ELSEVIER

Thermochimica Acta 256 (1995) 261–270

thermochimica
acta

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

Yan Lu *, Wei Xie, Ze Lu [1], Jinsuo Lu, Haihong Wang

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

Received 14 February 1994; accepted 24 July 1994

Abstract

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

Keywords: Glycine; Halide; Heat of solution; Protein; Salt; Stability

1. Introduction

Salts can have marked effects on the stability of protein structures. The effects, however, are different with different salts. Some elctrolytes tend to disrupt protein structures whereas others protect them [1]. There is evidence which seems to indicate that the discriminatory effects of salts on proteins arise principally from interactions of the ions with hydrophobic groups in the amino acid side chains [2]. Therefore, it is interesting to investigate the interactions of amino acids with salts in water. Many studies have been carried out on these interactions using enthalpic effects [3–7], and some interesting results have been obtained. However, most of the

---

* Corresponding author.

[1] Present address: Henan Medicine School, Kaifeng, Henan, China.

SSDI 0040-6031(94)02037-X

studies only relate to the enthalpic interaction between one amino acid molecule and an electrolyte, which, according to McMillan–Mayer theory [8], is described by the enthalpic pair interaction parameter. There is no doubt that the contribution of triplet interactions to the thermodynamic properties of multicomponent systems is not negligible. Therefore, it is necessary to take into account both enthalpic pair and triplet interactions when investigating the interactions of amino acids with salts in water.

According to the McMillan–Mayer approach, the enthalpies of transfer of a non-electrolyte (y) in pure water to an electrolyte (x) in solution can be expressed as [9,10].

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

where m_x and m_y are the molalities defined per kilogram of pure water, h_{xy} is the enthalpic pair interaction parameter and is equal to the sum of the two coefficients $(h_{My} + h_{Ay})$ (M = cation, A = anion), and h_{xyy} and h_{xxy} are the enthalpic triplet interaction parameters, where $h_{xyy} = h_{Myy} + h_{Ayy}$ and $h_{xxy} = h_{MMy} + 2h_{MAy} + h_{AAy}$ [5]. Eq. (1) can be rewritten as

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

We have measured the enthalpies of solution of glycine in pure water and in LiCl, NaCl and KCl solutions at 298.15 K, and have obtained the enthalpic pair and triplet interaction parameters of glycine with the three salts [11]. The purpose of the present paper is to obtain the enthalpic pair and triplet interaction parameters of glycine with various sodium halides in water by measuring the enthalpies of solution of glycine in the salt solutions.

2. Experimental

The analytical grade glycine used in the experiment was recrystallized from a water–methanol mixture and dried at 383 K. Analytical grade NaF and NaBr were recrystallized from water and dried at 383 K. Analytical grade NaI was recrystallized from a water–acetone mixture and dried under vacuum for several days at 335 K. All the salts and glycine were stored over P_2O_5 prior to use. All the water used was double-distilled.

The enthalpies of solution were measured at 298.15 K using a C-80 calorimeter (Setaram). The details of the experimental technique and the calibration have been described elsewhere [12]. The total uncertainty in the enthalpy of solution was about ±0.5%.

3. Results and discussion

The enthalpies of solution of glycine in NaF, NaBr and NaI solutions are given in Tables 1–3. We have measured the enthalpies of glycine in water in the

Table 1
The enthalpies of solution ΔH_m (in J mol^{-1}) of glycine in NaF aqueous solutions at 298.15 K

m_y in mol kg^{-1}	ΔH_m $m_x = 0.4986$	m_y in mol kg^{-1}	ΔH_m $m_x = 0.5913$	m_y in mol kg^{-1}	ΔH_m $m_x = 0.6944$	m_y in mol kg^{-1}	ΔH_m $m_x = 0.7994$
0.1397	14110	0.1796	14070	0.2021	14020	0.1612	14030
0.2501	14050	0.3136	14020	0.2918	13980	0.2628	14000
0.3788	13960	0.3873	13970	0.3355	13960	0.3710	13940
0.4652	13910	0.4330	13950	0.4425	13910	0.4387	13910
0.5706	13890	0.5484	13900	0.5198	13880	0.5341	13880
0.6498	13860	0.6361	13830	0.6113	13810	0.63113	13810

