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Dissolution enthalpy of NaCl in water at 25°C, 45°C and 60°C. Determination of the Pitzer's parameters of the {H_2O–NaCl} system and the molar dissolution enthalpy at infinite dilution of NaCl in water between 25°C and 100°C

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Abstract

The dissolution enthalpy of sodium chloride in water was measured until saturation at 24.4°C, 44.3°C and 59.2°C using a C80D differential calorimeter (SETARAM). The experimental data were fitted using Pitzer's ion interaction model and the value of the dissolution enthalpy per mole of salt at infinite dilution was found at each temperature by treating $\overline{\Delta_{\mathrm{sol}}H^{\infty}}$ as adjustable parameter. Using these calorimetric measurements, the analytical expression of the variation of Pitzer's parameters were established with respect to temperature. The validation of this expression is made by the measurement of vapour equilibrium of binary solution {H_2O–NaCl} closed to saturation. Excellent agreement between experimental and calculated values of water activity has been found using our Pitzer's model parameters. © 1997 Elsevier Science B.V.

1. Introduction

The thermodynamic properties of aqueous solutions have been under investigation for many years. However, with few exceptions, the available experimental data are limited to temperatures close to the ambient temperature and generally, the data are obtained from V.L.E. measurements. In order to increase thermodynamic information, we present experimental results of dissolution enthalpy of NaCl in water as a function of molality at 298.15, 317.45 and 332.35 K. A classical electrolyte thermodynamic model, such as proposed by Pitzer (1979), can be used to calculate thermodynamic properties of the solutions.

2. Thermodynamical background

The Gibb's energy $\hat{G}$ of an electrolyte solution containing 1 kg of water is expressed with chemical potential of each solute, $\bar{g}_i$ and of the solvent, $\bar{g}_{\mathrm{w}}$:

$$\hat{G} = \hat{n}_{\mathrm{w}}\bar{g}_{\mathrm{w}} + \sum_i m_i\bar{g}_i \qquad (1)$$

in which m_i is the molality (mol kg^{-1} of solvent) of each species (ionic or molecular) dissolved and $\hat{n}_{\mathrm{w}}$ the amount of water corresponding to 1 kg of water ($\hat{n}_{\mathrm{w}} = 1000/M_{\mathrm{w}}$, M_{w} = molar mass of water in g mol^{-1}, $\hat{n}_{\mathrm{w}}$=55.508 mol kg^{-1}).

Chemical potentials can be related to activity by defining reference state. In the case of water, the reference potential is that of pure liquid water, $\bar{g}^*_{\mathrm{w}}$,

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and in the case of solutes, it is the hypothetical state defined from one molal ideal solution for solute $\bar{g}_{\mathrm{i}}^{\mathrm{ref}}$.

Then,

$$\bar{g}_{\mathrm{w}}(T,P,\ldots) = \bar{g}_{\mathrm{w}}^{*}(T,P) + RT\ln a_{\mathrm{w}}, \tag{2}$$

$$\bar{g}_{\mathrm{i}}(T,P,\ldots) = \bar{g}_{\mathrm{i}}^{\mathrm{ref}}(T,P) + RT\ln a_{i}, \tag{3}$$

a_{w}, a_i = activity of water and component i using unsymetric convention in molality scale. For an ideal solution, we can consider the same relationships and the same reference states:

$$\hat{G}^{\mathrm{id}} = \hat{n}_{\mathrm{w}}\bar{g}_{\mathrm{w}}^{\mathrm{id}} + \sum_i m_i\bar{g}_i^{\mathrm{id}}, \tag{4}$$

with

$$\bar{g}_{\mathrm{w}}^{\mathrm{id}}(T,P,\ldots) = \bar{g}_{\mathrm{w}}^{*}(T,P) + RT\ln a_{\mathrm{w}}^{\mathrm{id}}, \tag{5}$$

$$\bar{g}_i^{\mathrm{id}}(T,P,\ldots) = \bar{g}_i^{\mathrm{ref}}(T,P) + RT\ln a_i^{\mathrm{id}}. \tag{6}$$

The excess Gibbs energy, $\hat{G}^{\mathrm{E}}$, is, by definition, the difference between Gibbs Energy of real solution (Eq. (1)) and Gibbs Energy of the ideal solution (Eq. (4)).

