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Enthalpies of transfer of amino acids from water to aqueous solutions of formamide

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Abstract

Enthalpies of solution of glycine, L-alanine, L-serine in water and aqueous solutions of formamide were measured at 298.15 K. Transfer enthalpies of amino acids from water to aqueous solutions of formamide were derived and interpreted qualitatively with hydration co-sphere overlap model. The results show that the structure interaction between formamide and zwitterionic head-group and hydrophilic side chain of amino acids make a negative contribution to transfer enthalpy, while that with the hydrophobic side chain is positive. In the solvent composition range studied, transfer enthalpies decrease overall with the increasing concentration of formamide, with the relative order of L-serine < glycine < L-alanine.

Keywords: Glycine; L-Alanine; L-Serine; Enthalpy of transfer; Formamide

1. Introduction

Amino acids have been useful models for understanding the thermodynamic behavior of proteins, especially in determining functional group contributions to the biopolymers conformational stability [1–5]. It is well recognized that transfer enthalpy often provides useful information regarding the solute–solvent interaction [1]. Although much work has been done regarding these quantities of amino acids in aqueous solutions of mono- or poly-ols and electrolytes [2–4], such studies are still lacking for a series of amide–water mixtures. In this paper, transfer enthalpies of glycine, L-alanine and L-serine, from water to aqueous solutions of formamide, the simplest molecule containing an amide linkage, are reported and discussed with the hydration co-sphere overlap model.

2. Experimental

Glycine, L-alanine, L-serine, obtained from Sino-American Biotechnology Co. (Shanghai, China), were ground in an agate motor, sifted through a 48 μm mesh sieve, and dried in vacuum at 90 °C for several hours before use. Analytical grade formamide was distilled twice under reduced pressure. Aqueous formamide was prepared by weight using deionized and distilled water.

The measurement of enthalpies of solution was done with an RD496-III calorimeter at 298.15 K, using mixing vessels as previously described [5]. All the substances were weighed on a METTLER AE200 balance with a sensitivity of 0.1 mg. The final molality of amino acids was 0.1000 mol kg^{-1} with an uncertainty of about ±0.25%. The total uncertainty in the enthalpy of solution is about ±1%.

3. Results and discussion

Table 1 is a summary of enthalpies of solution, $\Delta_{sol}H$, of glycine, L-alanine and L-serine in aqueous solutions of

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Table 1
Enthalpies of solution of glycine, L-alanine and L-serine in aqueous solutions of formamide at 298.15 K, $m_{\text{amino acid}} = 0.1000\ \text{mol kg}^{-1}$

Glycine		L-Alanine		L-Serine	
$m_{\text{formamide}}$ (mol kg^{-1})	$\Delta_{\text{sol}}H$ (kJ mol^{-1})	$m_{\text{formamide}}$ (mol kg^{-1})	$\Delta_{\text{sol}}H$ (kJ mol^{-1})	$m_{\text{formamide}}$ (mol kg^{-1})	$\Delta_{\text{sol}}H$ (kJ mol^{-1})
0	14.16	0	7.80	0	11.25
0.5044	14.03	0.5193	7.72	0.5049	10.88
1.0037	13.79	0.9977	7.59	1.0037	10.54
2.0225	13.36	2.0016	7.52	1.9980	10.30
3.9012	12.77	3.7436	7.55	3.7508	9.69
5.9856	12.36	5.9856	7.50	5.9908	9.28
7.9963	11.95	8.0363	7.55	8.0799	8.77
10.0077	11.74	10.0292	7.57	10.0101	8.49
12.9843	11.74	12.0035	7.51	12.9785	8.37

formamide. Our results of glycine and L-alanine in pure water agree well with those of other reports [2,3,5]. The value for L-serine in water is a little higher than that reported by Lou [5], the discrepancy may be due to the difference in the purity of the amino acid. Fig. 1 shows the variation of transfer enthalpy, $\Delta_{\text{tr}}H$, which was obtained from the difference of $\Delta_{\text{sol}}H$ in aqueous solution of formamide and that in the pure water, with the molality of the co-solvent formamide.