Table 2
The enthalpies of solution ΔH_m (in J mol^{-1}) of glycine in NaBr aqueous solutions at 298.15 K

m_y in mol kg^{-1}	ΔH_m $m_x = 0.4947$	m_y in mol kg^{-1}	ΔH_m $m_x = 0.9879$	m_y in mol kg^{-1}	ΔH_m $m_x = 2.9970$	m_y in mol kg^{-1}	ΔH_m $m_x = 5.0020$
0.1573	13320	0.1846	12760	0.1767	11030	0.1880	10330
0.2744	13300	0.2701	12740	0.3026	11060	0.3411	10350
0.3450	13290	0.3688	12720	0.3979	11080	0.4271	10370
0.4528	13270	0.4634	12700	0.4811	11090	0.5394	10380
0.5367	13250	0.5693	12680	0.5932	11100	0.5791	10400
0.6244	13240	0.6339	12670	0.6828	11110	0.6898	10420

Table 3
The enthalpies of solution ΔH_m (in J mol^{-1}) of glycine in NaI aqueous solutions at 298.15 K

m_y in mol kg^{-1}	ΔH_m $m_x = 0.4902$	m_y in mol kg^{-1}	ΔH_m $m_x = 0.9986$	m_y in mol kg^{-1}	ΔH_m $m_x = 3.0070$	m_y in mol kg^{-1}	ΔH_m $m_x = 5.0700$
0.1589	12860	0.1794	11950	0.1475	9480	0.2038	8170
0.2552	12860	0.2883	11970	0.2823	9470	0.2664	8210
0.3625	12870	0.3654	11980	0.4097	9500	0.3604	8230
0.4410	12870	0.4600	12000	0.4883	9520	0.4599	8250
0.5123	12880	0.5374	12010	0.5896	9550	0.5322	8280

concentration range 0.1–0.5 *m* [11]. There is a very good linear relation between the molar enthalpies of solution of glycine in water and its molalities in the range of concentration measured.

$$\Delta H_m/(\mathrm{J\ mol^{-1}}) = 14\,140 - 248 m_y \tag{3}$$

The limiting molal enthalpy of solution in Eq. (3) agrees very well with literature values [6,13,14]. However, the concentration coefficient in Eq. (3) is different from that obtained by Humphrey et al. [15] using the method of measuring the dilution enthalpies at 0.4–3 m. This discrepancy may arise from the different methods and

Table 4
Enthalpic interaction parameters of glycine with NaX in water at 298.15 K

Electrolyte	h_{xy} in J kg mol^{-2}	h_{xxy} in J kg^2 mol^{-3}	h_{xyy} in J kg^2 mol^{-3}
NaF	13 ± 19	$-5 + 18$	$-134 + 13$
NaCl	(-504 ± 20)[a]	(45 ± 14)[a]	(-49 ± 31)[a]
	(-504 ± 8)[b]	(43 ± 25)[b]	(-15.5 ± 13.6)[b]
NaBr	-802 ± 17	57 ± 2	37 ± 24
NaI	-1268 ± 33	87 ± 4	114 ± 45

[a] Ref. [11]. [b] Ref [5].

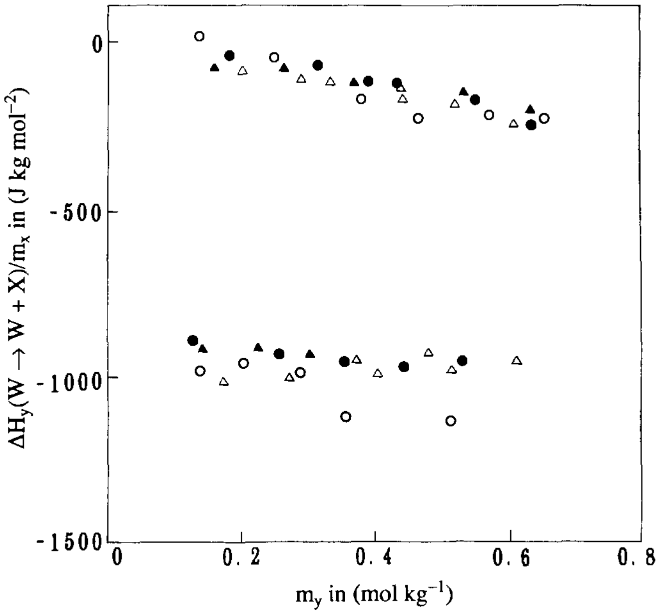

Fig. 1. Dependences of the function $\Delta H_y(w \to w + y)/m_x$ on m_x and m_y. Upper: for the NaF–water–glycine system; ▲, $m_x = 0.7994$; △, $m_x = 0.6944$; ●, $m_x = 0.5913$; ○, $m_x = 0.4986$. Lower: for the NaCl–water–glycine system; ▲, $m_x = 0.9637$; △, $m_x = 0.7422$; ●, $m_x = 0.4997$; ○, $m_x = 0.2498$.

