar alcohol in the aqueous solutions. The results are discussed in terms of solute−solute and solute−solvent interactions. The primary interactions between the zwitterionic group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule exhibit exothermic effects and make negative contributions to the transfer enthalpies. The hydrophilic side chains in the solute molecules also enhance these negative contributions effectively.

Introduction

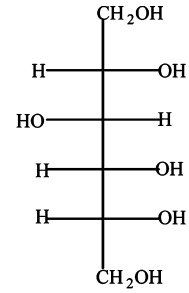
Sugar alcohols are widely distributed as artificial nutritive sweeteners in food and beverages (including diet drinks). Take sorbitol and mannitol for example, they are commonly used in the treatment of patients with oliguric renal failure. Administered as a hypertonic infusion solution, they enhance distal tubule delivery of Na^+ and water resulting in increased urine formation; i.e., they exhibit a diuretic effect.[1] Sugars and polyols are well-known stabilizing agents in their native state.[2−4] Amino acids and peptides, as model compounds of protein, are of fundamental importance in life system research.[5−10] Studies on the interaction between natural amino acids/peptides and sugar alcohols in water are helpful in understanding the essence of some biological phenomena.

In the present work, we investigate the transfer enthalpies of glycine, L-alanine, L-serine, L-threonine, diglycine, and triglycine from water to aqueous solutions of D-sorbitol, D-mannitol, and xylitol at 298.15 K. These sugar alcohols are similar in structure, offering an opportunity to evaluate thermodynamic properties in terms of different solute structures.

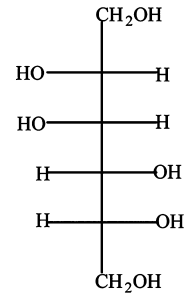
Experimental Section

Materials. Amino acids, glycine ($CH_2(NH_2)COOH$), L-alanine ($CH_3CH(NH_2)COOH$), L-serine ($HOCH_2CH(NH_2)COOH$), and L-threonine ($CH_3CH(OH)CH(NH_2)COOH$), were biological reagents with mass fraction > 99.0 % obtained from the Shanghai Chemical Co., China. They were twice recrystallized from aqueous ethanol solution and dried under vacuum at 348 K for 6 h before use. Peptides, diglycine ($H_2NCH_2CONHCH_2COOH$), and triglycine ($H_2NCH_2CONHCH_2CONHCH_2COOH$), and sugar alcohols, D-sorbitol, D-mannitol, and xylitol, were products of Fluka and Aldrich, respectively, and they were used as received. The structures of the sugar alcohols are shown in Scheme 1. All the solutions investigated were prepared freshly with twice-distilled water. The samples were weighed on a Mettler AE 200 balance with a sensitivity of 0.0001 g. The

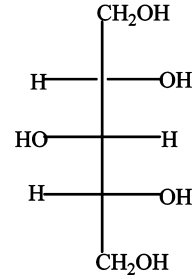
Scheme 1. Structures of D-Sorbitol, D-Mannitol, and Xylitol



D-sorbitol



D-mannitol



xylitol

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Table 1. Enthalpies of Solution ($\Delta_{sol}H_m$) of Amino Acids and Glycine Peptides in Aqueous Sugar Alcohol Solutions at 298.15 K

