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Short communication

Enthalpies of transfer of amino acids from water to aqueous solutions of *N*-methylformamide and *N*,*N*-dimethylformamide at $T = 298.15$ K

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Abstract

Enthalpies of solution of glycine, L-alanine and L-serine in aqueous solutions of *N*-methylformamide and *N*,*N*-dimethylformamide were measured at 298.15 K. Enthalpies of transfer ($\Delta_{tr}H$) of amino acids from water to aqueous solutions of amides were derived and interpreted in terms of structural interaction. The results were compared with those in aqueous formamide solutions.

Keywords: Amino acid; Enthalpy of transfer; *N*-Methylformamide; *N*,*N*-Dimethylformamide

1. Introduction

As a part of the continuation of our studies on the thermodynamics of amino acids in mixed amide aqueous solutions [1,2], this paper reports a study of the enthalpies of transfer of glycine, L-alanine and L-serine in aqueous solutions of *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide (DMF). The purpose is to understand the important role that no-bonding interactions play in biological systems.

2. Experimental

Glycine, L-alanine and L-serine (BR mass fraction >0.99, Shanghai Chem. Co.) were recrystallized from aqueous ethanol solutions and dried under vacuum at 348 K for 6 h. NMF (GR, Japan) and DMF (AR, Shanghai Chem. Co.) were stored over 4 Å molecular sieves for at least 48 h and used without further purification.

All solutions were prepared freshly by mass on a METTLER AE200 balance with a sensitivity of ±0.0001 g. The final molality of amino acids was 0.1000 mol kg^{-1} with an uncertainty of about ± 0.2%. The measurements of enthalpies of solution were carried out on a RD496-II microcalorimeter at 298.15 K as previously described [3]. The uncertainty of $\Delta_{sol}H$ was within ±1% based on the data of three iterations.

3. Result and discussion

The enthalpies of solution ($\Delta_{sol}H$) of amino acids in aqueous solutions of NMF and DMF are presented in Tables 1 and 2, respectively. The values for glycine, L-alanine and L-serine in water are 14.15, 7.57 and 11.34 kJ mol^{-1} [4], respectively. The enthalpies of transfer $\Delta_{tr}H$ were derived from the differences between $\Delta_{sol}H$ (s), the enthalpies of solution of amino acids in aqueous amides, and $\Delta_{sol}H$ (w), the enthalpies of amino acids in pure water:

$$\Delta_{tr}H = \Delta_{sol}H(s) - \Delta_{sol}H(w) \quad (1)$$

Figs. 1 and 2 show the variation of $\Delta_{tr}H$ of amino acids with the molality of NMF and DMF, respectively. The enthalpies of transfer of amino acids are positive and increase with the increasing concentration of amides except the $\Delta_{tr}H$ of L-serine in $m < 1.5$ mol kg^{-1} NMF solutions. The relative order of $\Delta_{tr}H$ of amino acids in the same concentration of NMF or DMF is L-serine < glycine < L-alanine.

In the ternary system of amino acid, amide and water the following interactions may be occurring: (a) the hydrophilic–hydrophilic interaction between the zwitterionic head group of

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Table 1
Enthalpy of solution of amino acids in aqueous solutions of *N*-methylformamide and enthalpy of transfer of amino acids from water to aqueous solutions of *N*-methylformamide at 298.15 K

m_{NMF} (mol kg^{-1})	$\Delta_{sol}H_{Gly}$ (kJ mol^{-1})	$\Delta_{tr}H_{Gly}$ (kJ mol^{-1})	m_{NMF} (mol kg^{-1})	$\Delta_{sol}H_{Ala}$ (kJ mol^{-1})	$\Delta_{tr}H_{Ala}$ (kJ mol^{-1})	m_{NMF} (mol kg^{-1})	$\Delta_{sol}H_{Ser}$ (kJ mol^{-1})	$\Delta_{tr}H_{Ser}$ (kJ mol^{-1})
0.4998	14.37	0.22	0.4999	7.94	0.37	0.4999	11.03	−0.31
0.9997	14.45	0.30	0.9992	8.29	0.72	1.0000	11.30	−0.04
1.4999	14.62	0.47	1.4996	8.50	0.93	1.4995	11.42	0.08
1.9997	14.71	0.56	1.9997	8.82	1.25	1.9999	11.51	0.17
2.4981	14.80	0.65	2.4990	9.12	1.55	2.4997	11.65	0.31
3.0010	14.89	0.74	2.9989	9.34	1.77	2.9991	11.82	0.48
3.4998	15.01	0.86	3.4982	9.52	1.95	3.4998	12.00	0.66
4.0005	15.17	1.02	4.0003	9.68	2.11	3.9979	12.12	0.78

