The enthalpic interaction parameters of NaCl, KCl and KI with acetone in water at 298.15 K

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Abstract

The enthalpies of solution of NaCl, KCl and KI have been measured in water and in mixtures of acetone with water at 298.15 K. The enthalpic interaction parameters h_{xy}, h_{xxy} and h_{xyy} of the three salts with acetone have been evaluated. The dependences of the enthalpic interaction parameters on the ionic size of the electrolyte have been discussed with respect to the electrostatic interaction and structural interaction.

INTRODUCTION

The interaction between electrolytes and non-electrolytes in water is very important in solution chemistry. The thermodynamic properties of electrolyte solutions in mixtures of water with non-electrolytes are frequently studied in many scientific centres. According to the McMillan–Mayer theory [1], all the thermodynamic properties of multi-component solutions can be expressed by using a virial expansion in m which relates the non-ideal contributions of any total thermodynamic function to a series of pair, triplet and higher order interaction parameters. The enthalpies of transfer of an electrolyte (x) from pure water (w) to a non-electrolyte (y) solution can be readily expressed as [2]

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

where m_x and m_y are the molalities defined per kg of pure water, v is the number of ions dissociated by the electrolyte (x), h_{xy} is the enthalpic pair interaction parameter, and h_{xxy} and h_{xyy} are the enthalpic triplet parameters.

Many studies [2–5] have been made on the interaction between electrolytes and non-electrolytes from the observed enthalpic effects. Most

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studies refer to the enthalpic pair interaction parameters. Only a few papers concern the triplet interaction parameters. There is no doubt that triplet interaction makes a non-negligible contribution to the thermodynamic properties of multi-component systems. Therefore, it is interesting to consider triplet interaction parameters when investigating the thermodynamic properties of multi-component systems.

The purpose of the present paper is to obtain the enthalpic pair and triplet interaction parameters of NaCl, KCl and KI with acetone in water by measuring the enthalpies of solution of the salts in water and in the mixtures of water and acetone.

EXPERIMENTAL

The NACl and KCl used in the experiment were high purity grade, with no 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 using Werner's method [6]. The water used was double-distilled.

The enthalpy of solution measurements were obtained using a C-80 calorimeter (Setaram) with reversed-mixing vessels. The reversed-mixing vessel has two chambers separated by a tilting lid. The salt was first introduced into the vessel, 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 before the solvent was introduced. The salts were weighed on a single-pan balance (Mettler) with a sensitivity of $10 \, \mu g$, and the solvent was weighed on an analytical balance with a sensitivity of 0.1 mg. The calibration of the calorimeter was performed with an EJ2 Joule-effect device (Setaram). The calibration of the enthalpy of evaporation of the solvent was made for the enthalpy of solution. The total uncertainty of ΔH_m is about ±0.5%. All measurements were made at 298.15 K.

RESULTS AND DISCUSSION

The enthalpies of solution of NaCl, KCl and KI in water and in water–acetone mixtures are given in Tables 1–3. The enthalpies of solution obtained for all three salts in water can be fitted by the equation

$$\Delta H_m \, (\text{J mol}^{-1}) = A + Bm^{1/2} + Cm \tag{2}$$

where m is the molality. The values of the parameters A, B and C were determined by the method of least squares and are listed in Table 4, the standard deviations being given in the last column. The enthalpies of transfer $\Delta H_x(w \rightarrow w + y)$ are the differences between the measured enthalpies of solution of the salts in water–acetone mixtures and the enthalpies of solution in water which were calculated using eqn. (2). The

enthalpies of transfer can be expressed in terms of pair and triplet interaction parameters of the electrolyte and non-electrolyte by eqn. (1).

Cassel and Wood [3] have compared some data and have pointed out that for a variety of solutes having a concentration of $1\,m$, the pair term makes a contribution of from $+300$ to $-300\,cal\,mol^{-1}$ to the excess enthalpy of a solution, the triplet terms contribute $\pm 30\,cal\,mol^{-1}$ and quadruplet terms contribute $\pm 5\,cal\,mol^{-1}$. Therefore, within experimental uncertainty, the contributions of quadruplet and higher order terms to the enthalpy of transfer will be negligible. Hence

