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Short communication

Enthalpies of transfer of amino acids from water to aqueous solutions of *N*-methylacetamide and *N*,*N*-dimethylacetamide 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*-methylacetamide and *N*,*N*-dimethylacetamide were measured at 298.15 K. Enthalpies of transfer ($\Delta_{tr}H$) of amino acids from water to aqueous solutions of amides were derived. It has been show that the enthalpies of transfer of amino acids are positive and increase with the increasing concentration of amides. The relative order of $\Delta_{tr}H$ of amino acids in the same concentration of NMA or DMA is L-serine < glycine < L-alanine. The influence of side group of L-alanine and L-serine on $\Delta_{tr}H$ has been discussed in terms of structural interaction. The results were compared with those in aqueous formamide, *N*-methylformamide and *N*,*N*-dimethylformamide solutions.

1. Introduction

“Non-bonding” interactions play an important role in biological systems. Enthalpy of transfer is a sensitive parameter which provides valuable information about these interactions. As a part of the continuation of our studies on the thermodynamics of amino acids in mixed amide aqueous solutions [1–3], this paper reports a study of the enthalpies of transfer of glycine, L-alanine and L-serine in aqueous solutions of *N*-methylacetamide (NMA) and *N*,*N*-dimethylacetamide (DMA).

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. NMA (mass fraction > 0.99, Acros) and DMA (HPLC/spectro, USA) 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 [4]. 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 NMA and DMA are presented in Tables 1 and 2, respectively. The enthalpies of transfer $\Delta_{tr}H$ were derived from the differences between $\Delta_{sol}H(\mathrm{s})$, the enthalpies of solution of amino acids in aqueous amides, and $\Delta_{sol}H(\mathrm{w})$, the enthalpies of amino acids in pure water:

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

Figs. 1 and 2 shows the variation of $\Delta_{tr}H$ of amino acids with the molality of NMA and DMA, respectively. The enthalpies of transfer of amino acids are positive and increase with the increasing concentration of amides. The relative order of $\Delta_{tr}H$ of amino acids in the same concentration of NMA or DMA is L-serine < glycine < L-alanine.

The three amino acids have similar structures but different side groups. So the difference in the transfer enthalpy of amino acids in the same amide solutions primarily comes from the influence of side group which reflects the change in the structure interaction between solute and cosolvent. Desnoyers et al. [6] and Visser et al. [7] have published a general discussion of structure interactions and believe that in most cases the net effect of cosphere overlap in the hydration is destructive. Structural interaction makes quite a large contribution to the enthalpic function and sometimes even becomes predominant [8,9]. Amino acids in aqueous solutions

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Table 1
Enthalpy of solution of amino acids in aqueous solutions of NMA and enthalpy of transfer of amino acids from water to aqueous solutions of NMA at 298.15 K.

m_{NMA} (mol kg^{-1})	$\Delta_{\text{sol}}H_{\text{Gly}}$ (kJ mol^{-1})	$\Delta_{\text{tr}}H_{\text{Gly}}$ (kJ mol^{-1})	m_{NMA} (mol kg^{-1})	$\Delta_{\text{sol}}H_{\text{Ala}}$ (kJ mol^{-1})	$\Delta_{\text{tr}}H_{\text{Ala}}$ (kJ mol^{-1})	m_{NMA} (mol kg^{-1})	$\Delta_{\text{sol}}H_{\text{Ser}}$ (kJ mol^{-1})	$\Delta_{\text{tr}}H_{\text{Ser}}$ (kJ mol^{-1})
0	14.15 [5]	–	0	7.57 [5]	–	0	11.34 [5]	–
0.5001	14.55	0.40	0.4998	8.24	0.67	0.4998	11.56	0.22
0.9997	15.05	0.90	0.9998	8.67	1.10	0.9998	11.85	0.51
1.4991	15.41	1.26	1.4985	9.12	1.55	1.4985	12.34	1.00
1.9993	15.71	1.56	1.9998	9.62	2.05	1.9998	12.71	1.37
2.5000	16.02	1.87	2.4993	10.04	2.47	2.4993	13.05	1.71
2.9981	16.42	2.27	2.9991	10.57	3.00	2.9991	13.40	2.06
3.4962	16.71	2.56	3.4987	10.96	3.39	3.4987	13.62	2.28
3.9957	16.98	2.83	3.9989	11.35	3.78	3.9989	13.98	2.64

