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The enthalpic interaction parameters of NaCl, KCl and KI with acetone in water at 303.15 and 308.15 K

Yan Lu *, Shaoqiang Zhen and Jinsou Lu

Department of Chemistry, Henan Normal University, Xinxiang, Henan 453002 (People's Republic of China)

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Abstract

The enthalpies of solution have been measured for NaCl, KCl and KI in water and in acetone–water mixtures at 303.15 and 308.15 K. The enthalpic interaction parameters h_{xy}, h_{xxy} and h_{xyy} of the three salts with acetone have been evaluated at the two temperatures. The concepts of electrostatic interaction and structural interaction can be used to explain the dependences of the enthalpic interaction parameters on the ionic size of the electrolytes. The structural interaction is responsible for the temperature dependences of the enthalpic interaction parameters.

INTRODUCTION

Electrolytes are known to modify the properties of non-electrolytes in water. Therefore it is very important to study the interaction between electrolytes and non-electrolytes in water; many studies have been made in the fields of chemistry, biology and industry and some theories have been proposed. One very useful way to investigate the interactions is by measuring the enthalpies of solution of electrolyte in aqueous non-electrolyte [1]. According to the McMillan–Mayer theory [2], all the thermodynamic properties of a multi-component solution can be expressed as a series of pair, triplet and higher order interaction terms between like and unlike solutes. The enthalpies of transfer of electrolyte (x) from pure water (w) to aqueous non-electrolyte (y) can be expressed [3]

$$\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y}) = 2vh_{xy}m_y + 3v^2h_{xxy}m_xm_y + 3vh_{xyy}m_y^2 + \ldots \quad (1)$$

where m_x and m_y are the molalities defined per kg of pure water, v is the

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* Corresponding author.

number of ions dissociated by x, h_{xy} is the enthalpic pair interaction parameter, and h_{xxy} and h_{xyy} are the enthalpic triplet interaction parameters.

So far, most investigations into the interactions between electrolyte and non-electrolyte have concentrated on the pair interaction parameters. The pair interaction parameters only reflect the interaction between electrolyte and non-electrolyte in very low concentrations. When the concentration is not very low, triplet and higher order interaction parameters are required to express the thermodynamic properties of multi-component solutions. We have measured the enthalpies of solution of NaCl, KCl and KI in pure water and in acetone–water mixtures at 298.15 K and have obtained the enthalpic pair and triplet interaction parameters of the three salts with acetone in water at that temperature [4]. The h_{xy} and h_{xxy} values show certain dependences on the size of the ions; h_{xyy} is small and does not show evident dependence on the size of the ions.

In the present work, we expand the investigations of the enthalpic interaction parameters of the three salts with acetone in water and their temperature dependences, on the basis of the previous work, by measuring the enthalpies of solution of NaCl, KCl and KI in pure water and in acetone–water mixtures at 303.15 and 308.15 K.

EXPERIMENTAL

The NaCl and KCl used in the experiment were high purity grade, used without further treatment after drying for 10 h at 383 K. Analytical grade KI was recrystallized from double-distilled water and dried for a day at 383 K. All the salts were stored over P_2O_5 prior to use. Analytical grade acetone was further purified by Werner's method [5]. The water used was double-distilled.

The enthalpies of solution were measured at 303.15 and 308.15 K using a C-80 calorimeter (Setaram). The details of the experimental technique and the calibration of the data have been described elsewhere [4]. The total uncertainty in the enthalpy of solution was about ±0.5%.

RESULTS AND DISCUSSION

The enthalpies of solution of NaCl, KCl and KI in water and in acetone–water mixtures at 303.15 and 308.15 K are given in Tables 1–6. The enthalpies of solution obtained for all three salts in water at the two temperatures can be fitted to the equation

$$\Delta H_s(\mathrm{J\ mol^{-1}}) = A + Bm_x^{1/2} + Cm_x \qquad (2)$$

Values of the parameters A, B and C have been determined by a

TABLE 1

The enthalpies of solution ΔH_m of NaCl in water–acetone mixtures at 303.15 K (in J mol^{-1})

