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Thermochimica Acta 319 (1998) 11–15

thermochimica acta

The enthalpic interaction of α-alanine with alkali metal halides in water at 298.15 K

Yan Lu*, Tongchun Bai, Wei Xie, Jinsuo Lu

Department of Chemistry, Henan Normal University, Xinxiang, Henan 453002, China

Received 9 December 1997; received in revised form 3 June 1998; accepted 12 June 1998

Abstract

The enthalpies of solution have been measured for α-alanine in NaBr, KBr and KI aqueous solutions at 298.15 K. The enthalpic interaction parameters h_{xy}, h_{xyy} and h_{xxy} of α-alanine with these salts have been evaluated. Combining the previous studies for other alkali metal halides, the experimental results are discussed in view of electrostatic and structural interactions.

Keywords: α-Alanine; Enthalpy of solution; Halide; Interaction parameter

1. Introduction

We have measured the enthalpies of solution of α-alanine in water and in LiCl, NaCl, KCl and NaI aqueous solutions [1,2] and obtained the pair and triplet enthalpic interaction parameters between α-alanine and the salts by using the McMillan–Mayer approach [3]. In order to investigate the behaviour of interaction of α-alanine with alkali metal halides more completely, we have further measured the enthalpies of solution of α-alanine in NaBr, KBr and KI aqueous solutions and obtained the enthalpic interaction parameters between them. We will report the experimental results in this paper and attempt to give a reasonable explanation for the behaviour of enthalpic interaction between α-alanine and alkali metal halides.

2. Experimental

The analytical grade α-alanine used in the experiments was recrystallized from water–methanol mixture and dried at 383 K. Analytical grade NaBr, KBr and KI were recrystallized from water and dried at 383 K. All the water used was deionized and double-distilled.

The enthalpy of solution measurements were made using a C-80 calorimeter (SETARAM). The experimental procedure has been described in an earlier publication [4]. The total uncertainty in the enthalpy was about ±0.5%.

3. Results and discussion

According to the McMillan–Mayer theory [3], all the thermodynamic properties of multi-component solutions can be expressed by using a virial expansion in m which relates the non-ideal contributions of any

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*Corresponding author. Fax: +86-373-3383145.

PII S0040-6031(98)00411-0

total thermodynamic function to a series of pair, triplet and higher order interaction parameters. The enthalpies of transfer of a non-electrolyte (Y) from pure water (W) to an electrolyte (X) aqueous solution can be expressed as mentioned in Refs. [5,6].

$$\Delta H\mathrm{y}(\mathrm{W} \rightarrow \mathrm{W}+\mathrm{X}) = 2h_{xy}m_x + 3h_{xyy}m_xm_y + 3h_{xxy}m_x^2 + \cdots \qquad (1)$$

For the studied system, we used the truncated form of the equation as mentioned in Refs. [1,2].

$$\Delta H\mathrm{y}(\mathrm{W} \rightarrow \mathrm{W}+\mathrm{X})/m_x = 2h_{xy} + 3h_{xyy}m_y + 3h_{xxy}m_x \qquad (2)$$

where m_x and m_y are the molalities defined in mole per kilogram of pure water, h_{xy} the enthalpic pair interaction parameter and h_{xxy} and h_{xyy} the enthalpic triplet interaction parameters. The molar enthalpies of solution of α-alanine in water can be expressed by the following equation as mentioned in Ref. [1].

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{J\,mol^{-1}}) = 9253 + 271m_y \qquad (3)$$

The molar enthalpies of solution of α-alanine in NaBr, KBr and KI aqueous solution are given in Table 1–3. The enthalpies of transfer of α-alanine from water to the aqueous solutions of three salts have been calculated and fitted to Eq. (2) using a least-squares method

Table 1
The enthalpies of solution ΔH_{m} of α-alanine in water–NaBr mixtures at 298.15 K (in J mol^{-1})

m_y/ (mol kg^{-1})	ΔH_{m} (m_x=0.9992)	m_y/ (mol kg^{-1})	ΔH_{m} (m_x=2.997)	m_y/ (mol kg^{-1})	ΔH_{m} (m_x=4.989)
0.1427	8873	0.1502	8622	0.1572	9176
0.2100	8904	0.2254	8656	0.2331	9225
0.2833	8939	0.2945	8680	0.3152	9272
0.3458	8960	0.3711	8737	0.3920	9311
0.4236	8985	0.4418	8764	0.4658	9346
0.4884	9001	0.5791	8782	0.5480	9393

Table 2
The enthalpies of solution ΔH_{m} of α-alanine in water–KBr mixtures at 298.15 K (in J mol^{-1})

m_y/ (mol kg^{-1})	ΔH_{m} (m_x=0.9971)	m_y/ (mol kg^{-1})	ΔH_{m} (m_x=2.995)	m_y/ (mol kg^{-1})	ΔH_{m} (m_x=4.989)
0.1488	8772	0.1610	8427	0.1629	8687
0.2187	8806	0.2362	8481	0.2475	8702
0.2864	8833	0.3087	8517	0.3313	8753
0.3558	8858	0.3917	8532	0.4075	8803
0.4273	8879	0.4597	8577	0.4936	8857
0.4993	8905	0.5350	8599	0.5623	8872

