ELSEVIER

Thermochimica Acta 385 (2002) 1–4

thermochimica acta

www.elsevier.com/locate/tca

The enthalpic interaction parameters of α-aminobutyric acid and alkali metal halides in water at 298.15 K

Yan Lu*, Wei Xie, Jinsuo Lu

College of Chemistry and Environmental Science, Henan Normal University, Xinxiang, Henan 453002, PR China

Received 11 April 2001; received in revised form 25 July 2001; accepted 27 July 2001

Abstract

The enthalpies of solution have been measured for α-aminobutyric acid in LiCl, NaCl, KCl and NaBr aqueous solutions at 298.15 K. The enthalpic interaction parameters h_{xy}, h_{xxy} and h_{xyy} of α-aminobutyric acid with these salts have been evaluated. Combining the previous studies for the enthalpic interaction parameters of glycine and α-alanine with alkali metal halides, the experimental results are discussed in view of electrostatic and structural interactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: α-Aminobutyric acid; Enthalpy of solution; Halide; Interaction parameter

1. Introduction

In solution chemistry and biological chemistry, it is very important to study interaction between electrolyte and amino acids. We have measured the enthalpies of solution of glycine and α-alanine in water and in some alkali metal halides aqueous solutions [1–5], and obtained the pair and triplet enthalpic interaction parameters between the amino acids and the salts by using the McMillan and Mayer approach [6]. In the present work, we expand the investigations of enthalpic interaction to α-aminobutyric acid with alkali metal halides in water at 298.15 K.

2. Experimental

Analytical grade α-aminobutyric acid used in the experiment were recrystallized from water + methanol mixture. Analytical grade LiCl was recrystallized from acetic acid + benzene mixture. Analytical grade NaBr was recrystallized from water. NaCl and KCl were of high purity, warranting no further treatment. All the materials were dried and stored over P_2O_5 prior to use. The water used was deionized and double-distilled.

The enthalpy of solution measurements were done using a C-80 calorimeter (Setaram). The experimental procedure has been described in earlier publication [7]. The total uncertainty in the enthalpy was ±0.5%.

3. Results and discussion

According the McMillan and Mayer approach the enthalpy of transfer of a non-electrolyte (y) from pure water (w) to an electrolyte (x) aqueous solution can be expressed as follows [1].

$$\Delta H_y(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{x})/m_x = 2h_{xy} + 3h_{xxy}m_x + 3h_{xyy}m_y \quad (1)$$

where m_x and m_y are the molalities defined per kilogram of pure water, and h_{xy}, h_{xxy} and h_{xyy} are the enthalpic pair and triplet interaction parameters. The

* Corresponding author. Fax: +86-373-3869901.
E-mail address: luyan88@263.net (Y. Lu).

0040-6031/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(01)00700-6

molar enthalpies of solution of α-aminobutyric acid in water can be expressed by the following Eq. (2).

$$\Delta_{sol}H_m\,(\mathrm{J\,mol^{-1}}) = 1392 + 754m_y \quad (2)$$

The molar enthalpies of solution of α-aminobutyric acid in LiCl, NaCl, KCl and NaBr aqueous solutions are given in Tables 1–4. The molar enthalpies of transfer of α-aminobutyric acid from water to the aqueous solutions of the salts have been calculated and fitted to Eq. (1) by using a least-squares method. The enthalpic interaction parameters obtained are given in Table 5.

Lilley et al. [8] considered that the interaction between electrolyte and amino acid is composed of three effects: (a) electrostatic interaction; (b) partial

Table 1
The enthalpies of solution $\Delta_{sol}H_m$ of α-aminobutyric acid in water–LiCl mixtures at 298.15 K (in J mol^{-1})

m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 0.9995)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 2.998)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 4.998)
0.1182	2209	0.1228	3221	0.1344	3862
0.1886	2252	0.1909	3264	0.2075	3913
0.2616	2301	0.2565	3303	0.2776	3967
0.3242	2337	0.3216	3329	0.3468	4002
0.3858	2380	0.3890	3351	0.4136	4038
0.4632	2416	0.4548	3376	0.4837	4086