m_x (mol kg^{-1})	ΔH_m Water	m_x (mol kg^{-1})	ΔH_m $m_y = 0.9138$	m_x (mol kg^{-1})	ΔH_m $m_y = 1.9195$	m_x (mol kg^{-1})	ΔH_m $m_y = 3.0432$	m_x (mol kg^{-1})	ΔH_m $m_y = 4.3395$	m_x (mol kg^{-1})	ΔH_m $m_y = 7.3791$
0.0964	3631	0.1288	3733	0.0079	3766	0.1271	3961	0.1278	4098	0.1196	4394
0.1909	3693	0.2340	3831	0.2261	3935	0.2131	4037	0.2830	4240	0.2871	4622
0.3088	3716	0.3897	3809	0.4109	3931	0.4274	4080	0.4650	4241	0.4823	4672
0.4959	3666	0.5444	3760	0.5650	3888	0.5888	4051	0.6353	4212	0.7376	4629
0.6156	3607	0.6767	3711	0.7179	3838	0.7715	3970	0.7965	4156	0.9443	4528
0.7626	3535	0.8379	3618	0.9202	3734	0.9708	3877	1.0263	4053	1.2004	4436

TABLE 2

The enthalpies of solution ΔH_m of NaCl in water–acetone mixtures at 308.15 K (in J mol^{-1})

m_x (mol kg^{-1})	ΔH_m Water	m_x (mol kg^{-1})	ΔH_m $m_y = 0.9310$	m_x (mol kg^{-1})	ΔH_m $m_y = 1.9174$	m_x (mol kg^{-1})	ΔH_m $m_y = 3.0337$	m_x (mol kg^{-1})	ΔH_m $m_y = 4.3152$	m_x (mol kg^{-1})	ΔH_m $m_y = 7.3826$
0.1118	3091	0.1315	3180	0.1250	3285	0.1380	3410	0.1845	3597	0.1702	3933
0.2346	3154	0.2296	3252	0.3053	3385	0.2893	4503	0.3503	3694	0.3196	4092
0.3768	3176	0.3325	3279	0.4859	3387	0.4427	4542	0.5718	3720	0.5232	4132
0.4603	3170	0.5233	3265	0.6603	3363	0.6320	3512	0.7158	3688	0.7813	4130
0.5978	3122	0.6401	3215	0.7618	3310	0.7418	3491	0.8778	3650	0.9627	4088
0.7922	3068	0.8553	3184	0.8932	3282	0.9745	3422	0.0398	3600	1.2113	3946

TABLE 3

The enthalpies of solution ΔH_m of KCl in water–acetone mixtures at 303.15 K (in J mol^{-1})

m_x ($mol\ kg^{-1}$)	ΔH_m Water	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 1.6925$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 3.0743$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 4.3072$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 7.3861$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 11.5313$
0.0903	17000	0.0846	16530	0.0814	16330	0.1124	16210	0.1220	15970	0.1137	15850
0.1414	17060	0.1966	16650	0.1986	16460	0.2353	16360	0.2504	16250	0.2788	16380
0.2525	17100	0.2845	16710	0.3483	16560	0.4032	16470	0.4580	16380	0.4495	16480
0.3933	17120	0.4578	16710	0.4981	16580	0.5229	16470	0.6193	16440	0.7434	16580
0.5343	17070	0.6188	16670	0.6632	16550	0.7445	16460	0.8688	16430	1.0336	16600
0.7170	16990	0.7567	16640	0.8733	16500	0.9021	16430	1.0393	16430	1.2361	16600

TABLE 4

The enthalpies of solution ΔH_m of KCl in water–acetone mixtures at 308.15 K (in J mol^{-1})

m_x ($mol\ kg^{-1}$)	ΔH_m Water	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 0.9062$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 1.9110$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 3.0480$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 4.3152$	m_x ($mol\ kg^{-1}$)	ΔH_m $m_y = 7.3826$
0.0832	16260	0.0991	16040	0.1302	15840	0.1231	15660	0.1274	15580	0.1252	15420
0.1513	16330	0.1707	16100	0.2416	15930	0.1680	15720	0.2689	15710	0.2726	15610
0.3077	16360	0.2909	16130	0.3613	15950	0.3518	15820	0.4272	15810	0.4192	15700
0.4150	16350	0.4515	16150	0.5099	15970	0.5308	15860	0.5702	15850	0.6258	15770
0.5320	16340	0.5388	16140	0.5915	15950	0.6362	15860	0.7137	15850	0.7850	15790
0.7169	16300	0.6594	16110	0.7085	15930	0.7485	15850	0.8075	15830	0.9477	15780