	m	$\Delta_{sol}H_m$/kJ·mol^{-1}					
sugar alcohol	mol·kg^{-1}	glycine	L-alanine	L-serine	L-threonine	diglycine	triglycine
	0	14.17[a] ± 0.02	7.60[a] ± 0.01	11.30[a] ± 0.03	10.35[a] ± 0.01	11.81[a] ± 0.03	16.06[a] ± 0.01
	0	14.20[b]	7.67[b]	11.49 [c]	10.33[c]		
D-sorbitol	0.0999	14.10 ± 0.01	7.55 ± 0.01	11.21 ± 0.02	10.30 ± 0.01	11.41 ± 0.03	14.89 ± 0.02
	0.1997	13.90 ± 0.02	7.52 ± 0.01	10.98 ± 0.01	10.23 ± 0.03	10.92 ± 0.02	14.26 ± 0.01
	0.2998	13.73 ± 0.02	7.46 ± 0.02	10.73 ± 0.01	10.14 ± 0.04	10.44 ± 0.01	13.59 ± 0.03
	0.3997	13.51 ± 0.01	7.39 ± 0.01	10.50 ± 0.03	10.02 ± 0.04	9.97 ± 0.03	12.96 ± 0.01
	0.4999	13.35 ± 0.01	7.28 ± 0.01	10.32 ± 0.01	9.88 ± 0.01	9.60 ± 0.03	12.28 ± 0.01
	0.6003	13.21 ± 0.03	7.20 ± 0.01	10.21 ± 0.01	9.77 ± 0.04	9.19 ± 0.04	11.63 ± 0.01
	0.6999	13.02 ± 0.04	7.09 ± 0.02	10.04 ± 0.01	9.68 ± 0.01	8.79 ± 0.02	11.21 ± 0.02
	0.7998	12.81 ± 0.01	6.97 ± 0.01	9.85 ± 0.01	9.60 ± 0.03	8.37 ± 0.01	11.04 ± 0.02
D-mannitol	0.0998	14.14 ± 0.02	7.59 ± 0.01	11.27 ± 0.01	10.34 ± 0.02	11.53 ± 0.03	15.46 ± 0.04
	0.1996	14.08 ± 0.04	7.58 ± 0.04	11.15 ± 0.01	10.29 ± 0.01	11.20 ± 0.02	15.02 ± 0.02
	0.2997	13.96 ± 0.01	7.54 ± 0.03	10.98 ± 0.04	10.24 ± 0.01	10.87 ± 0.01	14.52 ± 0.04
	0.3999	13.80 ± 0.04	7.47 ± 0.01	10.79 ± 0.01	10.16 ± 0.01	10.42 ± 0.03	13.99 ± 0.01
	0.4999	13.65 ± 0.03	7.39 ± 0.01	10.55 ± 0.03	10.09 ± 0.03	10.15 ± 0.03	13.46 ± 0.01
	0.5997	13.43 ± 0.04	7.32 ± 0.01	10.33 ± 0.01	9.99 ± 0.03	9.93 ± 0.04	12.89 ± 0.02
	0.6998	13.23 ± 0.01	7.23 ± 0.03	10.18 ± 0.02	9.85 ± 0.01	9.66 ± 0.02	12.41 ± 0.03
	0.7996	13.02 ± 0.02	7.15 ± 0.01	9.95 ± 0.04	9.73 ± 0.01	9.49 ± 0.01	11.99 ± 0.03
xylitol	0.1002	14.11 ± 0.01	7.56 ± 0.01	11.22 ± 0.01	10.31 ± 0.01	11.43 ± 0.03	15.11 ± 0.02
	0.1996	13.96 ± 0.01	7.54 ± 0.01	11.01 ± 0.01	10.25 ± 0.04	11.03 ± 0.02	14.44 ± 0.02
	0.3001	13.79 ± 0.02	7.47 ± 0.02	10.77 ± 0.02	10.17 ± 0.03	10.55 ± 0.01	13.85 ± 0.03
	0.3997	13.59 ± 0.01	7.41 ± 0.01	10.57 ± 0.01	10.05 ± 0.04	10.13 ± 0.03	13.29 ± 0.01
	0.5001	13.41 ± 0.03	7.29 ± 0.01	10.32 ± 0.01	9.92 ± 0.01	9.79 ± 0.03	12.57 ± 0.03
	0.6002	13.26 ± 0.01	7.21 ± 0.02	10.23 ± 0.01	9.82 ± 0.03	9.36 ± 0.04	11.96 ± 0.01
	0.6998	13.08 ± 0.01	7.18 ± 0.04	10.09 ± 0.02	9.73 ± 0.02	8.94 ± 0.02	11.49 ± 0.01
	0.7998	12.86 ± 0.03	7.02 ± 0.02	9.88 ± 0.01	9.64 ± 0.02	8.61 ± 0.01	11.24 ± 0.04

[a] This work. [b] Ref 6. [c] Ref 7.

molality of each amino acid or glycine peptide solution was prepared at 0.1000 mol·kg^{-1} of water.

Microcalorimetric Measurements. Measurements on the enthalpies of solution at 298.15 K were carried out with an RD 496-II microcalorimeter, which was manufactured by the 2905 factory of the Nuclear Industry Department of China, as previously described.[5] During the experiments, the mixing vessel of the microcalorimeter was divided into two parts by a drop partition. The partition was first placed into the vessel with a special device. Then the solid sample was introduced into the lower part and the solvent into the upper part. The lower part of the reference vessel was empty, and the upper part contained the same solvent as the sample vessel. The apparatus was calibrated by the solution enthalpy of KCl in water with the mole ratio of 1:500. The calorimetric curves were recorded automatically, and the enthalpies of solution were reported on the basis of three replicates. The calorimeter had a high temperature control precision (± 0.001 K) and a high stability (± 0.1 μV for baseline).