concentrations. Even if there is a systematic error in the concentrations measured in our experiment, this will not affect the calculation of the enthalpies of transfer $\Delta H_y(w \to w + y)$; because ΔH_y is the difference in the enthalpies of solution of glycine in salt solution and in pure water at the same concentration, the error will be cancelled out. The enthalpies of transfer have been calculated and fitted to Eq. (2) using a least-squares method, and the enthalpic interaction parameters thus obtained are given in Table 4. Eq. (2) shows that when m_x is fixed, $\Delta H_y(w \to w + x)/m_x$ is a linear function of m_y and the slope is not dependent on m_x.

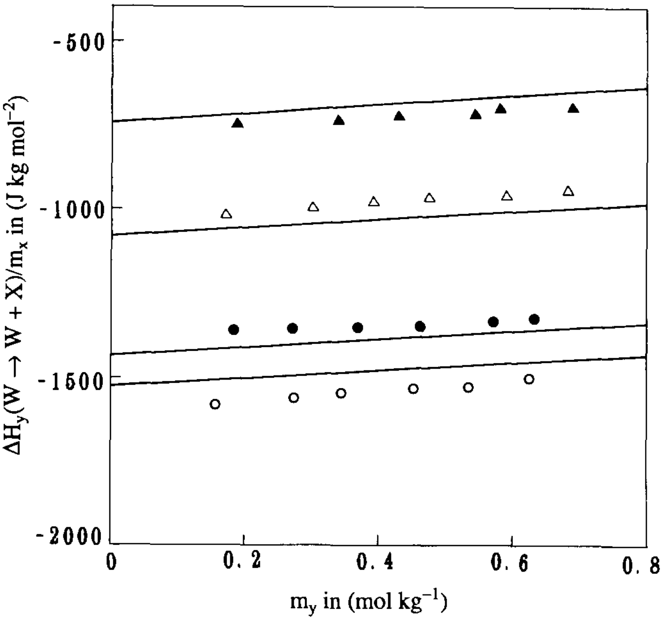

Fig. 2. Dependences of the function $\Delta H_y(\mathrm{w} \to \mathrm{w} + \mathrm{x})/m_x$ on m_x and m_y for the NaBr–water–glycine system. ▲, $m_x = 5.0020$; △, $m_x = 2.9970$; ●, $m_x = 0.9879$; ○, $m_x = 0.4947$; –, calculated from Eq. (2).

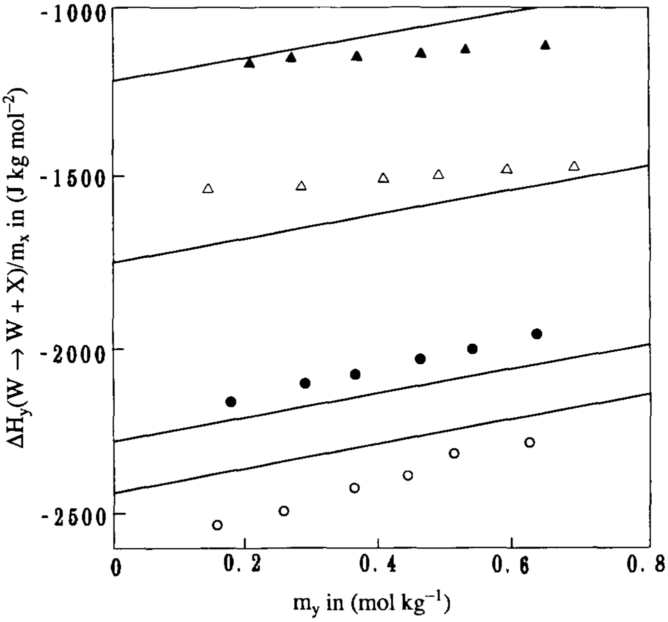

Fig. 3. Dependences of the function $\Delta H_y(\mathrm{w} \to \mathrm{w} + \mathrm{x})/m_x$ on m_x and m_y for the NaI–water–glycine system. ▲, $m_x = 5.0700$; △, $m_x = 3.0070$; ●, $m_x = 0.9986$; ○, $m_x = 0.4902$; –, calculated from Eq. (2).