TABLE 5

The enthalpies of solution ΔH_m of KI in water–acetone mixtures at 303.15 K (in J mol^{-1})

m_x (mol kg^{-1})	ΔH_m Water	m_x (mol kg^{-1})	ΔH_m $m_y = 0.9100$	m_x (mol kg^{-1})	ΔH_m $m_y = 1.9301$	m_x (mol kg^{-1})	ΔH_m $m_y = 3.0862$	m_x (mol kg^{-1})	ΔH_m $m_y = 4.3287$	m_x (mol kg^{-1})	ΔH_m $m_y = 5.7393$
0.0408	19530	0.0266	19020	0.0290	18250	0.0275	17230	0.0298	16010	0.0355	14430
0.0649	19650	0.0697	19230	0.0499	18420	0.0614	17520	0.0701	16350	0.0875	14880
0.1147	19710	0.1304	19320	0.0928	18540	0.1612	17710	0.1616	16490	0.1307	15050
0.1948	19730	0.2058	19360	0.1330	18680	0.2206	17740	0.2364	16590	0.1972	15170
0.2288	19730	0.2477	19390	0.2306	18710	0.2932	17780	0.3065	16660	1.3507	15290
0.2846	19700	0.2959	19370	0.3324	18710	0.3420	17830	0.3598	16650	1.3935	15310

TABLE 6

The enthalpies of solution ΔH_m of KI in water–acetone mixtures at 308.15 K (in J mol^{-1})

m_x (mol kg^{-1})	ΔH_m Water	m_x (mol kg^{-1})	ΔH_m $m_y = 0.9062$	m_x (mol kg^{-1})	ΔH_m $m_y = 1.9174$	m_x (mol kg^{-1})	ΔH_m $m_y = 3.0337$	m_x (mol kg^{-1})	ΔH_m $m_y = 4.3045$	m_x (mol kg^{-1})	ΔH_m $m_y = 5.7485$
0.0430	18800	0.0464	18330	0.0587	17640	0.0580	16660	0.0594	15390	0.0744	14040
0.0937	18940	0.0651	18420	0.1040	17800	0.1070	16920	0.0881	15610	0.1254	14330
0.1457	19020	0.1388	18590	0.1505	17900	0.1602	16990	0.1435	15740	0.1865	14480
0.1927	19070	0.1995	18620	0.1947	17990	0.2214	17050	0.2212	15900	0.2878	14580
0.2291	19050	0.2414	18640	0.2434	17960	0.2511	17080	0.2538	15960	0.3480	14640
0.2826	19050	0.2967	18610	0.3016	17980	0.3140	17110	1.3467	15990	0.3912	14650

TABLE 7

Parameters of eqn. (2)

Electrolyte	T	A	B	C	δ [a]
NaCl	303.15	3258	1691	−1578	6
NaCl	308.15	2742	1452	−1224	8
KCl	303.15	16594	1841	−1621	8
KCl	308.15	16008	1184	−997	9
KI	303.15	19019	3413	−4027	17
KI	308.15	18259	3294	−3391	13

[a] Standard deviation.

least-squares method and are listed in Table 7; the standard deviations are also given in the last column. The enthalpies of transfer $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})$ are the differences between the measured enthalpies of solution of the salts in acetone–water mixtures and the enthalpies of solution in water, calculated using eqn. (2). The relation between the enthalpies of transfer and the enthalpic interaction parameters has been expressed in eqn. (1). For the systems studied, we have indicated that because the quadruplet and higher order interactions make only small contributions to the enthalpy of transfer, they are negligible in eqn. (1). Therefore, eqn. (1) can be written

$$\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})/m_y = 2vh_{xy} + 3v^2h_{xxy}m_x + 3vh_{xyy}m_y \qquad (3)$$

The m_x, m_y and $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})/m_y$ data were fitted to eqn. (3) using a least-squares routine and the enthalpic interaction parameters obtained are given in Table 8.

Equation (3) indicates that when m_y is fixed, $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})/m_y$ is a linear function of m_x and the slope is not dependent on m_y. The interval

TABLE 8

Enthalpic interaction parameters of electrolytes with acetone in water

Electrolyte	T (K)	h_{xy} (J kg mol^{-2})	h_{xy} (J kg^2 mol^{-3})	h_{xyy} (J kg^2 mol^{-3})
NaCl [a]	298.15	24	5.9	−0.18
NaCl	303.15	24	5.5	0.05
NaCl	308.15	22	4.2	0.3
KCl [a]	298.15	−66	9.7	2.5
KCl	303.15	−69	8.1	2.6
KCl	308.15	−71	7.4	3.7
KI [a]	298.15	−106	42.7	−15
KI	303.15	−111	33.1	−13.6
KI	308.15	−125	24.6	−11.1

[a] From ref. 4.

