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The enthalpic interaction parameters of acetamide with sodium halides in water at 298.15 K ☆

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Abstract

The enthalpies of solution have been measured for acetamide in some sodium halide solutions at 298.15 K. The enthalpic interaction parameters h_{xy}, h_{xyy} and h_{xxy} of acetamide with sodium halides have been evaluated and are discussed with respect to the electrostatic interaction and structural interaction.

Keywords: Acetamide; Halide; Interaction parameter

1. Introduction

In solution chemistry and biological chemistry, it is very important to study the interaction between electrolytes and nonelectrolytes in water. It is quite effective to investigate the interaction between electrolytes and nonelectrolytes using an enthalpic effect method [1]. Therefore, much work has been done on this interaction by measuring enthalpic effects. According to the McMillan–Mayer theory [2], various excess thermodynamic properties of a multi-component solution can be expressed by a virial expansion. When the McMillan–Mayer theory is applied to the transfer

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enthalpy of a nonelectrolyte (y) from pure water (w) to an electrolyte (x) aqueous solution, it can be expressed as

$$\Delta H_y(w \rightarrow w + x) = 2h_{xy}m_x + 3h_{xyy}m_xm_y + 3h_{xxy}m_x^2 + \cdots \tag{1}$$

where m_x and m_y are the molalities, h_{xy} is the enthalpic doublet interaction parameter, and h_{xyy} and h_{xxy} are the enthalpic triplet parameters.

Proteins are responsible for many biological phenomena; the hydrogen bond link with amide is the most important secondary structure in proteins. Salts can have marked effects on the stability of proteins: some tend to destroy its structure and some may reinforce it [3]. We have investigated the enthalpic interaction parameters of some amino acids with alkali metal halides in water [4,5]. The present paper presents the enthalpies of solution of acetamide in water and in NaCl, NaBr, NaI aqueous solutions at 298.15 K, and the various enthalpic interaction parameters are evaluated. The results are discussed in terms of electrostatic and structural interactions.

2. Experimental

Analytical grade acetamide used in the experiments was recrystallized from methanol and dried under vacuum at 313 K. Analytical grade NaBr was recrystallized from water. Analytical grade NaI was recrystallized from water–acetone mixture. NaCl was of high purity, warranting no further treatment. The water used was deionized and redistilled. All the materials were stored over P_2O_5 prior to use.

The enthalpies of solution were measured in a C-80 calorimeter (Setaram) using reversed mixing vessels. The details of the experimental techniques and the calibration of the data have been described elsewhere [6]. The total uncertainty in the measurement is about ±0.5%.

3. Results and discussion

The molar enthalpies of solution of acetamide in water, and in NaCl, NaBr and NaI aqueous solutions are given in Tables 1–3. There is a very good linear relationship between the molar enthalpies of solution of acetamide in water and its molalities in the range of the concentration measured. The relationship was obtained with the method of least squares as

$$\Delta H_m/(\mathrm{J\ mol^{-1}}) = 9708 + 62m_y \tag{2}$$

with a standard deviation of ± 6 J mol^{-1}. The molar enthalpy of solution at infinite dilution of acetamide (9708 J mol^{-1}) is in good agreement with the literature values of 9.73 kJ mol^{-1} [7] and 9.644 kJ mol^{-1} [8].

In Eq. (1) the transfer enthalpy is expressed as the sum of a series of doublet, triplet and higher order terms. In the concentration range studied, the quadruplet and higher order interactions make only small and negligible contributions to the enthalpy of transfer [6,9]. Thus Eq. (1) can be rewritten as

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

Table 1
Molar enthalpies of solution of acetamide in NaCl aqueous solution at 298.15 K in J mol^{-1}

m_y/ (mol kg^{-1})	ΔH ($m_x = 0.4983$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 1.0003$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 2.0000$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 3.0000$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 3.9990$)
0.3403	9677	0.3367	9660	0.3687	9686	0.3544	9848	0.4068	10017
0.4847	9686	0.5816	9678	0.5086	9724	0.5433	9808	0.5422	10004
0.6826	9702	0.6954	9680	0.7060	9698	0.7195	9827	0.7254	9986
0.8393	9708	0.8617	9690	0.8729	9705	0.8903	9789	0.9078	10000
1.0086	9709	1.0063	9680	1.0859	9716	1.0642	9815	1.0684	9959

Table 2
Molar enthalpies of solution of acetamide in NaBr aqueous solution at 298.15 K in J mol^{-1}

m_y/ (mol kg^{-1})	ΔH ($m_x = 0.4993$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 1.9995$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 1.9990$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 2.9970$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 3.9930$)
0.3429	9652	0.3514	9601	0.3368	9549	0.3982	9616	0.4024	9760
0.5205	9656	0.5323	9595	0.5362	9545	0.5640	9614	0.5527	9671
0.6653	9663	0.7021	9592	0.6735	9572	0.7377	9605	0.7931	9755
0.8618	9673	0.8659	9608	0.8858	9561	0.9460	9587	0.9615	9709
1.0230	9685	1.0321	9609	1.0426	9560	1.1375	9595	1.1410	9711