Table 2
Enthalpy of solution of amino acids in aqueous solutions of DMA and enthalpy of transfer of amino acids from water to aqueous solutions of DMA at 298.15 K.

m_{DMA} (mol kg^{-1})	$\Delta_{\text{sol}}H_{\text{Gly}}$ (kJ mol^{-1})	$\Delta_{\text{tr}}H_{\text{Gly}}$ (kJ mol^{-1})	m_{DMA} (mol kg^{-1})	$\Delta_{\text{sol}}H_{\text{Ala}}$ (kJ mol^{-1})	$\Delta_{\text{tr}}H_{\text{Ala}}$ (kJ mol^{-1})	m_{DMA} (mol kg^{-1})	$\Delta_{\text{sol}}H_{\text{Ser}}$ (kJ mol^{-1})	$\Delta_{\text{tr}}H_{\text{Ser}}$ (kJ mol^{-1})
0.4999	14.76	0.61	0.5000	8.43	0.86	0.5002	11.71	0.37
0.9988	15.15	1.00	1.0001	8.91	1.34	0.9995	12.02	0.68
1.5002	15.64	1.49	1.4995	9.50	1.93	1.5012	12.57	1.23
2.0004	15.93	1.78	2.0004	10.05	2.48	1.9988	12.96	1.62
2.4983	16.25	2.10	2.4999	10.65	3.08	2.5002	13.30	1.96
3.0005	16.67	2.52	2.9874	11.30	3.73	2.9997	13.72	2.38
3.5017	16.94	2.79	3.4988	11.72	4.15	3.4989	14.01	2.67
4.0005	17.33	3.18	4.0006	12.27	4.70	4.0005	14.35	3.01

occur in the form of zwitterions (NH_3^+–CHR–COO^-). So the structure interaction between amino acids and amides can be separated into:

(a) The hydrophilic–hydrophilic interaction between the zwitterionic head group of amino acid or the side group of L-serine and –CONH– or –CON< group of amide, which lead to a negative contribution to the transfer enthalpy [6].
(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, which gives a positive contribution to the transfer enthalpy [6].
(c) The hydrophobic–hydrophobic interaction between the side group of L-alanine and –CH_3 group of amides, which cause an overall positive contribution to transfer enthalpy [6].

The major interactions between glycine and NMA or DMA are type (a) and (b), the positive $\Delta_{\text{tr}}H$ suggested that the interaction of type (b) is predominant. With the increasing concentration of amides, the hydrophilic–hydrophobic interaction between glycine and amides increased which leading an enhancement of positive $\Delta_{\text{tr}}H$ 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 enthalpy of L-alanine is larger than that of glycine in the same concentration of NMA or DMA solutions.

In the case of L-serine, the side group (–CH_2OH) lead additional hydrophilic–hydrophilic and hydrophilic–hydrophobic interactions, the result suggested that the former interaction is predominant. The carbonyl bond of NMA and DMA has a strong electron pair donating ability, and is capable of forma-

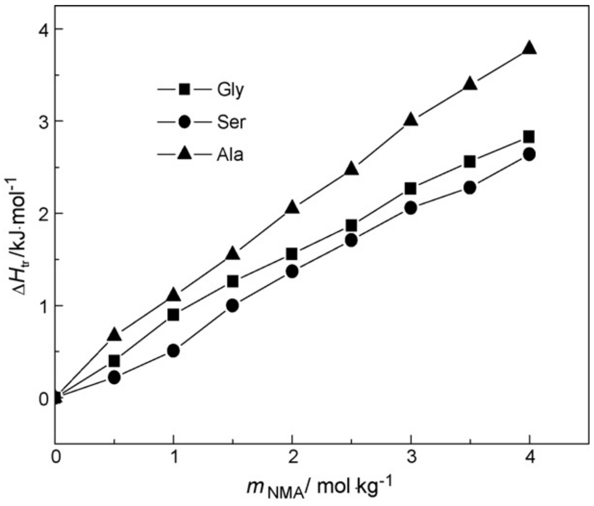


Fig. 1. Enthalpies of transfer of glycine (■), L-alanine (▲) and L-serine (●) from water to aqueous solutions of NMA at T = 298.15 K.