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

The m_x, m_y and $\Delta H_x(w \rightarrow w + y)/m_y$ data were fitted to eqn. (3) using a least-squares routine and the enthalpic interaction parameters obtained are given in Table 5. Equation (3) shows that $\Delta H_x(w \rightarrow w + y)/m_y$ is a linear function of m_x when m_y is fixed, and that the slope is not dependent on the value of m_y. Figures 1–3 give the relations of $\Delta H_x(w \rightarrow w + y)/m_y$ with m_x and m_y obtained from experiment. Figures 2 and 3 clearly show that there are linear relations between $\Delta H_x(w \rightarrow w + y)/m_y$ and m_x with the same slope at different m_y values. The straight lines in Figs. 2 and 3 are calculated from eqn. (3). In eqn. (3), it is clear that the distance between the two lines with different m_y is dependent on h_{xyy}. For the NaCl–acetone–water system (see Fig. 1), all the data fall on a line. This is because the h_{xyy} values are very small, so that the lines are very close; within experimental error, they join together.

Moldan [7] has measured the enthalpies of solution of some electrolytes in water and water–acetamide mixtures at 313.15 K. Figures 4 and 5 are drawn from his data. Most of the systems he investigated have relations similar to that of the systems investigated here, the system containing KNO_3 being an exception. Their enthalpic interaction parameters are also shown in Table 5.

It is generally believed that the interactions between electrolyte and non-electrolyte are composed of electrostatic and structural interactions. The concept of structural interactions, introduced by Frank and Robinson [8] has been used by many authors [9, 10] to explain the concentration dependence of transfer functions of electrolytes. For enthalpic functions, we shall consider that the structural interaction consists principally of two components, one arising from the partial desolvation of solutes which interact with each other, and the other from the effect of the electrolyte on the water structure in the neighborhood of hydrophobic groups of non-electrolyte. De Visser et al. [11] have published a general discussion on structural interactions and believe that, in most cases, the net effect of co-sphere overlap on the hydration structure is destructive. Structural interaction makes quite a large contribution to enthalpic functions and

TABLE 1

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

m_x (mol kg^{-1})	ΔH_m water	m_x (mol kg^{-1})	ΔH_m $m_y = 1.9259$	m_x (mol kg^{-1})
0.0813	4170	0.0922	4360	0.0863
0.1966	4232	0.1226	4400	0.1771
0.3031	4225	0.2651	4432	0.2431
0.4292	4172	0.3929	4431	0.3750
0.4821	4151	0.6406	4319	0.6149
0.7457	3979	0.8066	4160	0.8473

TABLE 2

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

m_x (mol kg^{-1})	ΔH_m water	m_x (mol kg^{-1})	ΔH_m $m_y = 0.9047$	m_x (mol kg^{-1})	ΔH_m $m_y = 1.8855$
0.0611	17520	0.0856	17330	0.0677	17160
0.1064	17590	0.1967	17400	0.1679	17240
0.1750	17630	0.2731	17410	0.2483	17260
0.2963	17620	0.3290	17400	0.3724	17280
0.3509	17600	0.4720	17360	0.4961	17230
0.5277	17520	0.5896	17300	0.6831	17170
0.6170	17460				

TABLE 3

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

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 $m_y = 1.9195$
0.0290	20180	0.0286	19730	0.0256	18900
0.0501	20240	0.0663	19880	0.0639	19100
0.0866	20290	0.1216	19980	0.0852	19180
0.1550	20330	0.1876	19990	0.1498	19260
0.2110	20300	0.2427	20000	0.2266	19320
0.2824	20230	0.3082	19920	0.2985	19340

at 298.15 K

ΔH_m $m_y = 3.0408$	m_x (mol kg^{-1})	ΔH_m $m_y = 4.3072$	m_x (mol kg^{-1})	ΔH_m $m_y = 5.7393$
4440	0.0952	4548	0.0897	4612
4557	0.2022	4714	0.2472	4842
4608	0.3100	4744	0.4723	4900
4589	0.4672	4730	0.6291	4845
4493	0.7335	4600	0.8007	4735
4358	0.9037	4507	0.9984	4665

298.15 K

m_x (mol kg^{-1})	ΔH_m $m_y =$ 2.9696	m_x (mol kg^{-1})	ΔH_m $m_y =$ 4.3029	m_x (mol kg^{-1})	ΔH_m $m_y =$ 7.3826
0.0854	16940	0.0985	16780	0.0842	16390
0.1255	17000	0.1424	16840	0.2303	16700
0.1992	17060	0.2184	16920	0.3662	16800
0.3279	17060	0.3523	16960	0.5759	16830
0.4400	17050	0.5105	16960	0.6944	16840
0.6603	16980	0.7427	16870	0.8773	16820

