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Article

Enthalpic Interaction for α-Amino Acid with Alkali Metal Halides in Water

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The studies of the enthalpic interaction parameters, h_{xy}, h_{xyy} and h_{xxy}, of alkali metal halides with glycine, α-alanine and α-aminobutyric acid were published. Synthetic considering of the results of the studies, some interesting behaviors of the interaction between alkali metal halides and the α-amino acids have been found. The values of h_{xy} will increase with the increase of the number of carbon atoms in alkyl side chain of amino acid molecules and decrease with the increase of the radius of the ions. The increasing of the salt's effect on the hydrophobic hydration structure as the radii of anion is more obvious than as that of cation. The value of h_{xxy} will regularly decrease with the increase of the number of carbon atoms in the alkyl chain of amino acids and linear increase with the increase of the radius. But the relation of h_{xxy} with the radius of cations is not evident. The value of h_{xyy} will increase with the increase of the radii of the ions. As the increase of the number of carbon atoms of amino acids, h_{xyy} is decreas for the ions which have lager size and there is a maximum value at α-alanine for the ions which have small size. The behaviors of the interaction mentioned above were further discussed in view of electrostatic and structural interactions.

Keywords α-amino acid, alkali metal halides, enthalpic interaction, aqueous solution

Introduction

The study of the properties of protein is very important in biological chemistry. Salts can have marked effects on the stability of structure of protein with the interactions between them.[1,2] The interactions are difficulty to study directly because of the complexity of protein structure. Many investigators studied the interaction by using the model molecules of protein such as amino acids or amides, instead of using the complex molecules of protein.[3-7] We chosen α-amino acids as the model molecules of protein and studied the enthalpic interaction of them with alkali metal halides in water.[8-13] In this paper the interaction between alkali metal halides and the α-amino acid with different alkyl side chain is further discussed in view of electrostatic and structural interactions.

Enthalpic interaction parameters

Enthalpies of solution of α-amino acids in water and in aqueous alkali metal halides solutions were measured in a C-80 calorimeter (Setaram) using reversed-mixing vessel. The reversed-mixing vessel has two chambers separated by a tilting lid. About 0.05—0.35 g of amino acids, which was weighed on a single-pan balance (Mettler) with a sensitivity of 10 μg , was introduced into the vessel and then the lid was put in place. In order to obtain a complete separation of the chambers, 0.5 g of mercury was put into the vessel to seal the gapping between the vessel and the lid. About 5 mL of solvent was weighed on an analytical balance with a sensitivity of 0.1 mg and introduced into the vessel. The calibration of the calorimeter was performed with an EJ2 Joule-effect device (Setaram). The total uncertainty in the measurement was about ±0.5%.

According to the McMillan-Mayer approach,[14] the enthalpies of transfer of amino acids (y) from pure water (w) to an electrolyte (x) aqueous solution can be expressed as follows[15,8]

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

where h_{xy} is the enthalpic pair interaction coefficient, h_{xyy} and h_{xxy} are the enthalpic triplet interaction coefficients, which can be obtained by using a least squares method.

Discussion

The enthalpic interaction parameters of α-amino acids with alkali metal halides in water are compiled in Table 1. The interaction between amino acids and ions of electrolyte can be considered to be composed of three effects.[16] (a) electrostatic interaction, (b) partial desolvation of solutes, (c) solvent reorganization. The elec-

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Table 1 Enthalpic interaction parameters of α-amino acids with alkali metal halides in water at 298.15 K