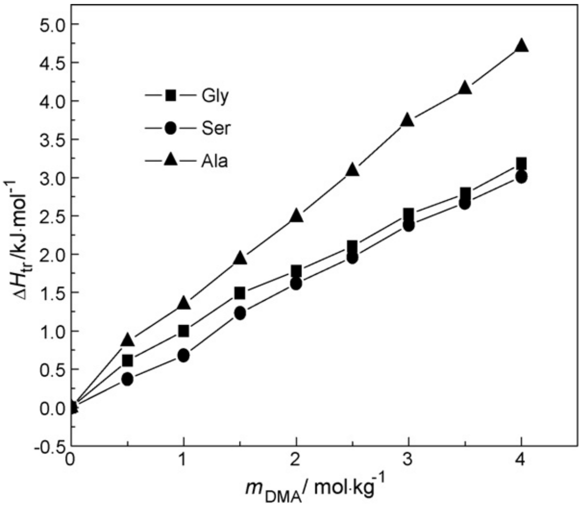
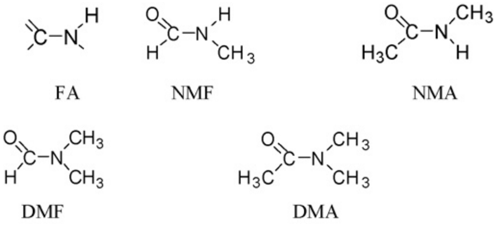


Fig. 2. Enthalpies of transfer of glycine (■), L-alanine (▲) and L-serine (●) from water to aqueous solutions of DMA at T = 298.15 K.



Scheme 1. Structures of FA, NMF, DMF, NMA and DMA molecules.

tion OH···OC hydrogen bonds between the side group of L-serine which enhanced the hydrophilic–hydrophilic interaction. But on the whole the positive transfer enthalpies of L-serine show that the major interaction between L-serine and the two amides is hydrophilic–hydrophobic interaction.

Compare the $\Delta_{\mathrm{tr}}H$ values of the three amino acids in the same concentration of formamide (FA) [1], NMF [3] and DMF [3] with in NMA and DMA solutions, it can be seen that the datas follow the trend: DMA > NMA > DMF > NMF > FA, which reflects the different structures of amides. The structures of the five amide molecules are displayed in Scheme 1, respectively.

The amides have the similar O═C–N bond but different number of $-\mathrm{CH_3}$ groups. With the increasing methyl groups in the sequence:

$$\mathrm{FA} \rightarrow \mathrm{NMF} \rightarrow \left\{ \begin{array}{l} \mathrm{NMA} \\ \mathrm{DMF} \end{array} \right. \rightarrow \mathrm{DMA},$$

the hydrophobicity of amide molecules increased and enhanced the hydrophilic–hydrophobic or hydrophobic–hydrophobic interactions between amino acids and amides which leading the $\Delta_{\mathrm{tr}}H$ values of amino acids increasing. NMA and DMF are isomers. The two $-\mathrm{CH_3}$ groups in DMF molecule are on the same side of N atom while on the different side of N atom in NMA molecule. The overlap of cospheres of two $-\mathrm{CH_3}$ groups in DMF weakens the structure-making influence of $-\mathrm{CH_3}$ on water, and hence decrease the hydrophobicity of DMF. But in NMA molecule the influence of the two $-\mathrm{CH_3}$ group on water is relatively independent.

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