298.15 K

m_x (mol kg^{-1})	ΔH_m $m_y =$ 3.0385	m_x (mol kg^{-1})	ΔH_m $m_y =$ 4.3045	m_x (mol kg^{-1})	ΔH_m $m_y =$ 5.7179
0.0246	18040	0.0255	16570	0.0373	15190
0.0745	18230	0.0910	17030	0.1020	15560
0.1582	18360	0.1671	17110	0.1705	15730
0.2105	18430	0.2560	17200	0.2689	15870
0.2532	18440	0.3325	17280	0.3320	15870
0.3371	18450	0.4162	17300	0.3972	15920

TABLE 4

Parameters of eqn. (2)

Electrolyte	A	B	C	S [a]
NaCl	3853	1595	−1680	5
KCl	17190	1796	−1863	8
KI	19836	2600	−3497	11

[a] Standard deviation.

TABLE 5

Enthalpic interaction parameters of electrolyte (x) with non-electrolyte (y) in water

| x	y	h_{xy} (J kg mol^{-2})	h_{xxy} (J kg^2 mol^{-3})	h_{xyy} (J kg^2 mol^{-3})	T (K)
NaCl	Acetone	24	5.9	−0.18	298.15
Kcl	Acetone	−66	9.7	2.5	298.15
KI	Acetone	−106	42.7	−15.0	298.15
NaCl	Acetamide	−18	−1.7	0.14	313.15
KBr	Acetamide	−75	1.9	0.76	313.15
CsI	Acetamide	−101	26.4	0.57	313.15
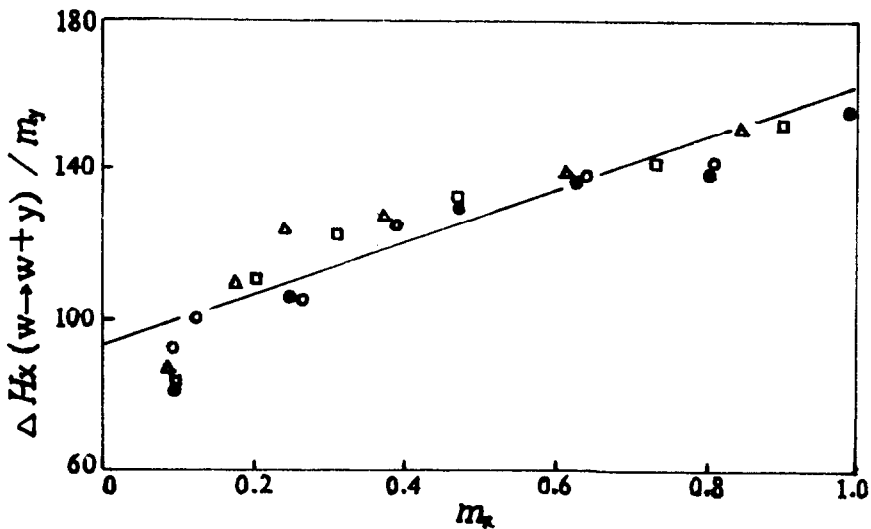
Fig. 1. Dependence of the function $\Delta H_x(w \rightarrow w + y)/m_y$ on m_x and m_y for the NaCl–water–acetone system at 298.15 K. ○, $m_y = 1.9259$; △, $m_y = 3.0408$; □, $m_y = 4.3072$; ●, $m_y = 5.7393$; ——, calculated from eqn. (3).
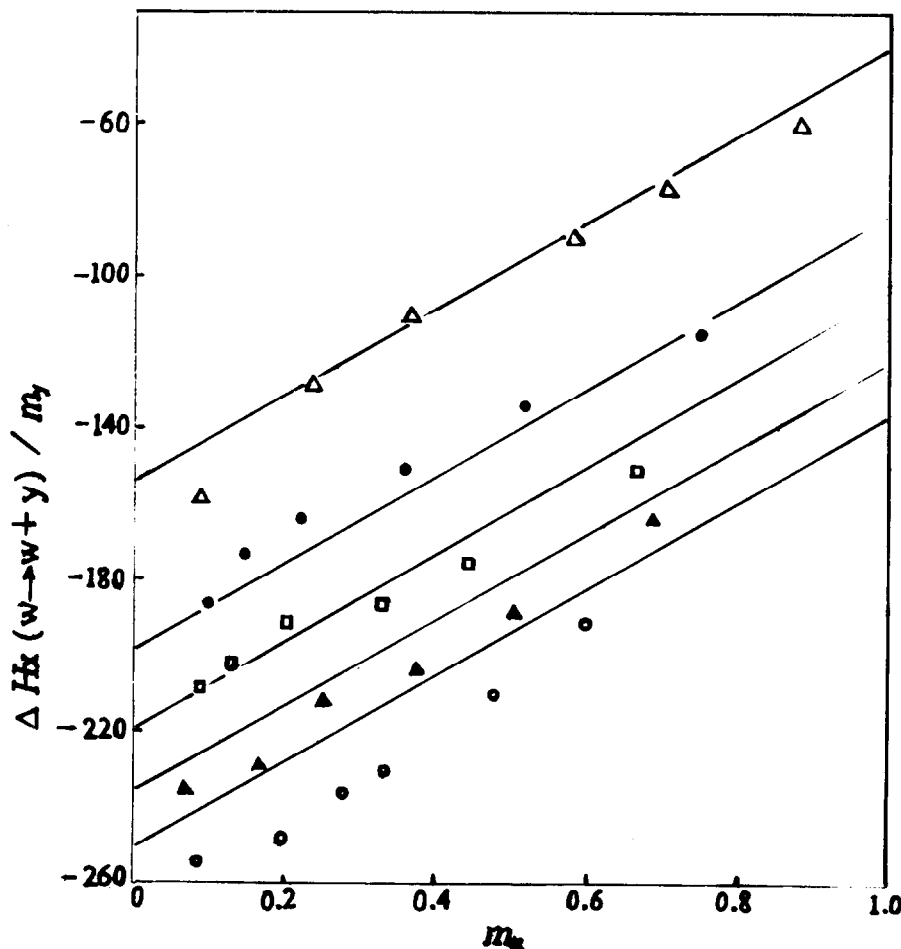
Fig. 2. Dependence of the function $\Delta H_x(w \rightarrow w + y)/m_y$ on m_x and m_y for the KCl–water–acetone system at 298.15 K. $\bigcirc$, $m_y = 0.9047$; $\blacktriangle$, $m_y = 1.8855$; $\square$, $m_y = 2.9696$; $\bullet$, $m_y = 4.3029$; $\triangle$, $m_y = 7.3826$; ——, calculated from eqn. (3).