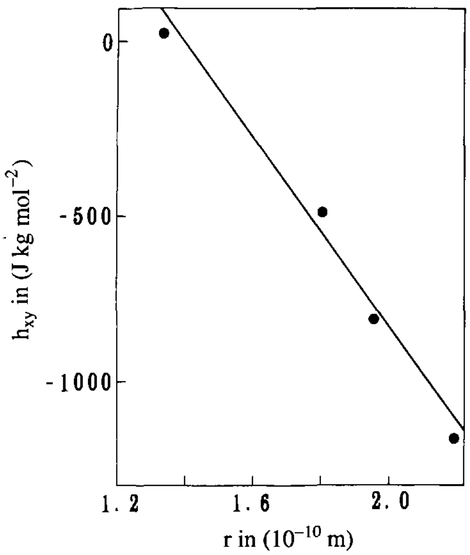

Fig. 4. Relationship between h_{xy} and anion radius.

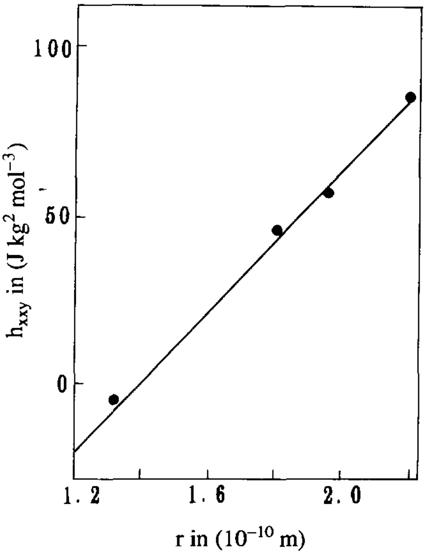

Fig. 5. Relationship between h_{xxy} and anion radius.

The interval between two lines with different m_x values is dependent on the h_{xxy} values and the difference between the two m_x values. Figs. 1–3 show the variation of $\Delta H_y(w \rightarrow w + x)/m_x$ with m_x and m_y obtained from the experiment. Figs. 2 and 3 clearly show that there are linear relations between $\Delta H_y(w \rightarrow w + x)/m_x$ and m_y,

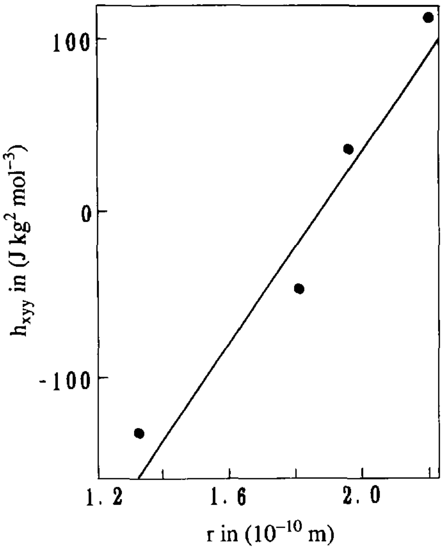

Fig. 6. Relationship between h_{xyy} and anion radius.

with the same slope at different m_x values. The straight lines in Figs. 2 and 3 are calculated from Eq. (3). For the glycine–NaF–water system (see Fig. 1), all the data fall on a straight line. This is because the h_{xxy} value is small and the differences among m_x are not large, so the lines are very close and coincide within the experimental error.