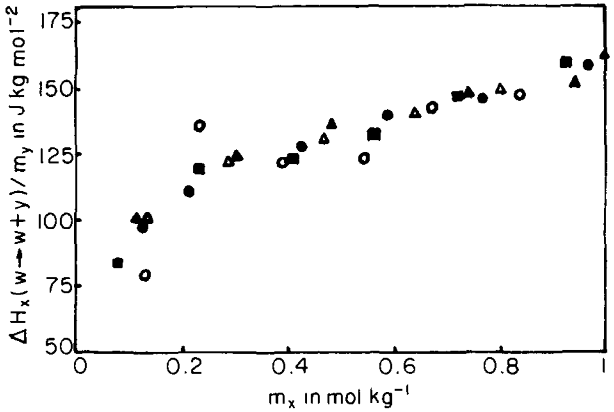

Fig. 1. Dependences of the function $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})/m_y$ on m_x and m_y for the NaCl–water–acetone system at 303.15 K. ▲, $m_y = 7.3791$; △, $m_y = 4.3395$; ●, $m_y = 3.0432$; ■, $m_y = 1.9195$; ○, $m_y = 0.9138$.

of two lines with different m_y values is dependent on the h_{xyy} value and the difference in the two m_y values. The experimental relations of $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})/m_y$ with m_x and m_y are shown in Figs. 1–6. The data of the KCl–acetone–water and KI–acetone–water systems at the two temperatures are clearly in agreement with eqn. (3) (Figs. 3–6). For the NaCl–acetone–water system, all the data fall on a line (Figs. 1 and 2). This is because the h_{xyy} values at the two temperatures are very small; therefore, the lines are very close, and, within experimental error, they are coincident.

The data for the parameters in Table 8 indicate that the values of h_{xy} decrease and of h_{xxy} increase as the ionic size of electrolytes increases; the values of h_{xyy} do not show evident dependence on the ionic size. This is also

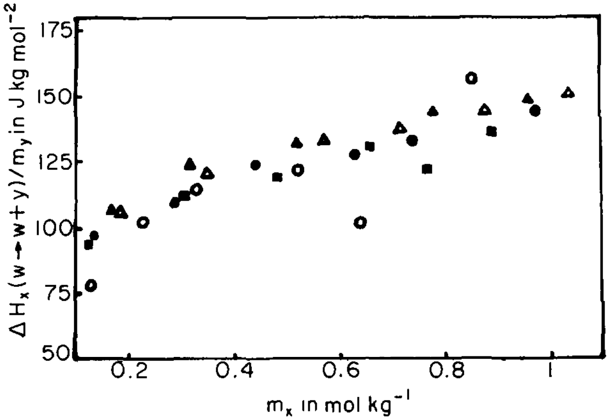

Fig. 2. Dependences of the function $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w} + \mathrm{y})/m_y$ on m_x and m_y for the NaCl–water–acetone system at 308.15 K. ▲, $m_y = 7.3526$: △, $m_y = 4.3152$; ●, $m_y = 3.0337$; ■, $m_y = 1.9174$; ○, $m_y = 0.9310$.

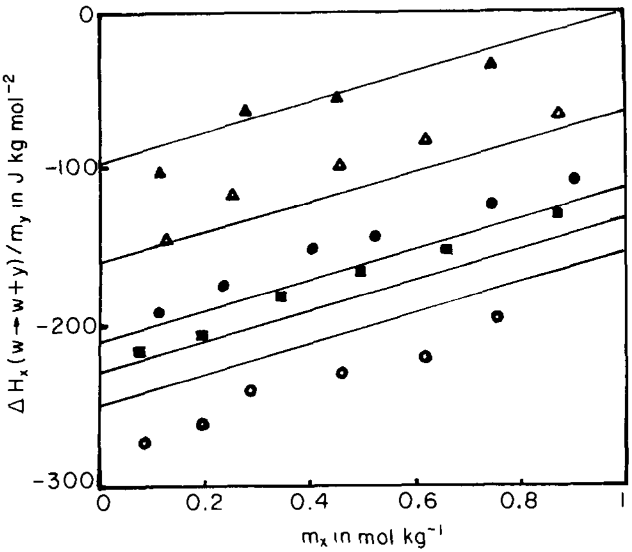

Fig. 3. Dependences of the function $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w}+\mathrm{y})/m_y$ on m_x and m_y for the KCl-water-acetone system at 303.15 K. ▲, $m_y = 11.5313$; △, $m_y = 7.3861$; ●, $m_y = 4.3072$; ■, $m_y = 3.0743$; ○, $m_y = 1.6925$; —, calculated from eqn. (3).