sometimes even becomes predominant [2]. It can be assumed that the interaction of electrolyte with the polar groups of non-electrolyte is mainly electrostatic, accompanied by the desolvation of the solutes, and that the interaction with the non-polar groups is mainly structural.

The data presented in Table 5 show that the values of h_{xy} decrease from positive to negative and that h_{xxy} increases as the ionic size of the electrolytes increases. The value of h_{xy} is the mean ionic pair interaction parameter of the ions dissociated by an electrolyte with a non-electrolyte. The electrostatic interaction between ions and the polar groups of non-electrolyte will give a negative contribution to h_{xy}. But this will be countered, to quite a considerable extent, by the contribution from the desolvation of solutes. Because the desolvation of the ions will become increasingly easier as the ionic size increases, one would expect that the
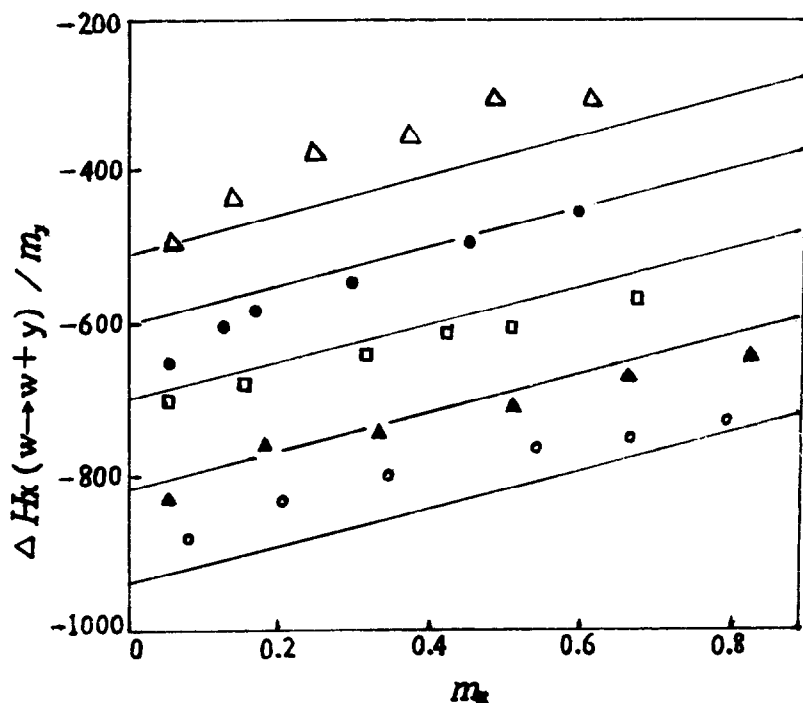
Fig. 3. Dependence of the function $\Delta H_x(w \rightarrow w + y)/m_y$ on m_x and m_y for the KI–water–acetone system at 298.15 K. $\triangle$, $m_y = 0.9062$; $\bullet$, $m_y = 1.9195$; $\square$, $m_y = 3.0385$; $\blacktriangle$, $m_y = 4.3045$; $\bigcirc$, $m_y = 5.7179$; ———, calculated from eqn. (3).