The concentration dependence of the transfer property is a measure of the solute-solvent interaction, which can be understood from the hydration co-sphere overlap model of Desnoyers and co-workers [6,7]. In this case, the interaction between amino acids and formamide involved structure interaction and electrostatic interaction, which is mostly dipole–dipole interaction. A number of studies in the literature support the idea that electrostatic interaction gives a negative contribution to transfer enthalpy [2,8]. According to the Kirkwood equation [9] and Fuoss's studies on dipole fields between solute molecules [10,11], it is reasonable to assume that the contribution of electrostatic interaction to transfer enthalpy of glycine, L-alanine and L-serine, whose dipole moment remains approximately constant, is almost the same at the same formamide concentration. A similar result was obtained from the study of interaction energy of amino acids with sodium chloride by Larson et al. [12]. Therefore, the difference in transfer enthalpies of amino acids is reflecting the change in the structure interaction between solute and co-solvent.

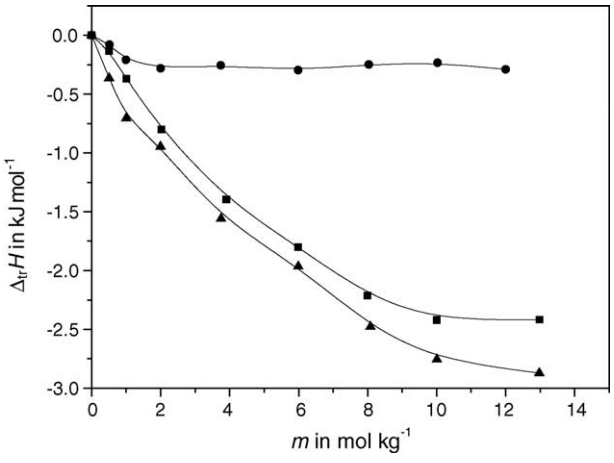

Fig. 1. Enthalpies of transfer of glycine (■), L-alanine (●) and L-serine (▲) from water to aqueous solutions of formamide at 298.15 K, $m_{\text{amino acid}} = 0.1000\ \text{mol kg}^{-1}$.

The interpretation of the structure interaction must be approached with the regard for the hydration of a separate molecule of solute and co-solvent. There is considerable evidence that formamide causes a net decrease in the structure in aqueous solutions, as compared with pure water [13,14]. The amino acid is presented as a zwitterion in water, NH_3^+-CHR-CO_2^-, so that the structure interaction between amino acid and formamide can be separated into: (a) The hydrophilic–hydrophilic interaction between the zwitterionic head-group of amino acid and formamide. (b) The hydrophilic–hydrophilic interaction between the hydrophilic side chain of amino acid and formamide. (c) The hydrophobic–hydrophilic interaction between the hydrophobic side chain of amino acid and formamide.

Desnoyers and co-workers [6,7] indicated that, in most cases, the net effect of co-sphere overlap is destructive. A negative contribution to transfer enthalpy for the hydrophilic–hydrophilic interaction is expected from the destructive overlap model, while that for the hydrophobic-hydrophilic interaction is positive. Thus, together with electrostatic interaction, the hydrophilic–hydrophilic interaction between the zwitterionic head-group and formamide plays a dominant role in the transfer process of glycine, leading to a negative transfer enthalpy. The hydrophobic-hydrophilic interaction between the apolar group $-CH_3$ with formamide make a positive difference between the transfer enthalpy of L-alanine and glycine. For L-serine, all the three types of structure interaction mentioned above are involved with formamide. The relative positions of $\Delta_{\text{tr}}H$ of glycine, L-alanine and L-serine indicate that the structure effect of the methyl group is overcome by that of –OH group of serine. The result shows that the $-CH_2OH$ group is partially hydrophilic, which is in accord with Kundu's study on the transfer thermodynamics of *p*-nitroaniline in aqueous solutions of isopropyl alcohol, propylene glycol and glycerol [15].

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