Amino acid	Electrolyte	h_{xy}/(J•kg•mol^{-2})	h_{xyy}/(J•kg^2•mol^{-3})	h_{xxy}/(J•kg^2•mol^{-3})
glycine	LiCl	35	−62	−7
glycine	NaCl	−504	−49	45
glycine	KCl	−698	49	150
glycine	NaF	13	−134	−5
glycine	NaBr	−802	37	57
glycine	NaI	−1268	114	87
alanine	LiCl	253	−25	−17
alanine	NaCl	−123	12	23
alanine	KCl	−160	23	26
alanine	NaBr	−257	21	31
alanine	NaI	−509	25	52
alanine	KBr	−303	22	32
alanine	KI	−531	25	63
aminobutyric acid	LiCl	390	−28	−19
aminobutyric acid	NaCl	90	−14	19
aminobutyric acid	KCl	36	−13	18
aminobutyric acid	NaBr	−31	−15	29
aminobutyric acid	NaI	−170	−20	41

trostatic interaction is mainly occurring between ions and the polar groups of amino acids. This interaction is exothermic and will give negative contribution to the enthalpic interaction parameters. The partial desolvation of solutes is caused by the cosphere overlap of solvation layer of solutes, which is destructive.[17,18] Therefore the partial desolvation of solutes will give positive contribution to enthalpic function. As for the contribution of solvent reorganization to enthalpic function, we should make a concrete analysis of concrete system. In general speaking, the solvent reorganization will make negative contribution if it enhances the solvent structure and make positive contribution if it weakens.

Discussion for h_{xy}

For the systems of α-amino acids and alkali metal halides in aqueous solution, the values of h_{xy} will decrease with the increases of the radii of the cations (Figure 1) and the anions (Figure 2). And will increase with the increases of the number of carbon atoms in alkyl side chain of amino acid molecules (Figure 3). In aqueous solution, electrolyte will be dissociated into cation (M) and anion (A), so h_{xy} can be expressed as the sum of h_{My} and h_{Ay}. Between the ions and the polar groups of the amino acid molecules, electrostatic interaction will be produced, which will make negative contribution to h_{xy}. However, this negative contribution will be counteracted to a quite large extent by the endothermic effect of the partial desolvation of the solutes. An ion with smaller size is more soluble, and consequently its endothermic effect on the partial desolvation is larger. This will be the main cause of the decrease in the negative values of h_{xy} as ionic size decreases.

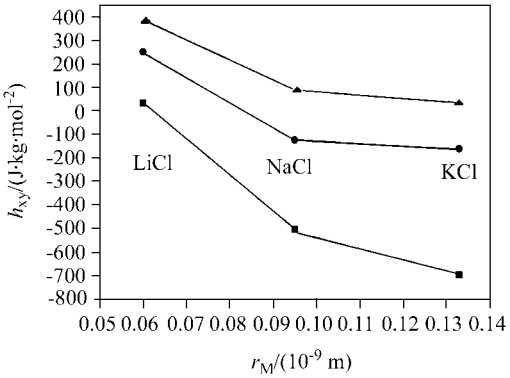

Figure 1 Variation of h_{xy} with the radii of cation (■, glycine; ●, alanine; ▲, aminobutyric acid).

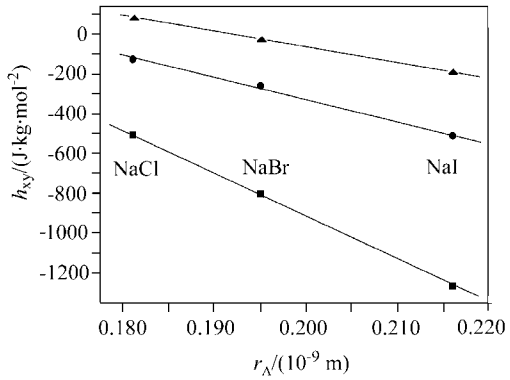

Figure 2 Variation of h_{xy} with the radii of anion (■, glycine; ●, alanine; ▲, aminobutyric acid).