Table 2
The enthalpies of solution $\Delta_{sol}H_m$ of α-aminobutyric acid in water–NaCl mixtures at 298.15 K (in J mol^{-1})

m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 1.002)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 2.999)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 4.952)
0.1241	1732	0.1282	2463	0.1370	3813
0.1858	1771	0.1928	2510	0.2021	3849
0.2432	1811	0.2593	2551	0.2625	3871
0.3013	1856	0.3150	2593	0.3314	3909
0.3599	1889	0.3774	2640	0.3938	3948
0.4160	1932	0.4418	2689	0.4526	3979

Table 3
The enthalpies of solution $\Delta_{sol}H_m$ of α-aminobutyric acid in water–KCl mixtures at 298.15 K (in J mol^{-1})

m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 1.997)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 3.001)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 3.988)
0.1265	1606	0.1394	2194	0.1393	2589
0.1888	1652	0.1968	2223	0.2019	2630
0.2469	1690	0.2594	2268	0.2692	2667
0.3120	1737	0.3235	2311	0.3383	2712
0.3614	1775	0.3866	2346	0.4113	2764
0.4210	1814	0.4521	2386	0.4814	2806

Table 4
The enthalpies of solution $\Delta_{sol}H_m$ of α-aminobutyric acid in water–NaBr mixtures at 298.15 K (in J mol^{-1})

m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 1.001)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 2.996)	m_y (mol kg^{-1})	$\Delta_{sol}H_m$ (m_x = 4.992)
0.1245	1516	0.1323	2048	0.1369	3270
0.1921	1548	0.2005	2091	0.2067	3323
0.2562	1598	0.2661	2141	0.2785	3369
0.3208	1642	0.3351	2182	0.3486	3414
0.3845	1688	0.4013	2224	0.4133	3452
0.4502	1729	0.4077	2265	0.4801	3489

Table 5
Enthalpic interaction parameters of α-aminobutyric acid with alkali metal halides in water at 298.15 K

Electrolyte	h_{xy} (J kg^2 mol^{-3})	h_{xxy} (J kg^2 mol^{-3})	h_{xyy} (J kg mol^{-2})
LiCl	390 ± 5	−28 ± 9	−19 ± 1
NaCl	90 ± 5	−14 ± 10	19 ± 1
KCl	36 ± 2	−13 ± 3	18 ± 1
NaBr	−31 ± 2	−15 ± 3	29 ± 1
NaI[a]	−170 ± 8	−20 ± 14	41 ± 1

[a] From [3].

desolvation of solutes; and (c) solvent reorganization. The latter two effects are structural interaction. In our previous studies [1–5], we have discussed the enthalpic interactions of glycine and α-alanine with alkali metal halides. It has been referred that the interaction of ions with the polar groups of amino acids is mainly electrostatic and make negative contribution to enthalpic function and that the interaction of ions with the apolar part of amino acid is mainly structural and make positive contribution to enthalpic function. These conclusions can also be used to explain the interaction of α-aminobutyric acid with alkali metal halides. Electrolyte (x) is composed of cation (M) and anion (A), so h_{xy} can be expressed as the sum of h_{My} and h_{Ay}. From Table 5, we can see that the values of h_{xy} for the systems studied here show a tendency to increase as the radius of ion decrease. This kind of tendency also take place in the systems of glycine and α-alanine [1–5]. Combining the previous studies for glycine and α-alanine, another tendency can be seen that the values of h_{xy} increase as the carbon number of amino acid molecules increases for all of the alkali metal halides investigated. The main cause of the first tendency is that the desolvation of ion will become increasingly easy as the ionic size increases and its endothermic effect of the partail desolvation will decrease. For the second tendency, we can make an analysis as follows. According to the well-known Savage and Wood group additivity mode [9], the interaction of electrolyte with the apolar CH_2 group will make positive contribution to enthalpic pair interaction parameter [10,11] and the contribution will increase with CH_2 group increase. Since the apolar part of glycine is very short, the interaction between ion and glycine molecule is mainly the electrostatic interaction and the partail desolvation. As the carbon atoms of amino acid molecules increases, the solvent reorganization effect of ion on the hydrophobic hydration structure of the molecules will manifest its influence. This effect is destructive and make positive contribution to h_{xy}. Therefore, the values of h_{xy} will increase as the carbon number increase.

