Enthalpies of Transfer of Amino Acids from Water to Aqueous Solutions of Alkali Metal Nitrates

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Enthalpies of solution of glycine, L-alanine, and L-serine in water and aqueous solutions of $LiNO_3$, $NaNO_3$, and KNO_3 were measured at 298.15 K. Enthalpies of transfer ($\Delta_{tr}H$) of amino acids from water to aqueous solutions of nitrate salts were derived. The effect of the ion type, concentration, and structure of amino acids on the magnitude of the transfer enthalpies are discussed in terms of the electrostatic interaction and the structural hydration interaction model.

Introduction

It is well-known that the type of salts and salts concentration greatly influence the interactions between proteins and hydrophobic or hydrophilic media.[1,2] Owing to the complexities of proteins, the direct interpretation from studies on proteins and media is very difficult. Amino acids have been quite useful as models for understanding the thermodynamic behavior of proteins in aqueous solutions. Many studies have been carried out in aqueous alkali metal and alkaline earths halide solutions,[3−13] and some interesting results have been obtained. For further understanding the role of salts on the conformational stability of proteins, this paper reports a systematic study of the enthalpies of transfer of glycine, L-alanine, and L-serine in aqueous solution of $LiNO_3$, $NaNO_3$, and KNO_3. The results are interpreted from the point of view of electrostatic interaction and structural interaction.

Experimental Section

Glycine, L-alanine, and L-serine (biological reagent, purity >99 %, Shanghai Chemical Co.) were twice recrystallized from aqueous ethanol solutions and dried under vacuum at 348 K for 6 h. Lithium nitrate (analytical reagent, purity >99 %, Tianjin Chemical Co.) was recrystallized from water acetone mixtures and dried in a vacuum at 393 K. $NaNO_3$ and KNO_3 (analytical reagents, purity >99 %, Tianjin Chemical Co.) were recrystallized from double-distilled water and dried at 373 K. All the materials were stored over P_2O_5 prior to use.

All solutions were prepared freshly by mass on a Mettler AE200 balance with a sensitivity of ± 0.0001 g. The molality of amino acids was constant at 0.1000 mol·kg^{-1} pure water. The uncertainty of the concentration was ± 0.0002 mol·kg^{-1}. The measurements of enthalpies of solution were carried out on a RD496 microcalorimeter at 298.15 K as previously described.[14] The uncertainty of $\Delta_{sol}H$ was within ± 1.2 % based on the data of three iterations.

Result and Discussion

The enthalpies of solution ($\Delta_{sol}H$) of glycine, L-alanine, and L-serine in aqueous solution of nitrate salts are presented in Tables 1 to 3. The values of glycine, L-alanine, and L-serine in water (14.15, 7.57, and 11.34, respectively) agree well with the reported values (14.20,[4] 7.67,[15] and 11.49[15] respectively). The solution processes are endothermic, and the values of solution decrease with the increased content of $LiNO_3$, $NaNO_3$, and KNO_3. 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 nitrates, and $\Delta_{sol}H(w)$, the enthalpies of amino acids in pure water:

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

Figures 1 to 3 show the variation of $\Delta_{tr}H$ of amino acids with the molality of one of the three cosolvent $LiNO_3$, $NaNO_3$, and KNO_3 respectively. All the transfer enthalpies are negative; in aqueous $NaNO_3$, KNO_3, and low concentration $LiNO_3$ solution, $\Delta_{tr}H$ varies in the sequence L-serine < glycine < L-alanine while glycine < L-serine < L-alanine in $LiNO_3$ solution at the concentration above 1.5 mol·kg^{-1}.

The substance molecules dissolved in aqueous solution interact with each other with participation of solvent molecules. Lilley et al.[16] considered that this effect between electrolyte and amino acid may be assumed to be a sum of three contributions: direct electrostatic interaction; partial desolvation of solutes; and solvent reorganization. The latter two effects are structural interactions. Desnoyers et al.[17] and Visser et al.[18] have published a general discussion of structure interactions, indicating that the overall influence of the solute on the structure of water is represented by a spherical shell and that the mutual interaction between the solute may cause some water molecules to be squeezed out from the hydration cosphere into the solvent and to assume the order of bulk water as illustrated in Figure 4. 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.[4,19]

The dipole moment of glycine, L-alanine, and L-serine remains approximately constant. According to the Kirk-

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Table 1. Enthalpies of Solution of Glycine in Aqueous Solutions of $LiNO_3$, $NaNO_3$, and KNO_3

m_{LiNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}	m_{NaNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}	m_{KNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}
0	14.15	0	14.15	0	14.15
0.2000	13.77	0.1997	13.68	0.1999	13.79
0.5000	13.45	0.4997	13.07	0.5000	13.26
0.7000	13.16	0.6996	12.69	0.7000	12.80
0.9999	12.57	0.9999	12.23	0.9992	12.40
1.5000	12.02	1.4967	11.27	1.4918	11.57
1.9998	11.21	2.0001	10.63	1.9988	10.97
2.4994	10.71	2.4433	10.25	2.4785	10.45
2.9998	10.35	2.9954	9.92	2.9819	10.18

