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The enthalpic interaction parameters of acetamide with some alkali-metal chlorides in water at 298.15 K[1]

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Abstract

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

Keywords: Acetamide; Alkalic metal chloride; Interaction parameter

1. Introduction

In solution chemistry and biological chemistry, it is very important to study the interaction between electrolyte and nonelectrolyte. Electrolytes can have marked effects on the stability of proteins: some tend to destroy its structure and some may reinforce it [1]. In order to study the effects of salts on the stability of proteins, it is needed to choose some organic molecules which have the same groups with proteins and to study the interaction of the organic molecules with the electrolytes. The hydrogen bond link with amide is the most important secondary structure in proteins, so we choose amides as the studied objects. We have investigated the enthalpic interaction parameters of acetamide with sodium halides in water at 298.15 K [2]. The present paper presents the enthalpies of solution of acetamide in alkali-metal chlorides 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 LiCl was recrystallized from acetic acid–benzene mixture. KCl 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 of acetamide in LiCl and in KCl aqueous solutions were measured in a C-80 calorimeter (Setaram) using reversed-mixing vessels. The reversed-mixing vessel has two chambers sepa-

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rated by a tilting lid. About 0.1–0.35 g of acetamide was introduced into the vessel, then the lid was put in place. The acetamide was weighed on a single-pan balance (Mettler) with a sensitivity of 10 μg. In order to obtained a complete separation of the chambers, 0.5 g of mercury was put into the vessel before the solvent was introduced. About 5 ml 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 measurements is about ±0.5%.

3. Results and discussion

The molar enthalpies of solution of acetamide in water at 298.15 K can be expressed by the following equation as mentioned in [2]:

$$\Delta H_m\ (\mathrm{J\ mol^{-1}}) = 9708 + 62m_\mathrm{y}. \tag{1}$$

The molar enthalpies of solution of acetamide in LiCl and KCl aqueous solutions are given in Tables 1 and 2.

According to the McMillan–Mayer theory [3], all the thermodynamic properties of multi-components solutions can be expressed by using a virial expansion in m which relates the nonideal contributions of any total thermodynamic function to a series of pair, triplet and higher order interaction parameters. The enthalpies of transfer of a nonelectrolytes (Y) from pure water (W) to an electrolyte (X) aqueous solution can be expressed as mentioned in [4,5]:

$$\Delta H_\mathrm{y}(\mathrm{w} \rightarrow \mathrm{w}+\mathrm{x}) = 2h_\mathrm{xy}m_\mathrm{x} + 3h_\mathrm{xyy}m_\mathrm{x}m_\mathrm{y} + 3h_\mathrm{xxy}m_\mathrm{x}^2 + \cdots \tag{2}$$

where m_x and m_y are the molalities of salts and acetamide defined in mole per kilogram of pure water, h_xy is the enthalpic pair interaction parameter and h_xyy and h_xxy are the enthalpic triplet interaction parameters representing interaction between the subscript species. For the studied system, we used the truncated form of the equation as mentioned in [6,7]:

$$\Delta H_\mathrm{y}(\mathrm{w} \rightarrow \mathrm{w}+\mathrm{x})/m_\mathrm{x} = 2h_\mathrm{xy} + 3h_\mathrm{xyy}m_\mathrm{y} + 3h_\mathrm{xxy}m_\mathrm{x}. \tag{3}$$

The enthalpies of transfer of acetamide from water to the electrolytes aqueous solutions have been calculated and fitted to Eq. (3) using a least-squares method

Table 1
The molar enthalpies of solution of acetamide in LiCl aqueous solution at 298.15 K (J mol^{-1})

m_y (mol kg^{-1})	ΔH_m(m_x = 0.5001)	m_y (mol kg^{-1})	ΔH_m(m_x = 1.0017)	m_y (mol kg^{-1})	ΔH_m(m_x = 2.0012)	m_y (mol kg^{-1})	ΔH_m(m_x = 3.0045)	m_y (mol kg^{-1})	ΔH_m(m_x = 4.0001)
0.3890	9633	0.3833	9509	0.4033	9275	0.3885	8998	0.414 2	8677
0.5491	9656	0.5700	9529	0.5843	9289	0.5953	9026	0.623 2	8693
0.7398	9655	0.7627	9539	0.8043	9298	0.7916	9034	0.8284	8701
0.9444	9679	0.9709	9534	0.9885	9314	0.9924	9012	1.014 2	8704
1.1213	9677	1.1527	9545	1.1813	9315	1.1965	9013	1.197 5	8721

Table 2
The molar enthalpies of solution of acetamide in KCl aqueous solution at 298.15 K (J mol^{-1})

m_y (mol kg^{-1})	ΔH_m (m_x = 0.4999)	m_y (mol kg^{-1})	ΔH_m (m_x = 0.995)	m_y (mol kg^{-1})	ΔH_m (m_x = 1.9950)	m_y (mol kg^{-1})	ΔH_m (m_x = 2.9950)	m_y (mol kg^{-1})	ΔH_m (m_x = 4.000)
0.3500	9645	0.3483	9593	0.3453	9594	0.3701	9655	0.3943	9773
0.5161	9659	0.5298	9614	0.5213	9616	0.5286	9660	0.5483	9758
0.6831	9661	0.6942	9624	0.7085	9641	0.7271	9653	0.6608	9773
0.8684	9659	0.8564	9627	0.8914	9619	0.9144	9640	0.8890	9767
1.0030	9670	1.0193	9619	1.0698	9642	1.1445	9652	1.1416	9773