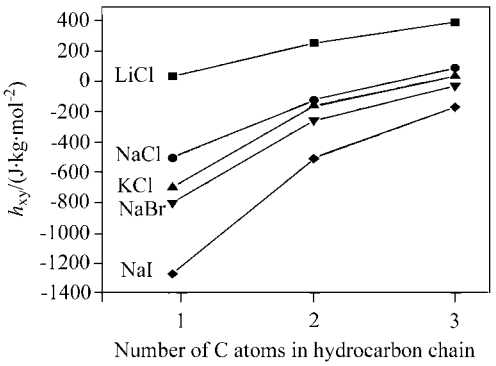

Figure 3 Variation of h_{xy} with the number of carbon atoms in the hydrocarbon chain.

In aqueous solution, there are hydrophobic hydration structures around the alkyl side chain of the amino acid molecules. The existence of ion will exert destructive solvent reorganization effect on the hydrophobic hydration structure, which the effect will give positive contribution to h_{xy}. As the alkyl side chain is lengthened, the destructive solvent reorganization effect will enlarge, therefore the values of h_{xy} will also increase. However, this increase of h_{xy} caused by one carbon atom extend in alkyl side chain is not a fixed value. Figure 4 gives the Δh_{xy} of alkali metal halides with different amino acids. In the figure, we can get two 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 that of cation.

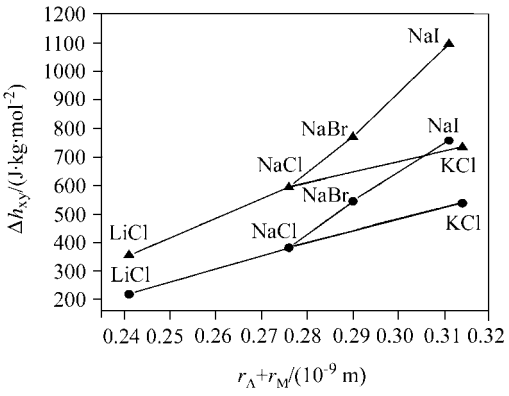

Figure 4 Dependences of the differences of h_{xy} on the sum of radii of cation and anion of salt [●, Δh_{xy} (alanine-glycine); ▲, Δh_{xy} (aminobutyric acid-alanine)].

Discussion for h_{xxy}

The value of h_{xxy} is a linear function of the radii of anions and the slope is positive (Figure 5). The relation of h_{xxy} with the radii of cations is not evident (Figure 6). And the value of h_{xxy} will regularly decrease as the number of carbon atoms in the alkyl chain of amino acids increase (Figure 7). These relations are also related with the form of interaction among the amino acid molecule and the ions.

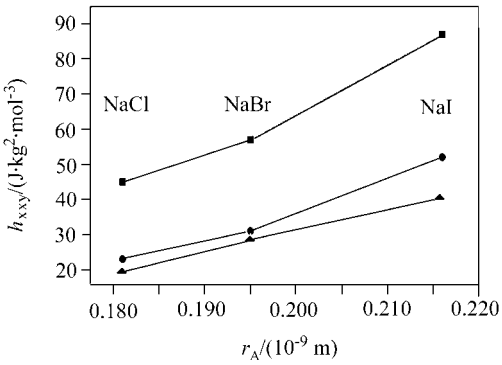

Figure 5 Variation of h_{xxy} with the radii of anion (■, glycine; ●, alanine; ▲, aminobutyric acid).

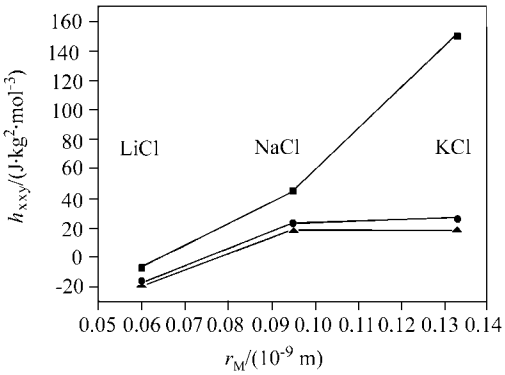

Figure 6 Variation of h_{xxy} with the radii of cation (■, glycine; ●, alanine; ▲, aminobutyric acid).