Table 2. Enthalpies of Solution of L-Alanine in Aqueous Solutions of $LiNO_3$, $NaNO_3$, and KNO_3

m_{LiNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}	m_{NaNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}	m_{KNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}
0	7.57	0	7.57	0	7.57
0.1989	7.35	0.1993	7.23	0.2000	7.39
0.5000	7.05	0.4988	6.93	0.5001	7.21
0.6916	6.86	0.7002	6.61	0.6999	7.17
0.9872	6.78	1.0004	6.46	0.9999	7.12
1.5000	6.72	1.4998	6.30	1.4991	7.02
1.9913	6.67	1.9906	6.26	1.9992	6.98
2.4927	6.58	2.5001	6.22	2.4996	6.96
2.9800	6.52	3.0005	6.18	2.9979	6.96

Table 3. Enthalpies of Solution of L-Serine in Aqueous Solutions of $LiNO_3$, $NaNO_3$, and KNO_3

m_{LiNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}	m_{NaNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}	m_{KNO_3} mol·kg^{-1}	$\Delta_{sol}H$ kJ·mol^{-1}
0	11.34	0	11.34	0	11.34
0.2000	10.64	0.1998	10.39	0.2000	10.57
0.4998	10.40	0.4997	9.56	0.4998	9.90
0.6998	10.05	0.6991	9.10	0.6999	9.56
0.9999	9.61	0.9999	8.64	1.0000	9.18
1.4995	9.18	1.4982	8.14	1.4765	8.46
1.9993	8.47	2.0572	7.57	2.0030	7.97
2.4997	8.20	2.5001	7.19	2.5000	7.54
2.9986	8.09	2.9987	6.86	2.9973	7.25

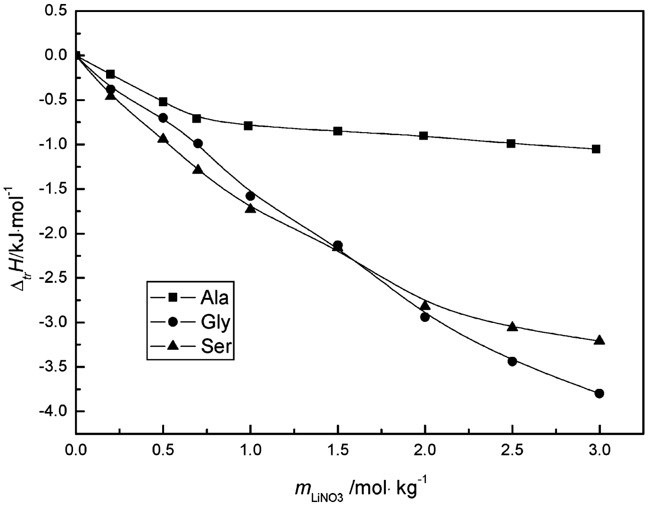

Figure 1. Enthalpies of transfer of ●, glycine; ■, L-alanine; and ▲, L-serine from water to aqueous solutions of $LiNO_3$ at 298.15 K.

wood equation[20] and Fuoss's studies on the dipole−dipole interaction,[21,22] the contribution of electrostatic interaction to the transfer enthalpy is almost the same at the same nitrate concentration, similar to that in water−NaCl system.[23] The difference in the transfer enthalpy of amino acids as can be seen in Figures 1 to 3 reflects the change in the structure interaction between solute and cosolvent.

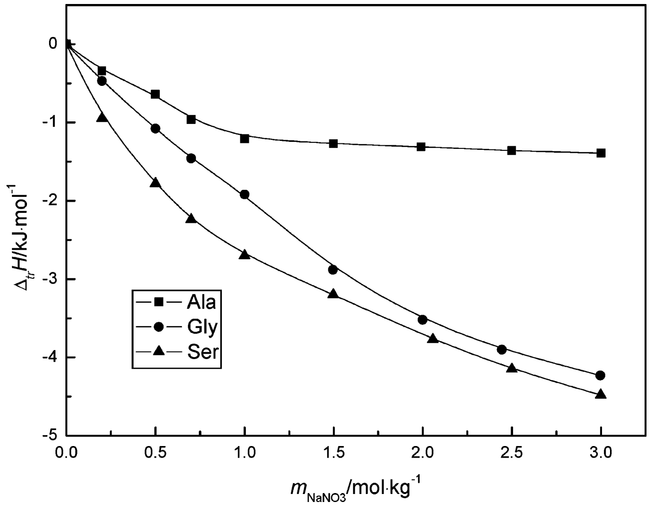

Figure 2. Enthalpies of transfer of ●, glycine; ■, L-alanine; and ▲, L-serine from water to aqueous solutions of $NaNO_3$ at 298.15 K.