Table 4 indicates that all three enthalpic interaction parameters are functions of the size of the electrolytes. Figs. 4–6 show that there are linear relations between the values of the three enthalpic interaction parameters and the radii of the anions. Davis and Lilley [7] obtained a similar relation between h_{xy} and the radii of the anions for the same systems [7]. Electrostatic and structural interactions between electrolyte and non-electrolyte were used to explain the dependence of h_{xy} on the solute. Lilley et al. [5] considered that the interaction between an electrolyte and glycine is composed of three effects: (a) electrostatic interaction, (b) partial desolvation of solutes, (c) solvent reorganization. The latter two effects are structural interactions. We can assume that the interaction of an electrolyte with the polar groups of glycine is mainly electrostatic, accompanied by the partial desolvation of the solutes, and that the interaction with the apolar part of glycine is mainly structural. Desnoyers and co-workers [10,16] gave a general discussion on structural interactions and believed that, in most cases, the net effects of cosphere overlap on the hydration structure are destructive. Therefore structural interactions will give a positive contribution to enthalpic functions. Piekarski and Tkaczyk [17] carried out a multiple linear–regression analysis for h_{xy} using the Abraham–Kamlet–Taft equation, and found that the electrostatic interaction, which was mostly due to ion–dipole type interactions, gave a negative contribution to h_{xy}. The enthalpic pair interaction parameters can also be correlated by means of the well-known Savage and Wood group additivity model [18], and the results show that the enthalpic pair interaction of the electrolyte with the apolar CH_2 group is positive and with some polar groups is negative [17,19]. Therefore, it can be inferred that the electrostatic interactions resulting mainly from the interactions between an electrolyte and polar groups of glycine will give a negative contribution to h_{xy}, and the structural interaction between the electrolyte and glycine will make a positive contribution to h_{xy}. Kirkwood [20] gave a theoretical treatment of the electrolyte with amino acids on the basis of Debye–Huckel theory. Kirkwood theory is successful for calculation of the interaction free energy of solutes, but it fails to describe the interaction enthalpy [4,5]. Perron et al. [10] provided an explanation, as follows. Electrostatic interactions may give the main contribution to g_{xy}, and these interactions do not vary significantly with temperature and pressure. Structural hydration interactions do not give a large contribution to g_{xy} but, being quite temperature dependent, rapidly become the dominating effect for h_{xy}. Although electrostatic interactions are not the dominating effect for h_{xy}, they should make a negative contribution as mentioned above. However, the theory calculation according to Kirkwood theory gave quite a large positive value [4,5,7]. This deviation may result from using an incorrect $\mathrm{d}\ln D/\mathrm{d}T$ value. The correct value should be related to the temperature dependence of the dielectric constant near the solutes. Since the water molecules which are in the first hydration layer of the ions cannot rotate freely due to the strong attraction of the ions, there is a region of dielectric saturation around each ion [21]. As the temperature increases, the water molecules in the first hydration layer of the ion will become freer due to increased thermal action, which will be accompanied by an increase in the dielectric constant in the neighbourhood of the ion. This increase in dielectric constant will counter the effect of the decrease in the dielectric constant of bulk water as the temperature increases on the enthalpic electrostatic interaction of ion with glycine. The effect of $\mathrm{d}\ln D/\mathrm{d}T$ on the theoretical value of the electrostatic interaction is very striking. When the experimental value of $\mathrm{d}\ln D/\mathrm{d}T$ for water ($-4.55 \times 10^{-3}\ \mathrm{K}^{-1}$) was used, quite a large positive electrostatic contribution was obtained for the pair enthalpic interaction parameter [4,5,7]. Assuming that the structure of water does not change will result in $\mathrm{d}\ln D/\mathrm{d}T \approx 1/T$ ($-3.35 \times 10^{-3}\ \mathrm{K}^{-1}$ for 298.15 K) and a very small positive electrostatic contribution [4]. If one takes the counteractive effect of the first hydration layer of the ion on the temperature dependence of the dielectric constant into account, it is rational that $\mathrm{d}\ln D/\mathrm{d}T$ will be much smaller and the theoretical value of the electrostatic interaction will be negative.

h_{xy} is the sum of h_{My} and h_{Ay}. The ions will undergo electrostatic interactions with the polar groups of glycine and make a negative contribution to h_{xy}. However, this will be counteracted to a quite large extent by the effect of the partial desolvation of the solutes. An ion of smaller size is a more soluble, and consequently its endothermic effect on the partial desolvation is larger. This will be the main cause of the decrease in the negative values of h_{xy} as ionic size decreases. In addition, the effect of ions on the water structure around glycine will also tend to make h_{xy} more positive. In the anion series, fluorine has the greatest solubility, so that most of the energy will be supplied to the desolvation of the fluorine ion. The positive value of h_{xy} for the system of glycine with NaF indicates that structural interactions have a larger effect on h_{xy} than electrostatic interactions have in the system.