Hence, the Excess Gibbs Energy of an electrolyte solution containing 1 kg of water can be expressed as follows:

$$\hat{G}^{\mathrm{E}}/RT = \hat{n}_{\mathrm{w}}\ln\gamma_{\mathrm{w}} + \sum_i m_i\ln\gamma_i \tag{7}$$

in which γ_{w} and γ_i are the activity coefficient of water and component i defined by

$$\gamma_{\mathrm{w}} = a_{\mathrm{w}}/a_{\mathrm{w}}^{\mathrm{id}}, \qquad \gamma_i = a_i/a_i^{\mathrm{id}}.$$

Given a binary solution containing 1 kg of water and m molecules of an electrolyte [MX], completely dissociated according to the reaction:

$$[\mathrm{MX}] = \nu_{\mathrm{X}}\mathrm{X} + \nu_{\mathrm{M}}\mathrm{M}.$$

The dissociation of one mole of solute leads to the formation of $\nu = \nu_{\mathrm{X}} + \nu_{\mathrm{M}}$ moles of ions with $m_{\mathrm{X}} = \nu_{\mathrm{X}}m$ and $m_{\mathrm{M}} = \nu_{\mathrm{M}}m$.

The mean activity coefficient is defined by

$$\nu\ln\gamma_{\pm} = \nu_{\mathrm{X}}\ln\gamma_{\mathrm{X}} + \nu_{\mathrm{M}}\ln\gamma_{\mathrm{M}}. \tag{8}$$

Then

$$\hat{G}^{\mathrm{E}}/RT = \hat{n}_{\mathrm{w}}\ln\gamma_{\mathrm{w}} + \nu m\ln\gamma_{\pm}. \tag{9}$$

It can be shown that:

$$\ln\gamma_{\pm} = \frac{1}{\nu RT}\left(\frac{\partial\hat{G}^{\mathrm{E}}}{\partial m}\right)_{T,P}. \tag{10}$$

In the molality scale, standard states are defined according to unsymetric convention. The activity of a component i in an ideal solution is identical to its molality:

$$a_i^{\mathrm{id}} = m_i/m^0,$$

in which m^0 is the unit molality.

The application of the Gibbs–Duhem relation to the ideal solution, leads to:

$$\hat{n}_{\mathrm{w}}d\left(\ln a_{\mathrm{w}}^{\mathrm{id}}\right) + \sum_i d\left(\ln\left(m_i/m^0\right)\right) = 0, \tag{11}$$

and integration of this equation, gives the expression of activity $a_{\mathrm{w}}^{\mathrm{id}}$

$$a_{\mathrm{w}}^{\mathrm{id}} = \exp\left(-\frac{1}{\hat{n}_{\mathrm{w}}}\sum_i m_i\right). \tag{12}$$

The osmotic coefficient of the solution, defined as follows:

$$\phi = \ln(a_{\mathrm{w}})/\ln\left(a_{\mathrm{w}}^{\mathrm{id}}\right).$$

Using Eq. (12), ϕ can be expressed in the molality scale by

$$\phi = -\frac{\hat{n}_{\mathrm{w}}}{\sum_i m_i}\ln a_{\mathrm{w}}$$

$$\text{(practical osmotic coefficient).} \tag{13}$$

Thus, the activity coefficient of water is related to the osmotic coefficient with the following expression:

$$\ln\gamma_{\mathrm{w}} = -(\phi - 1)\frac{\sum_i m_i}{\hat{n}_{\mathrm{w}}} \tag{14}$$

and whence, from Eq. (9),

$$\hat{G}^{\mathrm{E}}/RT = \nu m(\ln\gamma_{\pm} + 1 - \phi). \tag{15}$$

Consequently, we have from Eq. (10),

$$\phi - 1 = \frac{1}{\nu RT}\left[\left(\frac{\partial\hat{G}^{\mathrm{E}}}{\partial m}\right)_{T,P} - \frac{\hat{G}^{\mathrm{E}}}{m}\right]. \tag{16}$$

The last expression allows the calculation of the osmotic coefficient from a model of Excess Gibbs Energy, $\hat{G}^{E}(T,P,m)$.