Table 3
The enthalpies of solution ΔH_{m} of α-alanine in water–KI mixtures at 298.15 K (in J mol^{-1})

m_y/ (mol kg^{-1})	ΔH_{m} (m_x=0.4998)	m_y/ (mol kg^{-1})	ΔH_{m} (m_x=0.9938)	m_y/ (mol kg^{-1})	ΔH_{m} (m_x=2.994)
0.1455	8802	0.1544	8436	0.1632	7878
0.2190	8831	0.2227	8488	0.2452	7910
0.2903	8858	0.2925	8511	0.3178	7925
0.3532	8863	0.3519	8546	0.4010	7952
0.4281	8884	0.4346	8568	0.4742	7973
0.4919	8917	0.5062	8590	0.5506	8003

Table 4
Enthalpic interaction parameters of α-alanine with alkali metal halides in water at 298.15 K

Electrolyte	h_{xy}/(J kg mol^{-2})	h_{xyy}/(J kg mol^{-2})	h_{xxy}/(J kg mol^{-2})
LiCl	253±3	−25±5	−17±1
NaCl	−123±2	12±3	23±1
KCl	−160±5	23±8	26±1
NaBr	−257±3	21±5	31±1
NaI	−509±10	25±15	52±1
KBr	−303±6	22±10	32±1
KI	−531±8	25±15	63±2

and the enthalpic interaction parameters thus obtained are given in Table 4.

It is generally believed that the interactions between electrolyte and non-electrolyte are composed of electrostatic and structural interactions. Lilley et al. [7] considered that the interaction between electrolyte and amino acid is composed of three effects: (a) electrostatic interaction; (b) partial desolvation of solutes; and (c) solvent reorganization. The latter two effects are structural interactions. De Visser et al. [8] indicated that, in most cases, the net effect of co-sphere overlap on the hydration structure is destructive. The data presented in Table 4 show that the enthalpic interaction parameters between α-alanine and alkali metal halides are related with the radii of anion (r_A) and cation (r_M). We will try to explain the relation on the basis of the electrostatic and structural interaction concepts.

Piekarski and Tkaczyk [9] carried out a multiple linear-regression analysis for h_{xy} using the Abraham–Kamlet–Taft equation [10,11] and found that the electrostatic interaction, which was mostly due to ion–dipole type interactions, gave a negative contribution to h_{xy}. The enthalpic pair interaction parameters can also be correlated by means of the well-known Savage and Wood group additivity model [12] and the results showed that the enthalpic pair interaction of electrolyte with the apolar CH_2 group is positive and with some polar groups is negative [8,13]. h_{xy} is the sum of h_{My} and h_{Ay}. We have discussed the contributions to h_{xy} of the ions with glycine in the view of electrostatic interaction, partial desolvation and solvent reorganization [14]. The conclusions obtained can also be used to explain the interaction between α-alanine and electrolytes. But the effect of the solvent reorganization will be larger as the hydrocarbon chain is longer. This can be seen from the positive differences between the pair enthalpic interaction parameters of salts with α-alanine and glycine. Fig. 1 shows that there are linear relations between the differences mentioned above and the ionic radius of cations and anions. From Fig. 1, we can get two other pieces of information. One is that the ion with larger size has larger dispersion force and can make a larger destructive effect on the hydrophobic hydration structure of non-electrolyte. The other is the increasing of the salt's effect on the hydrophobic hydration structure as the radius of anion is more obvious than as cation.

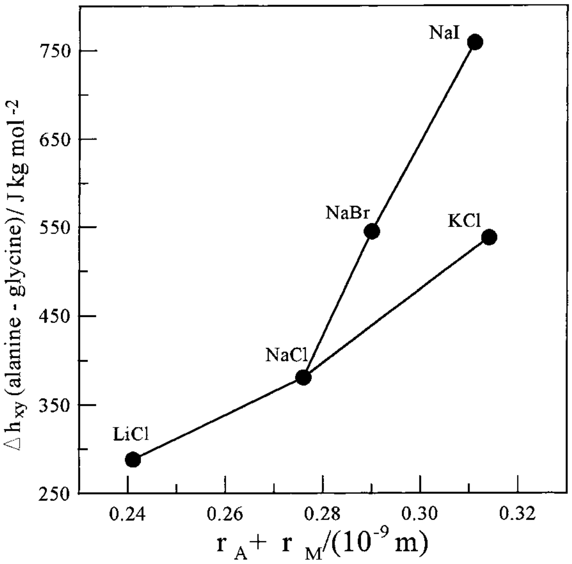

Fig. 1. Dependences of the difference Δh_{xy} (alanine–glycine) on the sum of radii of anion (r_A) and cation (r_M) of salt.