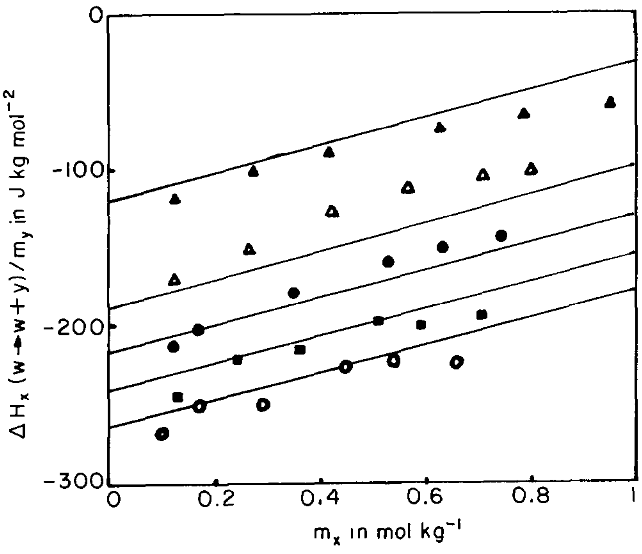

Fig. 4. Dependences of the function $\Delta H_x(\mathrm{w} \rightarrow \mathrm{w}+\mathrm{y})/m_y$ on m_x and m_y for the KCl-water-acetone system at 308.15 K. ▲, $m_y = 7.3826$; △, $m_y = 4.3152$; ●, $m_y = 3.0480$; ■, $m_y = 1.9110$; ○, $m_y = 0.9062$: —, calculated from eqn. (3).

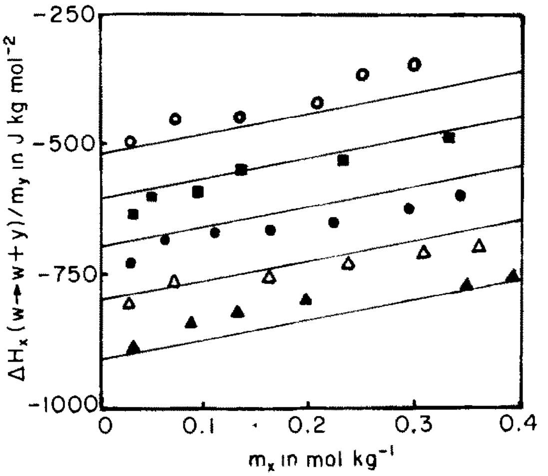

Fig. 5. Dependences of the function $\Delta H_x(w \rightarrow w+y)/m_y$ on m_x and m_y for the KI–water–acetone system at 303.15 K. ▲, $m_y = 5.7393$; △, $m_y = 4.3287$; ●, $m_y = 3.0862$; ■, $m_y = 1.9301$; ○, $m_y = 0.9100$; —, calculated from eqn. (3).

the case for the systems at 298.15 K [4]. We have discussed the dependences of the enthalpic interaction parameters on the ionic size of the electrolytes in the contexts of the electrostatic interaction and the structural interaction [4]. The electrostatic interaction of the ions with the polar groups of non-electrolytes will make a negative contribution to the enthalpic interaction parameters, and the destructive structural interaction [6] of ions with the non-polar groups of non-electrolytes will make a positive