In molality scale, the excess enthalpy, herein written $\hat{L}(m)$ is defined by:

$$\hat{L}(m) = \hat{G}^{E} - T\left(\frac{\partial \hat{G}^{E}}{\partial T}\right)_{P,m} = -T^{2}\left(\frac{\partial\left(\hat{G}^{E}/T\right)}{\partial T}\right)_{P,m} \quad (17)$$

If $\hat{H}(m)$ is the total enthalpy of the solution containing 1 kg of water, the excess enthalpy of this solution verifies the following relationship:

$$\hat{L}(m) = \hat{H}(m) - \hat{n}_{w}h_{w}^{*} - m\overline{h_{\mathrm{NaCl}}^{\infty}}, \quad (18)$$

with $\overline{h_{\mathrm{NaCl}}^{\infty}}$ and h_{w}^{*} are respectively partial molar enthalpy of NaCl at infinite dilution and molar enthalpy of pure liquid water.

The molar enthalpy of dissolution, $\Delta_{\mathrm{sol}}H(m)$, is the variation of enthalpy accompanying the dissolution of one mole of salt in enough water to make a solution of molality m. Thus we have the following relation:

$$\Delta_{\mathrm{sol}}H(m) = \left(\hat{H}(m) - \hat{n}_{w}h_{w}^{*} - mh_{\mathrm{NaCl}}^{*}\right)/m, \quad (19)$$

in which h_{NaCl}^{*} is the molar enthalpy of pure solid NaCl.

In the same manner, the partial molar enthalpy of dissolution at infinite dilution of NaCl can be defined by:

$$\overline{\Delta_{\mathrm{sol}}H^{\infty}} = h_{\mathrm{NaCl}}^{*} - \bar{h}_{\mathrm{NaCl}}^{\infty}. \quad (20)$$

From Eqs. (18) and (20), we can deduce that:

$$\Delta_{\mathrm{sol}}H(m) = \frac{\hat{L}(m)}{m} + \overline{\Delta_{\mathrm{sol}}H^{\infty}}. \quad (21)$$

Eq. (21) establishes a relationship between a model of representation of the excess Gibbs energy, $\hat{G}^{E}(T,P,m)$, and the experimental function, $\Delta_{\mathrm{sol}}H(m)$, measured, for example by calorimetric way.

In the case of the model proposed by Pitzer [1,2], expression for 1–1 electrolyte depends on the molal ionic strength, $I = \frac{1}{2}\sum_{i} m_{i}z_{i}^{2}$ (z_{i} being the charge on the ion), with the following relation:

$$\hat{G}^{E}/RT = -A_{\phi}\left(\frac{4I}{b}\right)\ln(1+bI^{1/2}) + m^{2}\left(2B+mC^{\phi}\right), \quad (22)$$

where

$$B = \beta^{(0)} + 2\beta^{(1)}\left[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})\right]/\alpha^{2}I,$$

A_{ϕ} is the Debye–Huckel coefficient associated with the model osmotic coefficient. The values of A_{ϕ} versus temperature were tabulated by Bradley and Pitzer [3]. The constants α and b have the values: $\alpha=2\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}$ and $b=1.2\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}$.

$\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} can be considered as adjustable parameters in the Pitzer's model.

Under the conditions of this work, we may admit that they are independent of pressure, and vary only with temperature. By application of Eq. (6) the corresponding equation for osmotic coefficient is

$$\phi - 1 = -A_{\phi}\left(\frac{I^{1/2}}{1+bI^{1/2}}\right) + 2m\left[\beta^{(0)} + \beta^{(1)}\exp\left(-\alpha I^{1/2}\right)\right] + m^{2}C^{\phi}. \quad (23)$$

Differentiating Eq. (22) with respect to temperature, and applying Eq. (21) we get the expression of molar enthalpy of dissolution given by the Pitzer's model:

$$\Delta_{\mathrm{sol}}H(m) = \overline{\Delta_{\mathrm{sol}}H^{\infty}} + A_{H}\ln(1+1.2I^{1/2}) - B(T)\left[1-(1+2I^{1/2})\exp(-2I^{1/2})\right] - A(T)m - C(T)m^{2}, \quad (24)$$