Table 3
Molar enthalpies of solution of acetamide in NaI aqueous solution at 298.15 K in J mol^{-1}

m_y/ (mol kg^{-1})	ΔH ($m_x = 0.6196$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 1.2390$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 2.4809$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 3.7123$)	m_y/ (mol kg^{-1})	ΔH ($m_x = 4.9631$)
0.3757	9628	0.3737	9547	0.3940	9574	0.4136	9685	0.4580	9870
0.5005	9635	0.5539	9583	0.5676	9577	0.6044	9686	0.6594	9871
0.7127	9648	0.7257	9602	0.7597	9584	0.8515	9695	0.8645	9854
0.8657	9664	0.9228	9612	0.9663	9589	1.0444	9680	1.0722	9827
1.0775	9654	1.0932	9605	1.1535	9575	1.1965	9695	1.2776	9808

Table 4
The enthalpic interaction parameters of acetamide (y) with electrolytes (x) in water at 298.15 K

Electrolyte	$h_{xy}/(\mathrm{J\ kg\ mol^{-2}})$	$h_{xxy}/(\mathrm{J\ kg^2\ mol^{-3}})$	$h_{xyy}/(\mathrm{J\ kg^2\ mol^{-3}})$
NaCl	-52.2 ± 2.7	15.7 ± 0.4	-8.9 ± 2.2
NaBr	-86.3 ± 1.7	16.1 ± 0.3	-10.5 ± 1.3
NaI	-88.1 ± 3.8	14.5 ± 0.5	-5.3 ± 2.9

The molar enthalpies of transfer of acetamide from pure water to electrolyte aqueous solutions are the differences between the measured enthalpies of solution in the electrolyte aqueous solutions and those in pure water which were calculated using Eq. (2). The enthalpies of transfer have been fitted to Eq. (3) using a least squares procedure, and the enthalpic parameters are given in Table 4. Eq. (3) shows that $\Delta H_y(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{x})/m_x$ is a linear function of m_y when m_x is fixed, and the slope is independent of m_x. Figs. 1–3 clearly indicate these linear relationships.

The interaction of nonelectrolyte with electrolyte consists of electrostatic and structural interactions. For the enthalpic functions, the structural interaction consists principally of the partial desolvation of solute and the solvent reorganization in the neighbourhood of hydrophobic groups of the nonelectrolyte [10,11]. Desnoyers and co-workers have given a general discussion for the structural interaction and suggested that in most cases the net effect of the co-sphere overlap on the hydration structure is destructive [12]. Structural interaction makes a fairly large

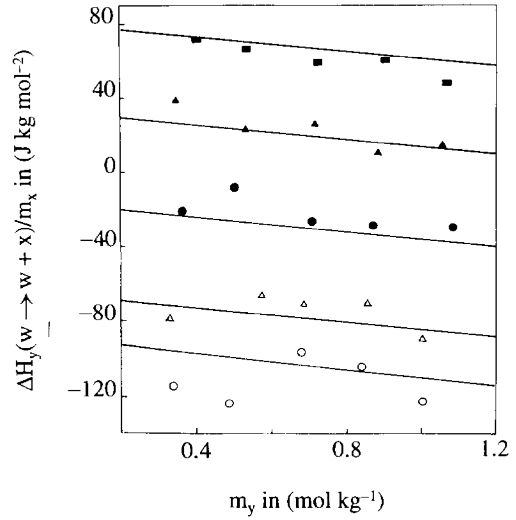

Fig. 1. Dependences of the function $\Delta H_y(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{x})/m_x$ on m_x and m_y for the NaCl–water–acetamide system. ■, $m_x = 3.999$; ▲, $m_x = 3.000$; ●, $m_x = 2.000$; △, $m_x = 1.0003$; ○, $m_x = 4983$; ——, calculated from Eq. (3).

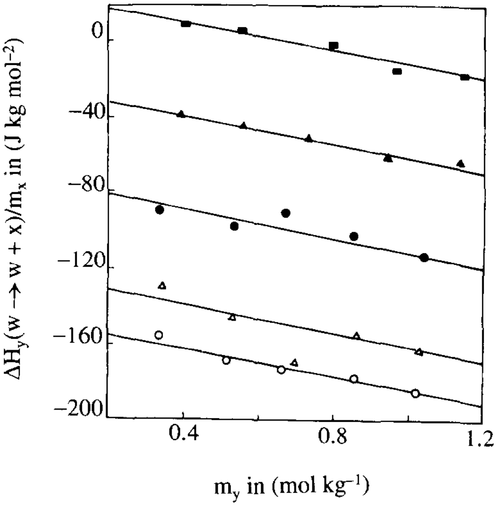

Fig. 2. Dependences of the function $\Delta H_y(w \rightarrow w + x)/m_x$ on m_x and m_y for the NaBr–water–acetamide system. ■, $m_x = 3.993$; ▲, $m_x = 2.997$; ●, $m_x = 1.999$; △, $m_x = 0.9995$; ○, $m_x = 4993$; ——, calculated from Eq. (3).