Results and Discussion

The calorimetric results of the enthalpies of solution, $\Delta_{sol}H_m$, for glycine, L-alanine, L-serine, L-threonine, diglycine, and triglycine in pure water and in aqueous solutions of sugar alcohol with different concentrations are given in Table 1. The values of $\Delta_{sol}H_m$ in pure water are in good agreement with those found in the literature.[6,7] The transfer enthalpy, $\Delta_{tr}H_m$, is derived from the difference between the enthalpy of solution in each aqueous solution of sugar alcohol, $\Delta_{sol}H_{m(s)}$, and that in pure water, $\Delta_{sol}H_{m(w)}$, respectively.[5]

$$\Delta_{tr}H_m = \Delta_{sol}H_{m(s)} - \Delta_{sol}H_{m(w)} \quad (1)$$

The changes of $\Delta_{tr}H_m$ of the amino acids and glycine peptides against the concentrations of the sugar alcohol solutions are shown in Figures 1, 2, and 3. It follows that the transfer enthalpies of the amino acids and glycine peptides from water to aqueous solutions of sugar alcohol are monotonically negative over the investigated concentration ranges.

Different interactions between the amino acid/peptide molecules and the sugar alcohol molecules are considered to explain the experimental phenomena. The types of intermolecular actions can be classified as follows:[8] (a) partial dehydration of the amino acid molecule and the sugar alcohol molecule (endothermic process); (b) direct interaction between the zwitterionic group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule (exothermic process); (c) interaction between the hydrophobic group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule (endothermic process). In the present systems, the primary interaction is that between the zwitterionic group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule. As a result, the transfer enthalpies of amino acids and glycine peptides from water to the aqueous solutions of sugar alcohol are negative and decrease with the increase of the concentration of sugar alcohols.

The value of the transfer enthalpy of glycine from water to the aqueous solutions of sugar alcohol is negative. The α carbon atom of an amino acid molecule is connected to the charged end groups ($-NH_3^+$, $-COO^-$) and a side group. The contributions of electrostatic interactions from the charged end groups should be similar for different amino acid molecules. So the different structures of the side groups play significant roles in the differences of the transfer enthalpies. The replacement of hydrogen with a polar/nonpolar group brings the transfer enthalpy increases in the sequence: L-serine < glycine < L-alanine ≈ L-threonine. The possible reason is that the interaction between the hydrophobic side group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule is endothermic, which counteracts part of the exothermic effects. In contrast, the interaction between the hydrophilic side group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule is exothermic. So, the

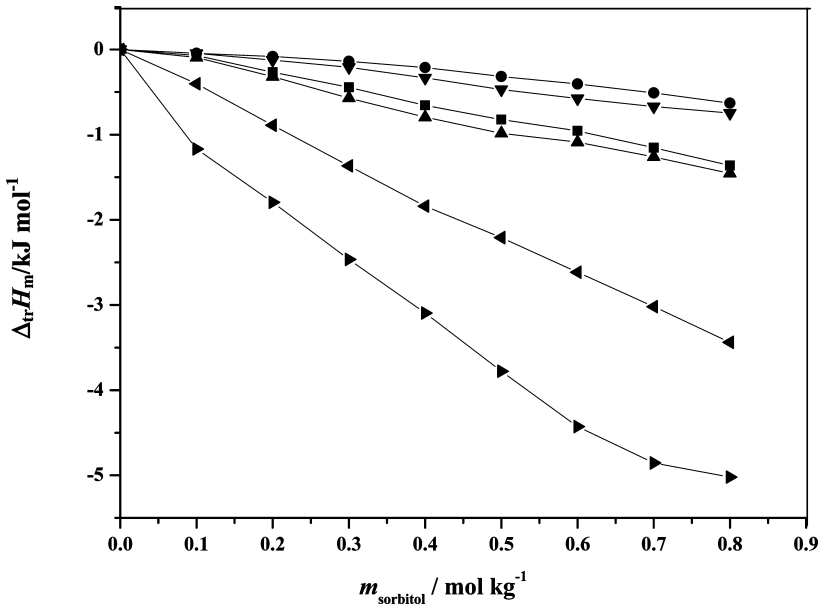

Figure 1. Enthalpies of transfer ($\Delta_{tr}H_m$) of amino acids and glycine peptides from water to aqueous solutions of D-sorbitol at 298.15 K (■, glycine; ●, alanine; ▲, serine; ▼, threonine; solid triangle pointing left, diglycine; solid triangle pointing right, triglycine).