negative contribution to h_{xy} arising from the interaction between the electrolyte and the polar group of the non-electrolyte will be greater as the ionic size increases. In addition, there is an interaction between the electrolyte and the non-polar groups of non-electrolyte. The larger ion has the larger dispersion force, so that it have a greater effect on the hydrophobic hydration structure of non-polar groups of non-electrolyte. Therefore the positive contribution to h_{xy} arising from the structural interaction between electrolyte and the non-polar groups of non-electrolyte will also be greater as the ionic size increases. The two interactions of electrolyte with polar and non-polar groups of non-electrolyte have opposite effects on the ionic size dependence of h_{xy}. The observed dependence suggests that the interaction of electrolyte with the carbonyl group of acetone is the main interaction in the systems studied, so that the values of h_{xy} decrease from positive to negative with increasing ionic size of electrolytes from NaCl to KCl and to KI. The h_{xxy} parameter is the mean ionic interaction of two electrolytes with a non-electrolyte. It can be imagined that after the interaction of an electrolyte with the polar group of a non-electrolyte, the other electrolyte will mainly interact with the non-polar groups of the non-electrolyte, with a resulting destructive effect. This will cause h_{xxy} to be positive. The larger the ionic size of an
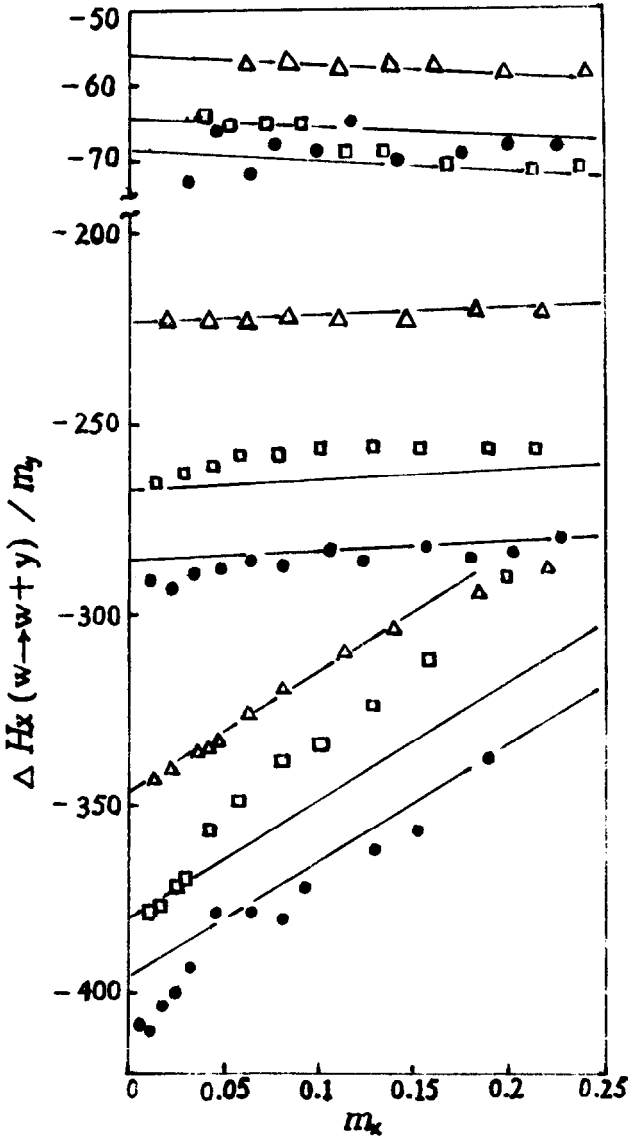
Fig. 4. Dependence of the function $\Delta H_x(w \to w + y)/m_y$ on m_x and m_y for some salt–water–acetamide systems at 313.15 K [7]. Upper data, NaCl; middle data, KBr; lower data, CsI, ●, $m_y = 2.9876$; □, $m_y = 7.2556$; △, $m_y = 16.9296$; ——, calculated from eqn. (3).

