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Thermochimica Acta 440 (2006) 57–59
thermochimica acta
www.elsevier.com/locate/tca

Enthalpies of transfer of amino acids from water to aqueous solutions of sodium nitrate and sodium perchlorate at $T = 298.15$ K

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Received 5 September 2005; received in revised form 11 September 2005; accepted 18 October 2005
Available online 18 November 2005

Abstract

Enthalpies of solution of glycine, L-alanine and L-serine in water and aqueous solutions of $NaNO_3$ and $NaClO_4$ have been determined at $T = 298.15$ K with a calorimeter. Enthalpies of transfer ($\Delta_{tr}H$) from water to aqueous solutions of salts were derived and interpreted in terms of electrostatic interaction and structural interaction. $\Delta_{tr}H$ decreases with increasing salt concentration in the composition range studied. The transfer enthalpies of amino acids from water to $NaNO_3$ solution and low concentration $NaClO_4$ solution vary in the sequence L-serine < glycine < L-alanine while glycine < L-serine < L-alanine in $NaClO_4$ solution above 2 mol kg^{-1}. The difference may be due to ion association at high concentration, weakening the interaction with L-serine more than with glycine.

Keywords: Amino acid; Enthalpy of transfer; Sodium nitrate; Sodium perchlorate

1. Introduction

Salts have large effects on the structure and properties of proteins. As a part of the continuation of our studies [1,2], this paper reports a systematic study of the enthalpies of transfer of glycine, L-alanine and L-serine in aqueous solutions of $NaNO_3$ and $NaClO_4$. Glycine is the simplest amino acid in nature. L-serine is the amino acid with polar side chain $-CH_2OH$. L-alanine is the amino acid with apolar side chain $-CH_3$. Studying the transfer properties of polar and apolar amino acids is helpful in understanding the effect of hydroxyl and alkyl group on the interactions in protein interiors.

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. Analytical grade $NaNO_3$ (AR mass fraction > 0.99, Tianjin Chem. Co.) was recrystallized from double-distilled water and dried at 373 K. Analytical grade $NaClO_4 \cdot H_2O$ (AR mass fraction > 0.995, Tianjin Chem. Co.) was recrystallized from water methanol mixtures and dried in vacuo at 423 K for 96 h. 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} of pure water. The measurements of enthalpies of solution were carried out on a RD496-II calorimeter at 298.15 K as previously described [3]. The uncertainty of $\Delta_{sol}H$ was within ±1% based on three replicates.

3. Result and discussion

The enthalpies of solution ($\Delta_{sol}H$) of glycine, L-alanine and L-serine in aqueous solutions of $NaNO_3$ and $NaClO_4$ are presented in Tables 1–3. The values for glycine, L-alanine and L-serine in water (14.15, 7.57, 11.34 respectively) agree well with the reported values (14.20 [4], 7.67 [5], 11.49 [5], respectively).

The enthalpies of transfer $\Delta_{tr}H$ were derived from the differences between $\Delta_{sol}H$(s) and $\Delta_{sol}H$(w), the enthalpies of solution of amino acids in salt solution and in pure water, respectively. Figs. 1 and 2 show the variation of $\Delta_{tr}H$ of amino acids with the molality of the salt.

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doi:10.1016/j.tca.2005.10.013

Table 1
Enthalpies of solution of glycine in aqueous solutions of $NaNO_3$ and $NaClO_4$ and enthalpies of transfer of glycine from water to aqueous solutions of $NaNO_3$ and $NaClO_4$ at $T = 298.15$ K

m_{NaNO_3} (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{tr}H$ (kJ mol^{-1})	m_{NaClO_4} (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{tr}H$ (kJ mol^{-1})
0	14.15	0	0	14.15	0
0.1997	13.68	−0.47	0.1989	13.32	−0.83
0.4997	13.07	−1.08	0.5000	12.75	−1.40
0.6996	12.69	−1.46	0.6995	12.08	−2.07
0.9999	12.23	−1.92	0.9995	11.10	−3.05
1.4967	11.27	−2.88	1.4994	10.19	−3.96
2.0001	10.63	−3.52	2.0020	8.95	−5.20
2.4433	10.25	−3.90	2.4998	8.35	−5.80
2.9954	9.92	−4.23	2.9981	7.72	−6.43

Table 2
Enthalpies of solution of alanine in aqueous solutions of $NaNO_3$ and $NaClO_4$ and enthalpies of transfer of alanine from water to aqueous solutions of $NaNO_3$ and $NaClO_4$ at $T = 298.15$ K

m_{NaNO_3} (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{tr}H$ (kJ mol^{-1})	m_{NaClO_4} (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{tr}H$ (kJ mol^{-1})
0	7.57	0	0	7.57	0
0.1993	7.23	−0.34	0.2000	7.20	−0.37
0.4988	6.87	−0.70	0.5000	6.74	−0.83
0.7002	6.61	−0.96	0.6955	6.41	−1.16
1.0004	6.46	−1.11	0.9996	6.14	−1.43
1.4998	6.30	−1.27	1.4992	5.62	−1.95
1.9906	6.23	−1.34	1.9891	5.35	−2.22
2.5001	6.18	−1.39	2.5006	5.13	−2.44
3.0005	6.14	−1.43	2.9955	5.07	−2.50

