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Enthalpy of the interaction of glycine, α-alanine and α-aminobutyric acid with sodium iodide at 298.15 K

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Abstract

A microcalorimetric method has been used to obtain the enthalpic interaction parameters for glycine, α-alanine and α-aminobutyric acid with sodium iodide in aqueous solutions at 298.15 K. It is found that the values of h_{xy} increase, whereas those of h_{xxy} and h_{xyy} decrease as the hydrocarbon chain increases in length (where x represents the non-electrolyte in pure water, and y the electrolyte in aqueous solution). The results are discussed in view of structural interactions.

Keywords: Amino acid; Enthalpy; Interaction

1. Introduction

Over the last decade, many studies have been done on the interactions occurring in aqueous solutions of amino acids [1–3]. Some interesting results have been obtained from various theories. The present paper will use the data obtained from our previous studies [4,5] to investigate the interactions of amino acids with sodium iodide in water. Enthalpic effects are studied in view of a structural interaction model.

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2. Experimental

Analytical grade glycine, α-alanine and α-aminobutyric acid used in the experiment were recrystallized from water + methanol and dried at 383 K. The sodium iodide, crystallized from a water + acetone mixture, was dried under vacuum for several days at 335 K. Water 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 publications [4,6].

The molality ranges over which the experiments were performed were as follows: amino acids 0.10–0.60 mol kg^{-1}; salts 0.5–5.0 mol kg^{-1}.

3. Results and discussion

The enthalpy of transfer of a non-electrolyte (y) in pure water to an electrolyte (x) in aqueous solution is given by [7,8]:

$$\Delta H_{\mathrm{tr}} = 2h_{\mathrm{xy}}m_{\mathrm{x}} + 3h_{\mathrm{xxy}}m_{\mathrm{x}}^2 + 3h_{\mathrm{xyy}}m_{\mathrm{x}}m_{\mathrm{y}} + \cdots \tag{1}$$

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, triplet, etc., interaction parameters.

ΔH_{tr} can be obtained from the differences between $\Delta H^{\mathrm{ws}}_{\mathrm{soln}}$, the enthalpies of solutions of amino acids in solution, and $\Delta H^{\mathrm{w}}_{\mathrm{soln}}$, the enthalpies of amino acids in pure water, i.e.

$$\Delta H_{\mathrm{tr}} = \Delta H^{\mathrm{ws}}_{\mathrm{soln}} - \Delta H^{\mathrm{w}}_{\mathrm{soln}} \tag{2}$$

The experimental data are given in Tables 1–3. The treatment of these data was the same as that used previously [4]. Our principal concern are pair and triplet enthalpic interaction parameters, and these are presented in Table 4.

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

m_{y} in mol kg^{-1}	ΔH_{m} water	m_{y} in mol kg^{-1}	ΔH_{m} $m_{\mathrm{x}} = 0.4902$	m_{y} in mol kg^{-1}	ΔH_{m} $m_{\mathrm{x}} = 0.9986$	m_{y} in mol kg^{-1}	ΔH_{m} $m_{\mathrm{x}} = 3.0074$
0.1025	14120	0.1589	12860	0.1794	11950	0.1475	9480
0.2349	14080	0.2552	12860	0.2883	11970	0.2823	9470
0.2618	14070	0.3625	12870	0.3654	11980	0.4079	9500
0.3427	14060	0.4410	12870	0.4600	12000	0.4883	9520
0.4954	14020	0.5123	12880	0.5374	12010	0.5896	9550
		0.6294	12870	0.6349	12030	0.6885	9560

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

m_y in mol kg^{-1}	ΔH_m water	m_y in mol kg^{-1}	ΔH_m $m_x = 0.9999$	m_y in mol kg^{-1}	ΔH_m $m_x = 3.0017$	m_y in mol kg^{-1}	ΔH_m $m_x = 4.9750$
0.1364	9284	0.1939	8434	0.1531	7784	0.1622	8071
0.2099	9317	0.2618	8463	0.2215	7780	0.2471	8116
0.2794	9330	0.3210	8487	0.3021	7826	0.3377	8156
0.3427	9351	0.3827	8510	0.3797	7878	0.4118	8226
0.4119	9359	0.4526	8530	0.4532	7918	0.4957	8273
0.4836	9385	0.4928	8552	0.5338	7970	0.5742	8295

Table 3
The enthalpies of solution ΔH_m of α-aminobutyric acid in water–NaI mixtures at 298.15 K (in J mol^{-1})

m_y in mol kg^{-1}	ΔH_m water	m_y in mol kg^{-1}	ΔH_m $m_x = 1.0000$	m_y in mol kg^{-1}	ΔH_m $m_x = 3.0000$	m_y in mol kg^{-1}	ΔH_m $m_x = 5.0013$
0.1209	1475	0.1338	1258	0.1366	1634	0.1486	2744
0.1765	1531	0.1966	1302	0.2055	1678	0.2222	2787
0.2401	1586	0.2585	1341	0.2719	1720	0.2952	2829
0.2958	1608	0.3287	1387	0.3419	1764	0.3703	2874
0.3562	1656	0.3915	1429	0.4160	1800	0.4451	2920
0.4203	1711	0.4558	1470	0.4850	1838	0.5172	2970