The enthalpic interaction parameters h_{xxy} is the sum of h_{MMy}, h_{AAy} and $2h_{MAy}$. From Table 5, one can see that all of the values of h_{xxy} are small positive except LiCl, and the value of h_{xxy} will increase as the ionic size increase. The α-amino acid molecule is present as a zwitter ion in water, therefore the MAy type interaction is very different with MMy and AAy types interaction. In the MAy type interaction, cation and anion will undergo electrostatic interactions with the carboxyl and amino groups of α-amino acid molecule, respectively, and make negative contribution to h_{xxy}. In the MMy and AAy types interactions, only one ion can undergo electrostatic interaction with the polar group of α-amino acid molecule which is opposite in polarity to the ion. Since the electrostatic rejection, the other one ion will be away from the polar head of α-amino acid molecule and produce structural interaction with the apolar part of α-amino acid molecule. The electrostatic rejection and the structural interaction will make quite large positive contribution to h_{xxy} and sometimes the structural interaction even become predominant [12]. Larger ion has larger dispersion force, so that it has greater destructive effect on the hydrophobic hydration structure of apolar part of α-amino acid molecule. This is the main cause of h_{xxy} increase as the ionic size increases.

The h_{xyy} is the sum of h_{Myy} and h_{Ayy}. On the base of our work and the work of Gallardo et al. [13], we have discussed the association fashions of two glycine molecules and two α-alanine molecules [1]. Since the apolar part of glycine is very short, the association of two glycine molecules is head-on-fashion and their self-interaction parameter h_{yy} is negative. For the α-alanine, its h_{yy} is positive and the association of two

molecules is side-by-side manner [1,13]. The association of two α-aminobutyric acid molecules should also be side-by-side manner since their h_{yy} is also positive [13,14]. For two α-amino acid molecules there are four polar groups, two amino groups whose polarity are positive and two carboxyl groups whose polarity are negative. For the side-by-side association manner, electrostatic attraction take place between the amino group of an amino acid molecule and the carboxyl group of the other amino acid molecule, but the other two polar groups keep free [1]. In Myy and Ayy types of triplet interactions, ion can still produce electrostatic interaction with the one of polar groups, which keep free, and give negative contribution to h_{xyy}. Therefore, h_{xyy} should be much smaller than h_{yy}. The experiments for α-alanine and α-aminobutyric acid all indicate the conclusion.

Acknowledgements

This project 29773011 is supported by the National Natural Science Foundation of China. The authors are grateful to this foundation for financial support.

References

[1] Y. Lu, T. Bai, W. Xie, J. Lu, Thermochim. Acta 319 (1998) 11.
[2] Y. Lu, W. Xie, Z. Lu, J. Lu, H. Wang, Thermochim. Acta 256 (1995) 261.
[3] W. Xie, Y. Lu, K. Zhuo, J. Lu, S. Zhan, Thermochim. Acta 254 (1995) 103.
[4] Y. Lu, W. Xie, J. Lu, Thermochim. Acta 246 (1994) 49.
[5] Y. Lu, S. Zhen, J. Lu, Acta Phys. Chem. Sin. 10 (1994) 281.
[6] W.G. McMillan, J.E. Mayer, J. Chem. Phys. 13 (1945) 276.
[7] Y. Lu, Q. Cheng, Y. Chen, T. Bai, J. Lu, Thermochim. Acta 334 (1999) 29.
[8] T.H. Lilley, E. Moses, I.R. Tasker, J. Chem. Soc., Faraday Trans. I 76 (1980) 906.
[9] J.J. Savage, R.H. Wood, J. Sol. Chem. 5 (1976) 733.
[10] C. de Visser, G. Perron, J.E. Desnoyers, J. Am. Chem. Soc. 99 (1977) 5894.
[11] K.G. Davis, M.A. Gallardo-Jimenez, T.H. Lilley, J. Chem. Soc., Faraday Trans. I 85 (1989) 2901.
[12] G. Perron, D. Joly, J.E. Desnoyers, Can. J. Chem. 56 (1978) 552.
[13] M.A. Gallardo, T.H. Lilley, H. Linsdell, S. Otin, Thermochim. Acta 223 (1993) 41.
[14] T.H. Lilley, R.P. Scott, J. Chem. Soc., Faraday Trans. I 72 (1976) 184.