Table 2
Enthalpy of solution of amino acids in aqueous solutions of *N*,*N*-dimethylformamide and enthalpy of transfer of amino acids from water to aqueous solutions of *N*,*N*-dimethylformamide at 298.15 K

m_{DMF} (mol kg^{-1})	$\Delta_{sol}H_{Gly}$ (kJ mol^{-1})	$\Delta_{tr}H_{Gly}$ (kJ mol^{-1})	m_{DMF} (mol kg^{-1})	$\Delta_{sol}H_{Ala}$ (kJ mol^{-1})	$\Delta_{tr}H_{Ala}$ (kJ mol^{-1})	m_{DMF} (mol kg^{-1})	$\Delta_{sol}H_{Ser}$ (kJ mol^{-1})	$\Delta_{tr}H_{Ser}$ (kJ mol^{-1})
0.4999	14.53	0.38	0.5000	8.14	0.57	0.5000	11.45	0.11
0.9999	14.82	0.67	0.9947	8.70	1.13	0.9947	11.66	0.32
1.5000	15.21	1.06	1.5000	9.13	1.56	1.5000	12.00	0.66
1.9999	15.42	1.27	2.0000	9.52	1.95	1.9999	12.32	0.98
2.4978	15.68	1.53	2.4978	10.08	2.51	2.4990	12.50	1.16
3.0002	15.87	1.72	2.9990	10.51	2.94	3.0002	12.80	1.46
3.4990	16.06	1.91	3.4991	10.73	3.16	3.4991	13.05	1.71
3.9994	16.21	2.06	3.9994	11.13	3.56	3.9994	13.25	1.91

amino acid or the side group of L-serine and –CONH– or –CON< group of amide. (b) The hydrophilic–hydrophobic interaction between the head group of amino acid or the side group of L-serine and $–CH_3$ group of amides or between the –CONH– or –CON< group of amides and side group of L-alanine. (c) The hydrophobic–hydrophobic interaction between the side group of L-alanine and $–CH_3$ group of amides. According to cosphere overlap model [5], interaction of type (a) would lead to a negative $\Delta_{tr}H$ while type (b) and (c) would lead to a positive $\Delta_{tr}H$.

The major interactions between glycine and NMF or DMF are type (a) and (b), the positive $\Delta_{tr}H$ suggested that the interaction of type (b) is predominant. With the increasing concentration of amides, the thermochemical repulsion (i.e. $\Delta H > 0$, $\Delta G > 0$) between zwitterionic head group of glycine and $–CH_3$ group of amides increased leading to the enhancement of positive $\Delta_{tr}H$ value.

For L-alanine, all the three types of structure interaction mentioned above are involved. The $–CH_3$ group of L-alanine provides a tendency of hydrophobic–hydrophilic and hydrophobic–hydrophobic groups to interact and as a result the transfer

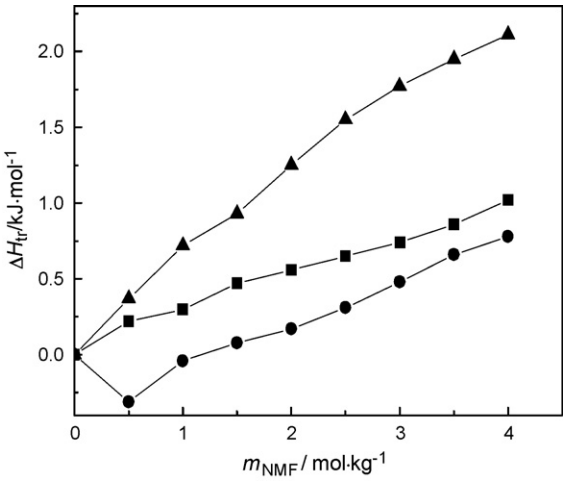

Fig. 1. Enthalpies of transfer of glycine (■), L-alanine (▲) and L-serine (●) from water to aqueous solutions of NMF at T =298.15 K.