Table 4
The enthalpic interaction parameters for the aqueous system NaI–amino acid at 298.15 K

Amino acid	h_{xy} in J kg mol^{-2}	h_{xyy} in J kg^2 mol^{-3}	h_{xxy} in J kg^2 mol^{-3}
Glycine	-1268 ± 14	114 ± 20	87 ± 1
α-Alanine	-509 ± 10	25 ± 15	52 ± 1
α-Aminobutyric acid	-170 ± 8	-20 ± 14	41 ± 1

It is generally believed that the interaction between non-electrolyte and electrolyte includes electrostatic and structural interactions. Lilley et al. [3] considered the interaction between electrolyte and amino acids to consist of three effects: (a) electrostatic interaction, (b) partial desolvation of solutes, (c) solvent reorganization [9]. The latter two effects belong to the class of structural interactions. Desnoyers and co-workers [10] gave a general discussion on structural interactions, and thought that in most cases the net effect of the cosphere on the hydration structure is destructive. Structural interactions make quite a large contribution to the enthalpic function, and sometimes even predominate [3,8,11].

Figs. 1–3 show the enthalpic interaction parameters as a function of the number of carbon atoms in the hydrocarbon chain.

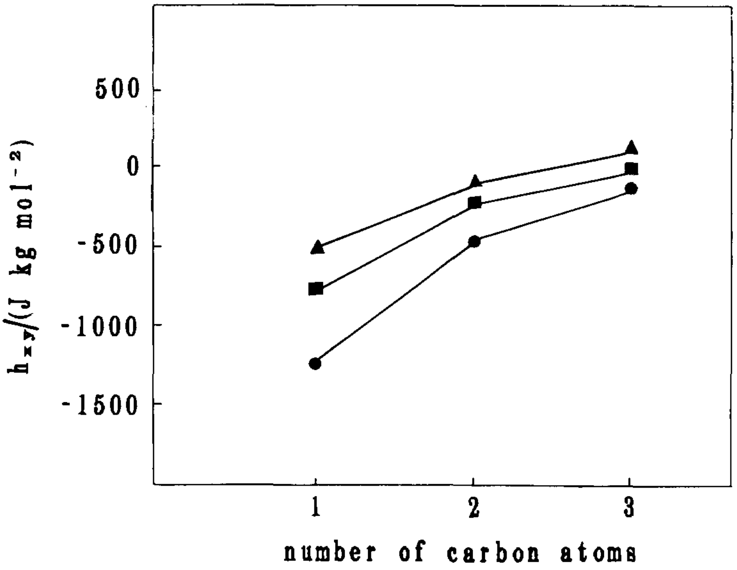

Fig. 1. Enthalpic pairwise parameter for the interaction of sodium halide with α-amino acids, as a function of the number of atoms in the hydrocarbon side chain. ●, NaI; ■, NaBr *; ▲, NaCl *. * From Ref. [5].

It is apparent from Table 4 that h_{xy} values increase, whereas h_{xxy} and h_{xyy} values decrease, as the carbon atoms in the hydrocarbon chain increase. This can be explained using the concepts of the electrostatic and structural interactions mentioned above.

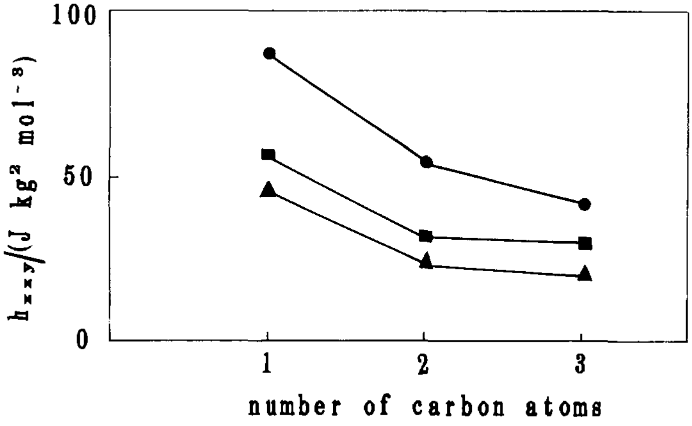

Fig. 2. Enthalpic triplet parameter for the interaction of sodium halide with α-amino acids, as a function of the number of atoms in the hydrocarbon side chain. ●, NaI; ■, NaBr *; ▲, NaCl *. * From Ref. [5].