Table 3
Enthalpies of solution of serine in aqueous solutions of $NaNO_3$ and $NaClO_4$ and enthalpies of transfer of serine from water to aqueous solutions of $NaNO_3$ and $NaClO_4$ at $T = 298.15$ K

m_{NaNO_3} (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{tr}H$ (kJ mol^{-1})	m_{NaClO_4} (mol kg^{-1})	$\Delta_{sol}H$ (kJ mol^{-1})	$\Delta_{tr}H$ (kJ mol^{-1})
0	11.34	0	0	11.34	0
0.1998	10.39	−0.95	0.2000	10.18	−1.16
0.4997	9.56	−1.78	0.5000	9.31	−2.03
0.6997	9.10	−2.24	0.7000	8.74	−2.60
0.9999	8.64	−2.70	0.9996	8.13	−3.21
1.4982	8.14	−3.20	1.5003	7.10	−4.24
2.0572	7.57	−3.77	1.9991	6.62	−4.72
2.5001	7.19	−4.15	2.500	6.12	−5.22
2.9987	6.86	−4.48	2.9970	5.61	−5.73

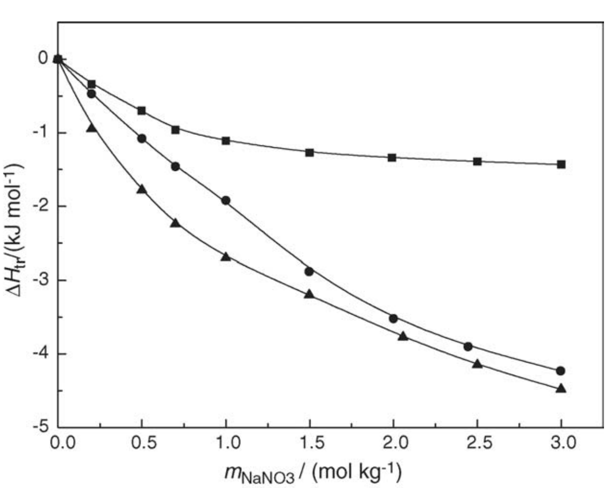

Fig. 1. Enthalpies of transfer of glycine (●), L-alanine (■), L-serine (▲) from water to aqueous solutions of $NaNO_3$ at $T = 298.15$ K.

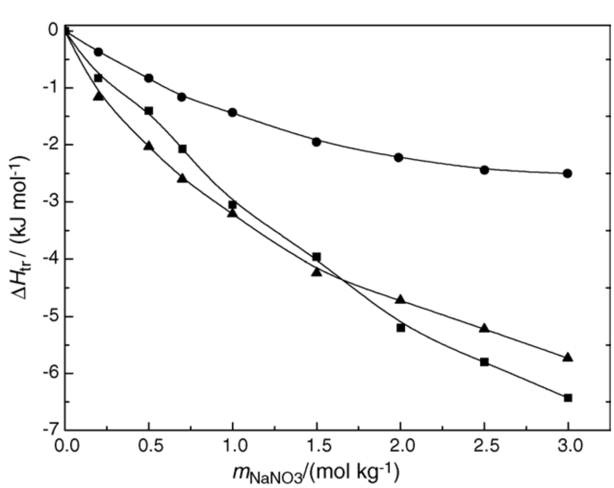

Fig. 2. Enthalpies of transfer of L-alanine (●), glycine (■), L-serine (▲) from water to aqueous solutions of $NaClO_4$ at $T = 298.15$ K.

The interaction between salt and amino acid may be assumed to be a sum of three contributions [6]: electrostatic interaction, partial desolvation of solutes and solvent reorganization. The latter two are structural interaction. Since the present amino acids have very similar dipole moment, the contribution of electrostatic interaction to the transfer enthalpy should be approximately the same. Therefore, it is the structure interaction that is responsible for the observed variation trends of ΔH_{tr}. The hydrophilic–hydrophilic interaction between the polar side chain (–OH) of L-serine and ions gives a negative contribution to the transfer enthalpy [7]. Whereas the hydrophobic–hydrophilic interaction between the apolar side chain ($–CH_3$) of L-alanine and ions cause a positive contribution to transfer enthalpy [7]. The observed succession L-serine < glycine < L-alanine of $\Delta_{tr}H$ in $NaNO_3$ and low concentration $NaClO_4$ solutions, can be well explained through the above different interactions. But in $NaClO_4$ solutions when $m > 2\,\mathrm{mol\,kg^{-1}}$, $\Delta_{tr}H$ of glycine and serine is abnormal. This is probably due to the interaction between ions in concentrated aqueous solutions of $NaClO_4$ [8], decreasing the interaction between L-serine and $NaClO_4$ more than that between glycine and $NaClO_4$. On the other hand for all the three amino acids the values of the transfer enthalpy are more negative in $NaClO_4$ solutions than in $NaNO_3$ solutions. This is probably due to the less contribution of dehydration of ClO_4^- than NO_3^- [9,10].

Acknowledgement

This work was supported by the National Science Foundation of China Grant 20273061.

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