A_{H} is the Debye–Hückel slope for enthalpy as defined by Bradley and Pitzer [3]. The variables $A(T)$, $B(T)$ and $C(T)$ are defined from the parameters of Pitzer's model:

$$A(T) = 2RT^{2}\left(\frac{\partial\beta^{(0)}}{\partial T}\right)_{P},$$

$$B(T) = RT^{2}\left(\frac{\partial\beta^{(1)}}{\partial T}\right)_{P},$$

$$C(T) = RT^{2}\left(\frac{\partial C^{\phi}}{\partial T}\right)_{P}. \quad (25)$$

If we measure, at temperature T, the enthalpy of dissolution of NaCl versus composition, we obtain an experimental curve, which can be represented with Eq. (24). This curve allows the determination of $\overline{\Delta_{\text{sol}}H^{\infty}(T)}$ at the considered temperature, considering it as an adjustable parameter in the light of $A(T)$, $B(T)$, and $C(T)$.

3. Experiment

The calorimetric system and procedure were the same as previously reported [4]. The calorimeter was calibrated by measuring the heat of fusion of indium. The precision of the results is about 2%. The lower value of the salt molality (0.06) was chosen according to the calorimeter sensitivity. Reagent grade NaCl (Aldrich) was dried at 110°C.

Table 1
The dissolution of NaCl in water at 24.4°C n_w = moles of water, n_l = moles of pure solid sodium chloride

n_w mol	$n_l \cdot 10^2$ mol	m mol kg^{-1}	ΔH_{exp} J	$\Delta H_{\text{exp}}/n_l \Delta_{\text{sol}}H(m)$ J·(mol NaCl)$^{-1}$
0.2798	0.0323	0.0642	1.33	4113
0.2839	0.0611	0.1194	2.63	4305
0.2797	0.1016	0.2017	4.45	4378
0.2754	0.1692	0.3411	7.27	4296
0.2937	0.2490	0.4705	10.46	4201
0.2222	0.2288	0.5716	9.49	4148
0.2720	0.3018	0.6160	12.34	4088
0.2798	0.3566	0.7075	14.62	4100
0.2841	0.4372	0.8542	17.03	3895
0.2779	0.4468	0.8923	17.82	3989
0.2744	0.4630	0.9366	18.48	3991
0.2775	0.4738	0.9477	18.53	3911
0.2602	0.5157	1.1003	19.32	3746
0.2223	0.5251	1.3115	19.10	3637
0.2263	0.6781	1.6629	23.34	3442
0.2730	0.9981	2.0294	31.75	3181
0.1640	0.6853	2.3201	20.86	3044
0.2708	1.2371	2.5359	35.85	2898
0.0835	0.4185	2.7820	11.66	2786
0.2234	1.2215	3.0350	32.78	2684
0.1943	1.1979	3.4221	30.21	2522
0.1112	0.6971	3.4811	17.29	2480
0.0915	0.7055	4.2813	15.53	2201
0.1779	1.4803	4.6199	30.83	2083
0.0919	0.8559	5.1702	17.07	1994
0.1380	1.3771	5.5404	26.71	1940
0.0764	0.8549	6.2112	15.96	1867

Table 2
The dissolution of NaCl in water at 44.3°C n_w = moles of water, n_l = moles of pure solid sodium chloride

n_w mol	$n_l \cdot 10^2$ mol	m mol kg^{-1}	ΔH_{exp} J	$\Delta H_{\text{exp}}/n_l \Delta_{\text{sol}}H(m)$ J·(mol NaCl)$^{-1}$
0.2241	0.0758	0.1878	1.80	2374
0.2242	0.1422	0.3571	3.48	2413
0.1946	0.1860	0.5306	4.18	2247
0.1676	0.2596	0.8598	5.79	2230
0.1663	0.4163	1.3899	8.72	2095
0.2170	0.6875	1.7582	14.04	2042
0.1662	0.5943	1.9853	11.44	1925
0.1702	0.7402	2.4136	13.90	1878
0.1668	0.8321	2.7698	14.89	1789
0.1118	0.6974	3.4681	12.10	1735
0.1389	1.0881	4.3486	18.04	1658
0.0922	0.8617	5.1859	13.88	1611
0.0776	0.8460	6.0520	14.24	1683
0.0771	0.8709	6.2666	14.53	1668