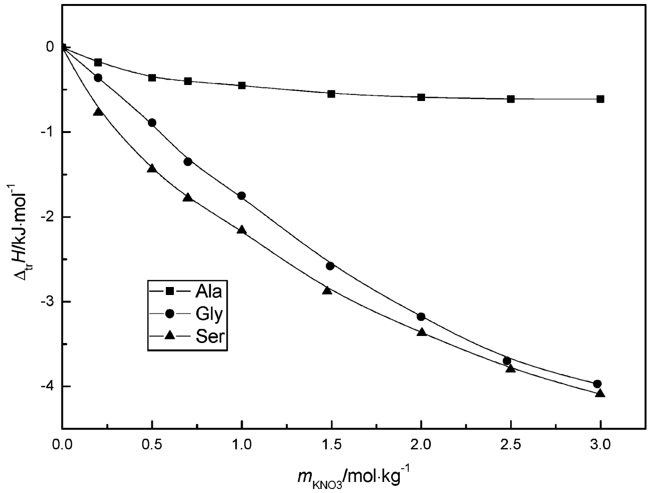

Figure 3. Enthalpies of transfer of ●, glycine; ■, L-alanine; and ▲, L-serine from water to aqueous solutions of KNO_3 at 298.15 K.

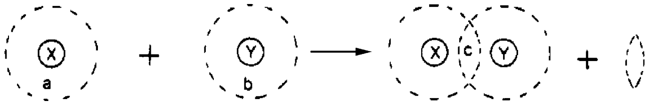

Figure 4. Structure interaction between two solute molecules through the overlap of hydration cospheres.

Amino acids in aqueous solutions occur in the form of zwitterions (NH_3^+−CHR−COO^-). So the structure interaction between amino acids and nitrates can be separated into the following:

(a) The hydrophilic−hydrophilic interaction between the zwitterionic headgroup of amino acids and ions, which leads to a negative contribution to the transfer enthalpy.[17]

(b) The hydrophilic−hydrophilic interaction between the polar side chain (−OH) of L-serine and ions, which gives a negative contribution to the transfer enthalpy.

(c) The hydrophobic−hydrophilic interaction between the apolar side chain ($-CH_3$) of L-alanine and ions, which causes an overall positive contribution to transfer enthalpy.[17]

The observed succession of $\Delta_{tr}H$ of amino acids in $NaNO_3$, KNO_3, and low concentration $LiNO_3$ solutions (viz., L-serine < glycine < L-alanine) can be well-explained through the difference of interaction of type (b) and (c). But in $LiNO_3$ solution, the enthalpy of transfer of glycine and

L-serine is abnormal when $m_E > 1.5\ \text{mol·kg}^{-1}$. This is probably due to the interaction between anions and cations in concentrated aqueous solutions of $LiNO_3$. Raman and infrared spectra studies of alkali metal nitrates solutions[24] found that, when the concentration rises above $1.5\ \text{mol·dm}^{-3}$, there is evidence of cation−anion contact with the increasing concentration of $LiNO_3$. Molecular orbital results also substantiate the bidentate structure of $Li^+NO_3^-$ with a high percent covalency for the Li−O bonds association.[25] The results of our study suggest that the contact between cations and anions decreases electrostatic interaction and hydrophilic−hydrophilic interaction between L-serine and $LiNO_3$ more than that between glycine and $LiNO_3$.

The cations examined by us differ in size. For all the three amino acids, $\Delta_{tr}H$ become more and more negative as follows: $Li^+ < K^+ < Na^+$. The differences in the energy of electrostatic interaction between zwitterions and ions should result from the difference in the charge surface density of the cations. The higher the charge surface density, the higher the ion−ion attraction energy, thus the negative contribution of cation−zwitterion interaction to $\Delta_{tr}H$ should be in the sequence: $K^+ < Na^+ < Li^+$. However, the result obtained by us is $Li^+ < K^+ < Na^+$. This apparent discrepancy also attributes to the predominance of structure interactions between Li^+ and amino acids. Li^+ orients water molecules so strong that its hydration cosphere contains more hydration bonds than bulk water (somewhat like a hydrophobic group, although the structure of water is not the same),[17] so the structure interactions between Li^+ and $-COO^-$ and between Li^+ and −OH of L-serine are similar to the interaction of type (c) and the interaction between Li^+ and $-CH_3$ of L-alanine is similar to the interaction of hydrophobic−hydrophobic interaction, which also gives a positive contribution to the enthalpy of transfer.[17] In a word, structure interactions between Li^+ and amino acids counteract part of electrostatic interactions and are responsible for the observed variation in trends in $\Delta_{tr}H$ for the systems investigated.

Conclusions

The transfer enthalpies of amino acids from water to alkali metal nitrates solutions reflect the effects of various interactions in these solutions. The relative order of transfer enthalpies of amino acids is consistent with the structure interaction model. Cations Li^+, Na^+, and K^+ exert markedly different influences on the enthalpy of transfer, which indirectly indicates the different effects of salts on the structure and properties of proteins.

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