Table 3
Enthalpic interaction parameters of acetamide with alkali alides in water at 298.15 K

Electrolyte	h_{xy} (J kg mol^{-2})	h_{xyy} (J kg^2 mol^{-3})	h_{xxy} (kg^2 mol^{-3})
LiCl	-91.2 ± 3.8	-3.4 ± 2.7	-6.3 ± 0.6
NaCl[a]	-52.2 ± 2.7	-8.9 ± 2.2	15.7 ± 0.4
KCl	-87.3 ± 5.6	-7.8 ± 4.5	17.3 ± 0.9
NaBr[a]	-86.3 ± 1.7	-10.5 ± 1.3	16.2 ± 0.3
NaI[a]	-88.1 ± 3.8	-5.4 ± 2.9	14.5 y$\pm$ 0.5

[a] Ref. [2].

and the enthalpic interaction parameters thus obtained are given in Table 3.

The enthalpic interaction parameters in Table 3 are the comprehensive reflection of the enthalpic effects produced by the electrostatic and the structural interaction between acetamide and the electrolytes. According to the well-known Savage and Wood [8] group additivity model, the interaction between electrolyte and nonelectrolyte can be divided into the interactions of ions with the various groups of nonelectrolyte. The interactions of ions with the polar groups of nonelectrolytes are mainly electrostatic and give negative contribution to the enthalpic function and with the apolar group, CH_2, is structural and give positive contribution [9,10].

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., $h_{My} + h_{Ay}$. The acetamide has two opposite polar groups: its carbonyl group (C=O) is a proton acceptor, which can easily interact electrostaticly with the cation; its amino group (CH_2) is a proton donor and will interact with the anion. The electrostatic interaction between ions and the polar groups of acetamide will make negative contribution to the h_{xy}, but the contribution will be partially counteracted by the partial desolvation of the solutes. Since the desolvation of the ions will become increasingly easier as the ionic size increases, its counteractive effect will also decrease. Therefore, the h_{xy} should be more negative as the ionic size increases. The values of h_{xy} of acetamide with sodium halides are agree with the explanation of above [2]. We can see from Table 3 that in alkali-metal chlorides system, the values of h_{xy} of acetamide with NaCl and KCl are also agree with the explanation, but the value of with LiCl is much more negative than it should be in the explanation. This because that lithium ion has the smallest radius and the largest surface charging density in the cations, therefore it will exert the largest attractive force on the water molecules which are in the first hydration layer of the lithium ion. Since the acetamide's dipole moment is quite small, the electrostatic interaction of lithium ion with acetamide is not bigger enough to destroy the first hydration layer of the lithium ion. In the meantime, the lithium ion has smaller structural interaction for the hydrophobic hydration structure acetamide molecule. The two reasons cause the value of the h_{xy} of LiCl with acetamide more negative. If the dipole moment of the nonelectrolyte is quite large, the electrostatic interaction between the nonelectrolyte and lithium ion will de able to destroy the primary hydration structure of lithium ion and make quite large positive contribution to h_{xy}. One of the nonelectrolytes is glycine. The value of h_{xy} of glycine with LiCl is positive [11,12].

The h_{xyy} parameter is the sum of the enthalpic interaction parameters of a pair of electrolyte ions with two acetamide molecules, i.e., $h_{Myy} + h_{Ayy}$. The data in Table 3 indicate that the values of h_{xyy} in the investigated systems are small negative. As mentioned in [2], the two acetamide molecules will combine with each other through intermolecular hydrogen bonding with their proton acceptors and donors, the enthalpic interaction parameter of two acetamide molecules, h_{yy}, is positive. Therefore, the ion cannot produce the electrostatic interaction with the polar groups of the acetamides, but produce structural interaction with the nonpolar groups through dispersion force. This kind of triplet interaction will enhance the hydrophobic structure peripheral to the associated acetamide molecules and make negative contribution to the value of h_{xyy} . Since the interaction through dispersion force is not strong enough to destroy the primary hydration structure of electrolyte ions, it only can make the partial desolvation effect on the secondary hydration layer of the ions. For most ions which belong to structure breaker, this kind of partial desolvation will make negative contribution to enthalpic function. Since Li^+ is a structure maker, it will make positive contribution to enthalpic function. This is the reason that the negative value of h_{xyy} of acetamide with LiCl is the smallest.

h_{xxy} is the sum of three types of enthalpic interaction parameters of an acetamide molecule with four ions dissociated from electrolytes and it can be expressed as $2h_{MAy} + h_{MMy} + h_{AAy}$. The h_{MAy} refers to the interaction of the pair of ions with the two opposite polar groups of the acetamide molecules; these electrostatic attractions lead to negative contributions to enthalpy. Whereas h_{MMy} and 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 and make 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 between the two same ions, making a positive contribution to enthalpy. From Table 3 we can see that the values of h_{xxy} of acetamide with all of the salts except LiCl are positive. The value of h_{xxy} of acetamide with LiCl is negative. This mainly because that the interaction between acetamide and LiCl produce larger negative contribution to enthalpy as discussed above for h_{xy}.

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