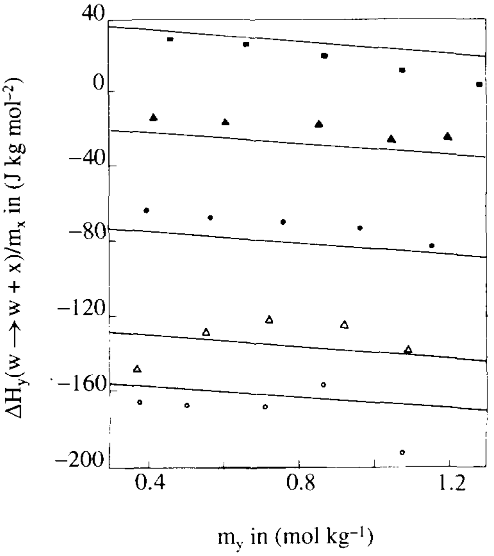

Fig. 3. Dependences of the function $\Delta H_y(w \rightarrow w + x)/m_x$ on m_x and m_y for the NaI–water–acetamide system. ■, $m_x = 4.9631$; ▲, $m_x = 3.7123$; ●, $m_x = 2.4809$; △, $m_x = 1.2390$; ○, $m_x = 6196$; ——, calculated from Eq. (3).

contribution to the enthalpic function and sometimes even surpasses the effect of electrostatic interaction and becomes a dominant factor [10,13,14]. It can be concluded that the interactions of the ions of electrolyte with the polar groups of nonelectrolyte are electrostatic, accompanied by partial desolvation of the solutes, whereas the interactions with the apolar groups are mainly structural.

In the system investigated, h_{xy} is a sum of the enthalpic interaction parameters of the pair of electrolytic ions, cation (M^+) and anion (A^+), with the acetamide molecule, i.e. $h_{xy} = h_{My} + h_{Ay}$. The acetamide molecule has two opposite polar groups: its carbonyl group (C=O) is a proton acceptor, which can easily interact electrostatically with the cation; its amino group (NH_2) is a proton donor, and will interact with the anion. These electrostatic interactions make negative contributions to the enthalpic parameters, so the values of h_{xy} tend to be negative [5]. However they are counteracted by the desolvation of the solutes. Because the desolvation of the ion will become increasingly easy as the ionic size increases, its counteractive effect on the electrostatic interaction will decrease as the ionic size increases. Therefore, h_{xy} decreases as the ionic size increases.

The h_{xyy} parameter is the sum of the enthalpic interaction parameters of a pair of electrolyte ions with two acetamide molecules, i.e. $h_{xyy} = h_{Myy} + h_{Ayy}$. In an acetamide molecule there is a proton acceptor together with a proton donor; therefore the two acetamide molecules will first interact with each other through intermolecular hydrogen bonding. There is a hydrophobic structure peripheral to the associated nonelectrolyte molecules. Both Eq. (3) and the studies Wood and Hiltzik [15] show that the enthalpic self-interaction parameter h_{yy} of the two acetamide molecules has a positive value, but in this experiment, the values of h_{xyy} are negative and small. Avedikian et al. [16] have indicated that 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 electrolyte ions will also enhance the hydrophobic bonding between the two acetamide molecules, and this enhancement makes a negative contribution to the h_{xyy} value. In the meantime, the dispersion force of ions upon the two acetamide molecules leads to partial desolvation of solutes, and reorganization of the hydration structure around acetamide molecules. Because this dispersion force is not strong enough to destroy the primary hydration structure of electrolyte ions, the partial desolvation effect can only destroy the secondary hydration layer structure and makes a negative contribution to enthalpic interaction parameters. The larger the size of the anion, the more the structure of water will be disrupted, and the stronger the dispersion force, the more negative will be the contribution from desolvation. On the contrary, the partial desolvation and the solvent reorganization of the apolar groups of acetamide will make positive contributions to enthalpy. These two opposite trends lead to h_{xyy} having only a small change with increasing ionic radius.

h_{xxy} is the sum of three types of enthalpic interaction parameter of an acetamide molecule with four ions dissociated from electrolytes, and it can be expressed as $h_{xxy} = 2h_{MAy} + h_{MMy} + h_{AAy}$, where h_{MAy} refers to the interaction of the pair of ions with the two opposite polar groups of the acetamide molecule; these electrostatic attractions lead to negative contributions to enthalpy. Whereas h_{MMy} or h_{AAy} are the enthalpic interaction parameters of an acetamide molecule with two identical ions, only one of the ions can electrostatically attract the polar group of the acetamide molecule which is opposite in polarity to the ion, making a negative contribution as discussed before; the other will only interact structurally with the apolar parts of the acetamide. At the same time, electrostatic repulsion occurs, making a positive contribution to enthalpy. From the h_{xxy} data, it can be concluded that these positive contributions are larger than the negative contributions. The contributions of structural interaction vary in two opposite trends as the ionic size increases, as discussed before, and the contributions of electrostatic interaction consist both of electrostatic attraction and repulsion, which means that h_{xxy} has no evident variation with the change of ionic radius.

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