electrolyte, the greater the destructive effect. Therefore the values of h_{xxy} increase as the ionic size of the electrolytes increases from NaCl to KCl and to KI.

The values of h_{xyy} (shown in Table 5) for most systems are small, in agreement with the result obtained by Perron et al. [2] that the h_{xyy} of NaCl–*tert*-butyl alcohol–water system is near zero. However, the h_{xyy}
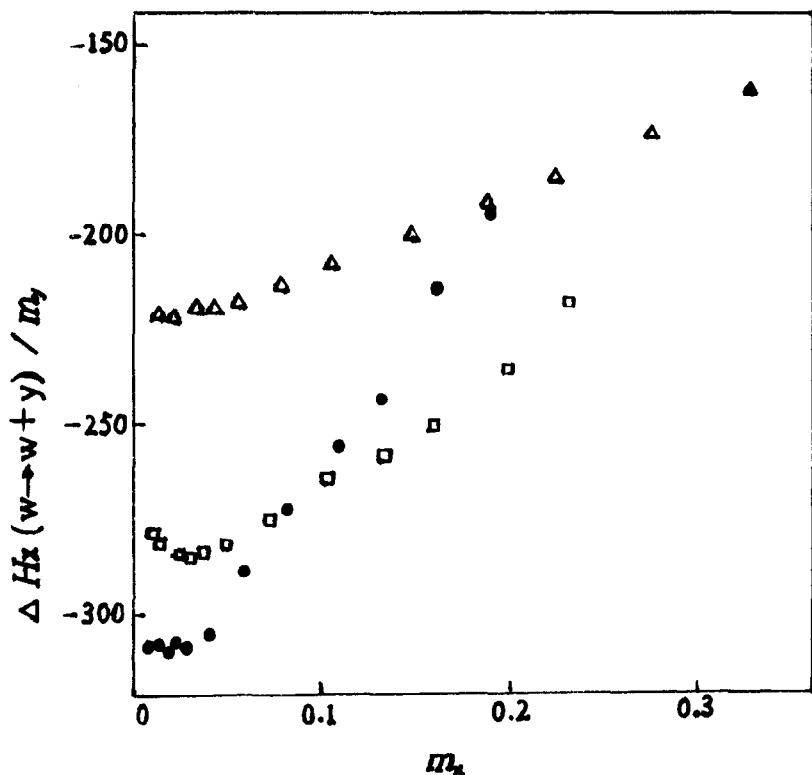
Fig. 5. Dependence of the function $\Delta H_x(w \rightarrow w+y)/m_y$ on m_x and m_y for the KNO_3–water–acetamide system at 313.15 K [7]. ●, $m_y = 2.9876$; □, $m_y = 7.2556$; △, $m_y = 16.9296$; ——, calculated from eqn. (3).

values given in Table 5 do not show any clear dependence on the ionic size of the electrolytes. The uncertainty in the measured enthalpies of solution is probably responsible for this. At present, we can make no further conclusions concerning h_{xyy}.

The $\Delta H_x(w \rightarrow w+y)/m_y$ of the KNO_3–acetamide–water system (see Fig. 4) shows different dependences on m_x and m_y from the other systems studied. This indicates that eqn. (3) cannot be used for this system, and suggests that the transfer enthalpy has a non-negligible relation with higher order interactions between electrolyte and non-electrolyte. More experiments are required for further explanations of this phenomenon.

ACKNOWLEDGEMENTS

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