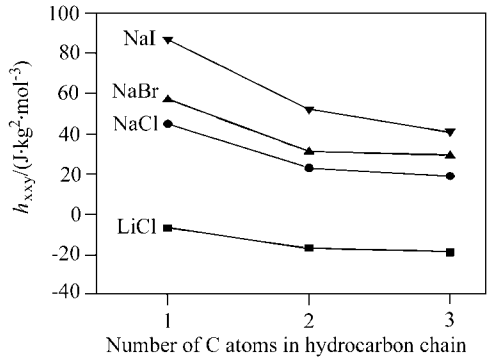

Figure 7 Variation of h_{xxy} with the number of carbon (atoms in the hydrocarbon chain).

h_{xxy} is the sum of h_{MMy}, h_{AAy} and 2 h_{MAy}. The M-A-y type interaction is different from that of the M-M-y and A-A-y types. For the M-A-y type, the anion and cation of electrolyte will all undergo electrostatic interaction with the carboxyl and amino groups of amino acid molecule respectively, in which total contribution to h_{xxy} is negative. But for the M-M-y and A-A-y types, since the two ions are the same, only one ion can undergo electrostatic interaction with the polar group of amino acid molecule which is opposite in polarity to the ion.

The other one will produce destructive structural interaction with the apolar part of amino acid molecule, which will make positive contribution to enthalpic functions. Apart from this destructive structural interaction, this ion will also produce electrostatic repulsion with the polar group of amino acid molecule. The electrostatic repulsion interaction will make larger positive contribution to enthalpic functions. For the same kind of amino acid, the destructive structural interaction, therefore the positive contribution to the enthalpic functions, will increase with the increase of radii of ions. For the same kind of electrolyte, the distance between the ion and the polar head of amino acid will be larger as the carbon chain of the amino acid increase. This will make the electrostatic repulsion effect between them decrease and the h_{xxy} decrease. But as the carbon chain of the amino acid increases, the destructive solvent reorganization effect of ion on the hydrophobic hydration structure of the alkyl group will increase. This will make h_{xxy} increase, which is opposite to the electrostatic repulsion effect. Therefore, we can think that the electrostatic repulsion effect will be gradually relegated to a secondary position and the h_{xxy} maybe will increase after the carbon chain is long enough.

Discussion for h_{xyy}

For glycine, the values of h_{xyy} increase with the increase of the radii of ions largely. For alanine and aminobutyric acid, the values of h_{xyy} also increase with the increase of the radii of ions, but the increment is small (Figure 8 and Figure 9). For KCl, NaBr and NaI, which have the ion with larger size, the values of h_{xyy} decrease with the increase of the carbon atoms in the alkyl chain of amino acid molecules. And for NaCl and LiCl, which the ions of all have small size, the largest values of h_{xyy} are at alanine (Figure 10).

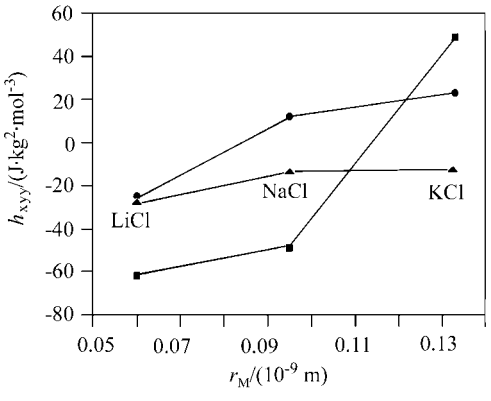

Figure 8 Variation of h_{xyy} with the radii of cation (■, glycine; ●, alanine; ▲, aminobutyric acid).