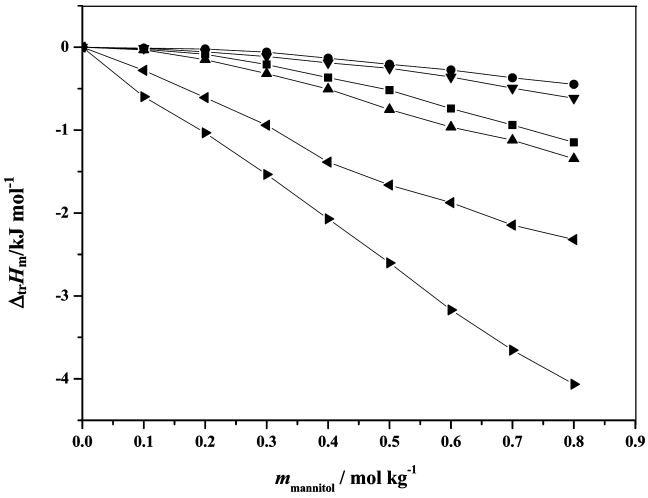

Figure 2. Enthalpies of transfer ($\Delta_{tr}H_m$) of amino acids and glycine peptides from water to aqueous solutions of D-mannitol at 298.15 K (■, glycine; ●, alanine; ▲, serine; ▼, threonine; solid triangle pointing left, diglycine; solid triangle pointing right, triglycine).

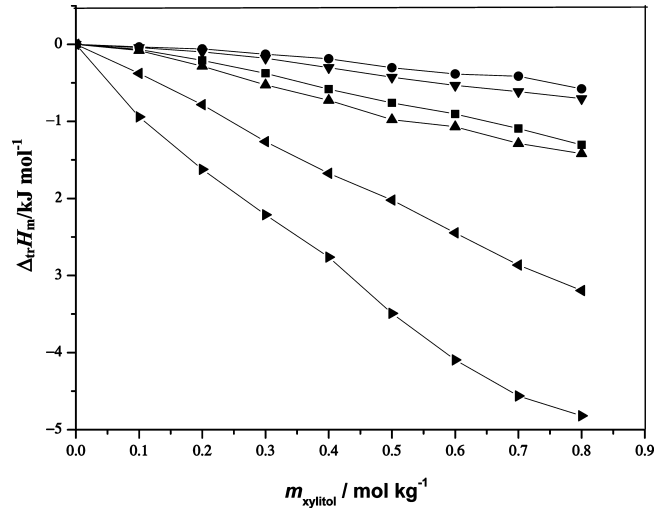

Figure 3. Enthalpies of transfer ($\Delta_{tr}H_m$) of amino acids and glycine peptides from water to aqueous solutions of xylitol at 298.15 K (■, glycine; ●, alanine; ▲, serine; ▼, threonine; solid triangle pointing left, diglycine; solid triangle pointing right, triglycine).

transfer enthalpy is a little more negative. For the glycine peptide, the peptide group is also a structure breaker. Therefore, the absolute value of the transfer enthalpy is larger than that of the amino acids.

It can be observed that subtle differences occur in the values of the transfer enthalpy due to hydroxyl number and stereochemical differences of sugar alcohols. Both D-sorbitol and xylitol have similar stereoconfigurations with the difference of one —CH(OH)— group. So, the transfer enthalpies of amino acids and glycine peptides from water to xylitol solution are only slightly larger than those to D-sorbitol solution. On the other hand, the order of the exothermic curve indicates that D-sorbitol is a stronger structure breaker than D-mannitol. It seems that D-mannitol can be more easily adopted into the hydrogen-bonded structure than D-sorbitol.[11] So, dehydration of the D-mannitol molecule needs more energy than that of the D-sorbitol molecule. Hence, the transfer enthalpies of amino acids and peptides from water to D-sorbitol are a little more negative than those in D-mannitol.

Conclusions

The solution processes of glycine, L-alanine, L-serine, L-threonine, diglycine, and triglycine in aqueous solutions of D-sorbitol, D-mannitol, and xylitol at 298.15 K have been investigated by calorimetry. It has been observed that the derived transfer enthalpies have negative values and decrease with increase of the concentration of sugar alcohol solutions, which indicate that the primary interactions are those between the zwitterionic group of the amino acid molecule and the hydroxyl group of the sugar alcohol molecule. The hydrophilic side chains also make negative contributions to the transfer enthalpies.

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