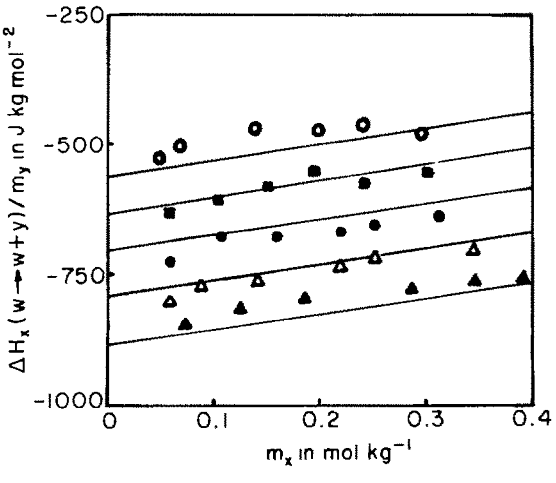

Fig. 6. Dependences of the function $\Delta H_x(w \rightarrow w+y)/m_y$ on m_x and m_y for the KI–water–acetone system at 308.15 K. ▲, $m_y = 5.7485$; △, $m_y = 4.3045$; ●, $m_y = 3.0337$: ■, $m_y = 1.9174$; ○, $m_y = 0.9062$; —, calculated from eqn. (3).

contribution to the enthalpic interaction parameters. This has been indicated by an analysis of the h_{xy} values between electrolytes and non-electrolytes with the group additivity concept [7]. The values of the enthalpic interaction parameters will be mainly dependent on the differences in the two kinds of interaction although there may be other kinds of interaction. The electrostatic interaction will be accompanied by a partial desolvation of the solutes which interact with each other and this will counteract the negative contribution of the electrostatic interaction to a great extent. Because the desolvation of the ion will become increasingly easier as the ionic size increases, its counteractive effect on the electrostatic interaction will decrease as the ionic size increases. This is why h_{xy} decreases as the ionic size increases. In this work, h_{xxy} is the mean enthalpic ionic interaction parameter of an acetone molecule with four ions: two positive ions and two negative ions. Because there is only one polar group in an acetone molecule, most of the ions will mainly produce structural interaction with the non-polar groups of the acetone molecule and bring about a destructive effect. This will cause h_{xxy} to be positive. The ion with the larger size has the larger dispersion force, so that it will have a larger destructive effect on the hydrophobic hydration structure of the non-electrolyte. Therefore the values of h_{xxy} increase as the ionic size of the electrolytes increases from NaCl to KCl to KI.

According to the thermodynamic relations, the temperature coefficients of the enthalpic interaction parameters are the interaction parameters of the molal heat capacity. We can see from Table 8 that all the h_{xy} and h_{xxy} values tend to increase and the h_{xyy} values tend to increase as the temperature increases. This means that the c_{xy} and the c_{xxy} values are negative and that the c_{xyy} value is positive. Piekarski et al. [8] have also determined that the c_{xys} values of NaI with some alcohols in water are negative. The interaction parameters of the heat capacity measure the fluctuation of the interaction energies with temperature. The electrostatic interaction does not vary significantly with temperature, the structural interaction is relatively temperature dependent [3]. Thus, the temperature dependence of the structural interaction is the contribution responsible for the interaction parameters of the heat capacity.

The contributions to the enthalpic effect from the structural interaction relate to the difference in energy between the hydrophobic hydration structure and the normal water structure. The hydrophobic hydration of a non-electrolyte is said to promote the structure of water [9, 10] and the structure of water near the hydrophobic solute is more temperature dependent than that of pure water [6]. That is to say that the difference in energy between the hydrophobic hydration structure and the normal water structure will decrease as the temperature increases. If the structural interaction destroys the hydrophobic hydration structure of the non-electrolyte, it will make a positive contribution to the enthalpic interaction parameters, and if the hydrophobic hydration structure is enhanced by the structural interaction, negative contribution will be made. The two kinds of contributions will all decrease in absolute value as the temperature increases. In other words, destroying the hydrophobic hydration structure makes the interaction parameters of the heat capacity negative, and enhancing the hydrophobic hydration structure makes it positive. As mentioned above, the structural interaction of the electrolyte with one acetone molecule will destroy the hydrophobic hydration structure; therefore the c_{xy} and the c_{xxy} values for the systems studied are negative.

The h_{xyy} parameter is the mean ionic enthalpic interaction parameter of two acetone molecules with one electrolyte molecule. Kato et al. and Ito et al. have pointed out that there is a clathrate hydrate structure around the non-electrolyte in aqueous solutions of acetone and in aqueous solutions of *t*-butyl alcohol [11, 12]. Chloride ions will promote the aggregation of the clathrate hydrate structure [13]. Avedikian et al. have 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 [14]. In the present study, it can be concluded that the structural interaction of an electrolyte with two acetone molecules will also enhance the hydrophobic bonding between the two acetone molecules. It is this enhancement of the hydrophobic bonding that makes the negative contribution to the h_{xyy} parameter and makes c_{xyy} positive.

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