Since the enthalpic interaction parameter h_{xyy} is the sum of h_{Myy} and h_{Ayy}, the interaction between two amino acid molecules is very important to h_{xyy}. Lilley[3] has given two modules of the association for the α-amino acids. One is in a side-by-side manner and the other is in a head-on-fashion. They have obtained the homotactic

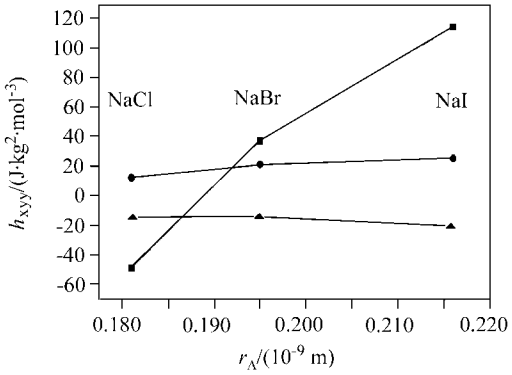

Figure 9 Variation of h_{xyy} with the radii of anion (■, glycine; ●, alanine; ▲, aminobutyric acid).

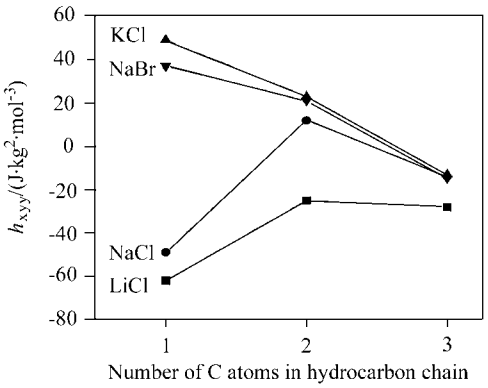

Figure 10 Variation of h_{xyy} with the number of carbon atoms in hydrocarbon chain.

pairwise enthalpic parameters of glycine, alanine and aminobutyric acid, which are −439, 217 and 505 J•kg•mol^{-2}, respectively. Since the apolar part of glycine is the shortest, it will take the head-on-module to associate with each other and hence render h_{yy} large negative value. If alanine and aminobutyric acid are also associated by head-on-module, their h_{yy} values will be similar to that of glycine. But the experimental data are not so, which are positive values. Therefore, they took the side-by-side manner to associate with each other.

In the interaction of head-on-module, all the carboxyl and amino groups of two glycine molecules have associated with each other and no one polar group keeps free. So, in the ion-glycine-glycine triplet interaction, the ion will only be able to undergo structural interaction with the apolar part of the two associated glycine molecules. This kind of structural interaction will give positive contribution to h_{xyy}, which makes the values of h_{xyy} more positive than those of h_{yy}. In the interaction of side-by-side manner, just one pair polar of group undergoes the electrostatic interaction. So, in the ion-amino acid-amino acid triplet interaction, the ion will still be able to undergo electrostatic interaction with the one of remaining polar groups and give negative contribution to h_{xyy}, which will make the values of h_{xyy} more negative than those of h_{yy}.

From a comparison we can see that the negative

contribution to h_{xyy} produced by the interaction of alkali metal halides with aminobutyric acid is bigger than the contribution with alanine. The reason is worth analysis here. The investigation of Kato[19,20] indicates that in the aqueous solution of some non-electrolyte, there is a clathrate hydrate structure around the non-polar part of the non-electrolyte. Ions will promote the aggregation of the clathrate hydrate structure.[21] Avedikian[22] has also indicated that, at intermediate *t*-butyl alcohol concentrations, there is an enhancement of the hydrophobic bonding in the *t*-BuOH-*t*-BuOH association by hydrophilic salts through triplet interaction. In the present study, it can be concluded that the structural interaction of an electrolyte with two amino acid molecules associated in side-by-side manner will also enhance the hydrophobic bonding between the two molecules. This enhancement will make negative contribution to h_{xyy} parameter. Since the non-polar part of aminobutyric acid molecule is larger than that of alanine molecule, the clathrate hydrate structure of aminobutyric acid molecules will be more easily enhanced by electrolyte. This is the reason that the negative contribution to h_{xyy} produced by the interaction of alkali metal halides with aminobutyric acid is bigger than the contribution with alanine.

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