The enthalpic interaction parameter h_{xxy} is the sum of h_{MMy}, h_{AAy} and $2h_{MAy}$. The α-alanine is present as a zwitter ion in water the formula of which is $^{+}H_3N\text{-}CH_2(CH_3)\text{-}COO^{-}$. In the M–A–y type interaction, cation and anion will undergo electrostatic interactions with the carboxyl and amino groups of α-alanine, respectively, and the electrostatic interaction will be accompanied by a partial desolvation of the solutes which interact with each other. The total contribution to h_{xxy} is negative as in the above discussion on h_{xy}. In the M–M–y and A–A–y types interaction, only one ion can undergo electrostatic interaction with the polar group of α-alanine which is opposite in polarity to the ion. The other one will produce electrostatic rejection with the same ion and the another polar group of α-alanine. Therefore, it will be away from the polar head of α-alanine and interact with apolar part of α-alanine. The structural interaction will make quite a large positive contribution to enthalpic functions and sometimes even become predominant [6]. The contributions from the M–M–y and A–A–y types of interaction will be larger than that from the M–A–y type of interaction, the net contribution to h_{xxy} will be positive. Since h_{xxy} is composed of three types of interaction, it is difficult to analyse the interaction in more detail. However, we can also see from Fig. 2 that there are quite good linear relation between the values of the h_{xxy} and the ionic size of the salts. This indicate that the ionic size of the salt also play an important role in x–x–y interaction.

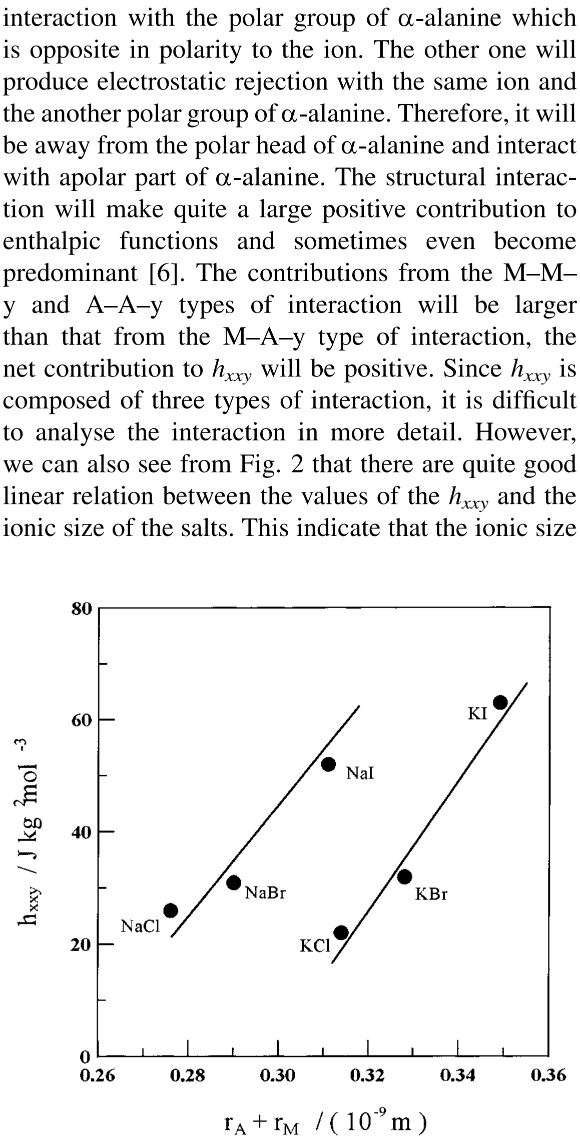

Fig. 2. Dependences of h_{xxy} on the sum of radii of anion (r_A) and cation (r_M) of salt.

The enthalpic interaction parameter h_{xyy} is the sum of h_{Myy} and h_{Ayy}. Gallardo et al. [15] have measured the homotactic pairwise enthalpic parameters of some amino acids in water and given two modules of the association for the α-amino acids. One is in a side-by-side manner and the other in a head-on-fashion. Since the apolar part of glycine is shortest, it will take the head-on-module to associate with one another and hence render h_{yy} large negative value. If α-alanine is also associated by the head-on-module, its h_{yy} value will be similar to that of glycine. But the experimental data are not so, the values of h_{yy} of glycine and α-alanine are −439 and 217 J kg mol^{-2} [15], respectively. Therefore, a reasonable guess would be the association of two α-alanine molecules takes the side-by-side manner. It is worth mentioning that the association in head-on-module has made all the polar groups of the two amino acid molecules interact with each other and in side-by-side manner just one pair polar group takes place the electrostatic interaction [15]. If the guess is true, we will get the conclusions as below. In the ion–glycine–glycine triplet interaction, the ion will only be able to interact with the apolar part of the two associated molecules and give positive contribution to h_{xyy} which will make the values of h_{xyy} more positive than h_{yy} [14]. And in the ion–α-alanine–α-alanine triplet interaction, the ion will still be able to undergo electrostatic interaction with the one of remaining polar groups of the two molecules and give negative contribution to h_{xyy} which will make the values of h_{xyy} more negative than h_{yy}. Our investigations support this guess and the data in Table 4 and Ref. [14] indicate the conclusions.

Acknowledgements

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

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