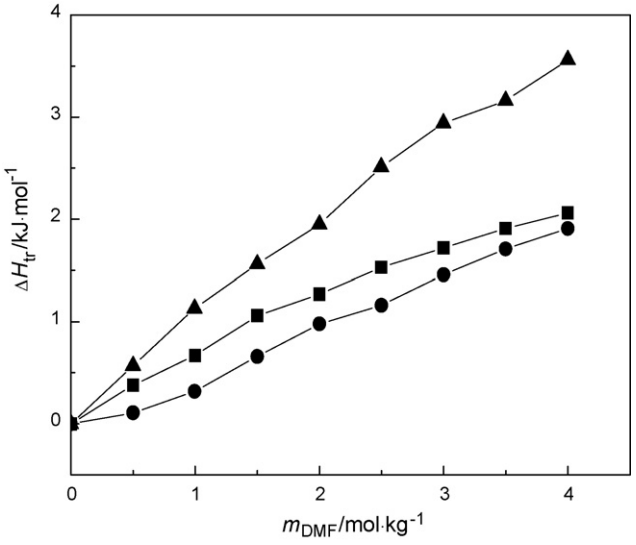

Fig. 2. Enthalpies of transfer of glycine (■), L-alanine (▲) and L-serine (●) from water to aqueous solutions of DMF at T =298.15 K.

enthalpy of L-alanine is larger than that of glycine in the same concentration of NMF or DMF solutions. Hydrophobic–hydrophobic interaction is enthalpic unfavorable but Gibbs energy favorable ($\Delta H > 0$, $\Delta G < 0$). The co-operation effect of repulsion interactions between L-alanine and amide will enhance the attraction between the hydrophobic groups of L-alanine and amide, leading to much larger $\Delta_{tr}H$ than that of glycine in higher concentration amides as can be seen in Figs. 1 and 2.

In the case of L-serine, the side group (–CH_2OH) lead to additional hydrophilic–hydrophilic and hydrophilic–hydrophobic interactions, the result suggested that the former interaction is predominant. The carbonyl bond of NMF and DMF has a strong electron pair donating ability, and is capable of forming OH···OC hydrogen bonds between the side groups of L-serine, which enhanced the hydrophilic–hydrophilic interaction. In $m < 1.5\,\mathrm{mol\,kg^{-1}}$ NMF solutions the hydrophilic–hydrophilic interaction between L-serine and –CONH– group of NMF surpassed the hydrophilic–hydrophobic interaction result in negative $\Delta_{tr}H$ value. NMF is liable to form chain-wise association by intermolecular hydrogen bonds [6]; with the increasing concentration of NMF, probably the association tendency increased and weakened the hydrogen bond between L-serine and NMF, the negative contribution to $\Delta_{tr}H$ decreased.

The $\Delta_{tr}H$ value of the three amino acids in the same concentration of formamide (FA) [1], NMF and DMF vary in the sequence DMF > NMF > FA, which is consistent with the –CH_2 number of amides. The $\Delta_{tr}H$ of amino acids from water to formamide solutions is negative which shows that the major interaction between amino acids and FA is type (a) and amino acids interact more favorably with FA than with the other amides. With the increasing number of –CH_2 group in amides, for glycine and L-serine increases the hydrophilic–hydrophobic interaction and for L-alanine increases hydrophilic–hydrophobic and hydrophobic–hydrophobic interaction which all give positive contribution to $\Delta_{tr}H$.

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