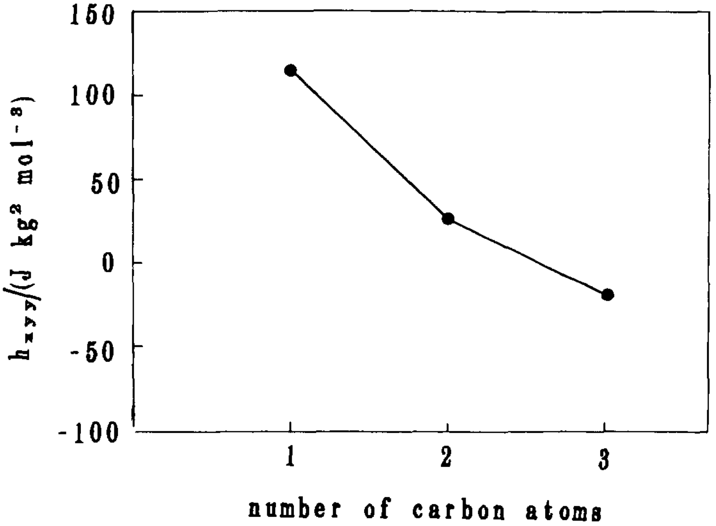

Fig. 3. Enthalpic triplet parameter for the interaction of sodium iodide with α-amino acids, as a function of the number of atoms in the hydrocarbon side chain.

For the interaction between electrolyte and zwitterionic ion, Kirkwood [12,13] proposed an electrostatic theory to estimate the contribution of electrostatic interactions to the pairwise interaction parameters. A feature of the Kirkwood approach is the dominant role played by the dipole moment of the amino acid in determining the pairwise interaction parameters. Since for the present system all of the amino acids have very similar dipole moments, one would imagine that their interaction parameters should be approximately the same. This has been verified by these and other authors [2,14]. Therefore, an assumption can be made that it is the structural interaction that is responsible for the observed variation in trends in h_{xy} for the systems investigated.

h_{xy} is the enthalpic interaction parameter of an electrolyte with an amino acid molecule. The move from large negative to small negative values signifies a decrease in the hydrogen-bonded structure of water due to the overlap of cospheres of amino acids and NaI. The principal contribution to the interaction between an electrolyte and an amino acid molecule occurs via the carboxylate region of the zwitterionic head of the amino acid. The overlap of structure-breaking regions of water in the cosphere close to the ions and the polar part of amino acid will make a higher negative contribution to the h_{xy} values. Apart from the hydrophilic hydration of the charged zwitterionic head group, there exists a hydrophobic hydration cosphere for the alkyl side chain; the contribution of hydrophobic structure-making will counteract that of hydrophilic structure-breaking, so as the side chain is lengthened, the addition of hydrophobic groups will greatly reduce the negative values of h_{xy}. This will be the major cause of increase in negativity of the value of h_{xy} with increase in amino acid size.

h_{xxy} is the enthalpic interaction parameter of an amino acid molecule with two electrolytes. It can be imagined that after an electrolyte has interacted with the polar groups of an amino acid molecule, the other electrolyte will mainly interact with the non-polar part of the amino acid with a destructive effect. The positive values of h_{xxy} show the net decrease of structured water in the region around the non-polar group. It is obvious that the h_{xxy} of the glycine system is larger than that for α-alanine and α-aminobutyric acid; whereas for the latter two the differences are small. A qualitative explanation of this feature would be that, after the ions of the salts primarily interact with the head groups, it will be hard for other ioins to interact with the short extension of a hydrocarbon chain such as glycine; in contrast, for α-acids, the interaction between ions and non-polar groups will become easier as the hydrocarbon chain is extended. For α-amino acids with other alkali metal halide systems [5] the results are the same.

h_{xyy} is the enthalpic interaction parameter of two amino acid molecules with an electrolyte. In the case of the self-interaction between α-amino acids, the interactions are mainly of a dipole–dipole nature and head group effects prevail side-chain interactions. However, as the side-chain is lengthened, the hydrophobic–hydrophobic interactions of non-polar parts increase; for glycine, α-alanine and α-aminobutyric acid, the h_{yy} values change sign, passing from negative to positive [15]. Thus the interaction of an electrolyte with a couple of amino acid molecules will mainly be structural, and the electrolyte ions will probably perturb the hydrophobic hydration cospheres of the amino acid molecules. If the structural interaction destroys the hydrophobic hydration structure of the amino acid molecules, a positive contribution will be made to the enthalpic interaction parameters; if the hydrophobic hydration structure is enhanced by the structural interaction, a negative contribution will be made. In the present study, it can be concluded that the longer the hydrocarbon chain, the greater the enhancement by the electrolyte ions of the hydrophobic hydration structure of the amino acid molecules. It is this enhancement effect that causes the h_{xyy} values to go from positive to negative as the side-chain length increases.

Acknowledgements

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