h_{xxy} is the sum of h_{MMy}, h_{AAy} and $2h_{MAy}$. h_{MAy} is the enthalpic interaction parameter of a glycine molecule with a pair of ions: cation and anion. The cation and the anion will undergo electrostatic interactions with the carboxyl and amino groups of glycine respectively, and make a negative contribution to h_{xxy}, as in the above discussion on h_{xy}. h_{MMy} and h_{AAy} are the enthalpic interaction parameters of a glycine molecule with two like ions. Only one ion can undergo electrostatic interactions with the polar groups of glycine, which is opposite in polarity to the ion. The other ion will only be able to interact with the apolar part of the glycine, which is mainly structural in nature, and between the two ions there will be an electrostatic rejection; the result will be a positive contribution to h_{xxy}. The values of h_{xxy} in Table 4 indicate that the contribution from the interaction of glycine with two like ions is larger than with two different ions. All the anions in the series are structure-breakers except for F^-. The larger the ion, the larger the dispersion force, and hence the larger disturbance made to the hydration structure of glycine, and the larger the positive contribution to h_{xxy}. This is the cause of h_{xxy} increasing with anion size. Because F^- is a structure-maker, it will enhance the hydration structure of glycine, and make a negative contribution to h_{xxy}. When this contribution exceeds the positive contribution, the h_{xxy} of glycine with NaF becomes negative.

h_{xyy} is the sum of h_{Myy} and h_{Ayy}. Franks et al. [22] indicated that for a non-electrolyte having hydrogen bonding or stronger dipolar interactions between its molecules, the enthalpic pair interaction parameter, h_{yy}, in water is negative. The concentration coefficient of the solution enthalpy of glycine in water showed that the h_{yy} of glycine molecules in water is negative. An analysis of the h_{xyy} values presented in Table 4 indicated that the principal interactions among one ion and two glycine molecules come from the interaction of the two glycine molecules, and the contribution to h_{xyy} is negative as for h_{yy}. The interaction of ions with the glycine molecules is structure-breaking and makes a positive contribution to h_{xyy}. The larger the ionic size, the greater the destructive effect. Therefore, the h_{xyy} parameters increase from negative to positive in the electrolyte series from NaF to NaI.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China and to the National Education Committee of China for the financial support.

References

[1] P.H. Von Hippel and T. Schleich, Acc. Chem. Res., 2 (1969) 257.
[2] A. Hamabata and P.H. Von Hippel, Biochemistry, 12 (1973) 1264.

[3] J.W. Larson and G. Morroson, J. Phys. Chem., 80 (1976) 1449.
[4] J.W. Larson, W.J. Plymade and A.F. Joseph, J. Phys. Chem., 81 (1977) 2074.
[5] T.H. Lilley, E. Moses and I.R. Tasker, J. Chem. Soc. Faraday Trans. 1, 76 (1980) 906.
[6] B.P. Kelley and T.H. Lilley, J. Chem. Thermodyn., 10 (1978) 703.
[7] K.G. Davis and T.H. Lilley, Thermochim. Acta, 107 (1986) 267.
[8] W.G. McMillan and J.E. Mayer, J. Chem. Phys., 13 (1945) 276.
[9] J.E. Desnoyers, G. Perron, L. Avedikian and J.-P. Morel, J. Solution Chem., 5 (1976) 631.
[10] G. Perron, D. Joly and J.E. Desnoyers, Can. J. Chem., 56 (1978) 552.
[11] Y. Lu, S. Zhen and J. Lu, Acta Phys. Chem. Sin., 10 (1994) 281.
[12] Y. Lu, S. Zhen and J. Lu, Thermochim. Acta., 210 (1992) 15.
[13] G.C. Kreshech and L. Benjamin, J. Phys. Chem., 68 (1964) 2476.
[14] C.H. Spink and M. Auker, J. Phys. Chem., 74 (1970) 1742.
[15] R.S. Humphrey, G.R. Hedwig, I.D. Watson and G.N. Malcolm, J. Chem. Thermodyn., 12 (1980) 595.
[16] C. Visser, G. Perron and J.E. Desnoyers, J. Am. Chem. Soc., 99 (1977) 5894.
[17] H. Piekarski and M. Tkaczyk, J. Chem. Soc. Faraday Trans., 87 (1991) 3661.
[18] J.J. Savage and R.H. Wood, J. Solution Chem., 5 (1976) 733.
[19] K.G. Davis, M.A. Gallardo-Jimenez and T.H. Lilley, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 2901.
[20] J.G. Kirkwood, Chem. Rev., 24 (1939) 233.
[21] R.A. Robinson and R.H. Stokes, Electrolyte Solution, Butterworths Scientific, London, 1955.
[22] F. Franks, M. Pedley and D.S. Reid, J. Chem. Soc. Faraday Trans. 1, 72 (1976) 359.