Table 3
The dissolution of NaCl in water at 59.2°C n_w = moles of water, n_l = moles of pure solid sodium chloride

n_w mol	$n_l \cdot 10^2$ mol	m mol kg^{-1}	ΔH_{exp} J	$\Delta H_{\text{exp}}/n_l \Delta_{\text{sol}}(m)$ J·(mol NaCl)$^{-1}$
0.2882	0.0917	0.1766	0.66	720
0.2872	0.2832	0.5474	2.78	982
0.2956	0.4741	0.8902	5.02	1059
0.2980	0.6011	1.1195	6.70	1115
0.2899	0.8721	1.6698	9.57	1097
0.2919	0.9170	1.7437	9.98	1088
0.2447	1.1762	2.6680	13.08	1112
0.2418	1.2306	2.8247	14.57	1184
0.2234	1.4575	3.6209	16.77	1151
0.2036	1.6389	4.4675	19.39	1183
0.0929	0.8644	5.1633	11.88	1374
0.1279	1.2520	5.4323	17.14	1369
0.0766	0.8545	6.1903	11.82	1383

The experimental results are reported in Tables 1–3.

4. Determination of the Pitzer's parameters

Using Eq. (24), each parameters $\overline{\Delta_{\text{sol}}H^{\infty}(T)}$, $A(T)$, $B(T)$ and $C(T)$ have been fitted in our experimental

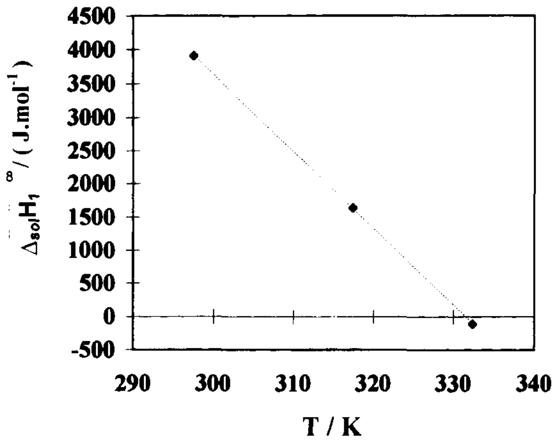

Fig. 1. Values of $\overline{\Delta_{sol}H_1^\infty}(T)$ versus temperature T for the {H_2O–NaCl} system.

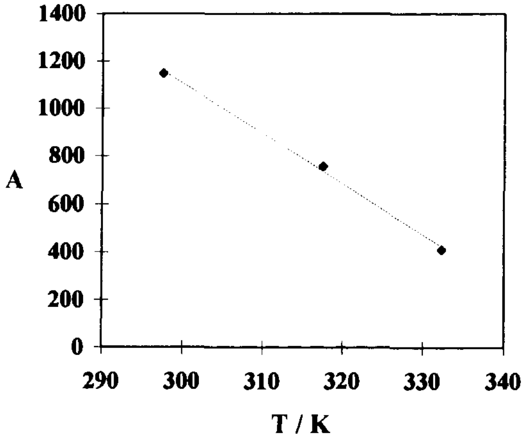

Fig. 2. Values of parameter A versus temperature T for the {H_2O–NaCl} system, with $A(T) = 2RT^2(\partial\beta^{(0)}/\partial T)_p\beta^{(0)}$ an adjustable parameter in the Pitzer model.

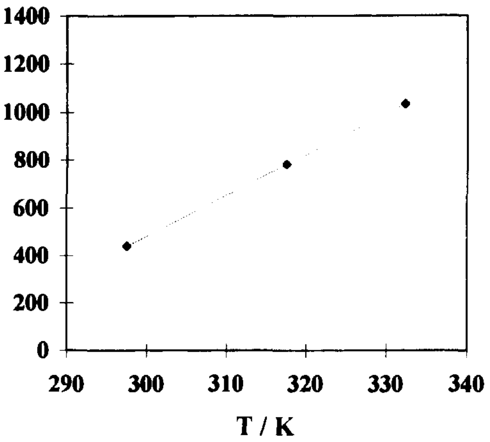

Fig. 3. Values of parameter B versus temperature T for the {H_2O–NaCl} system, with $B(T) = RT^2(\partial\beta^{(1)}/\partial T)_p\beta^{(1)}$ an adjustable parameter in the Pitzer model.

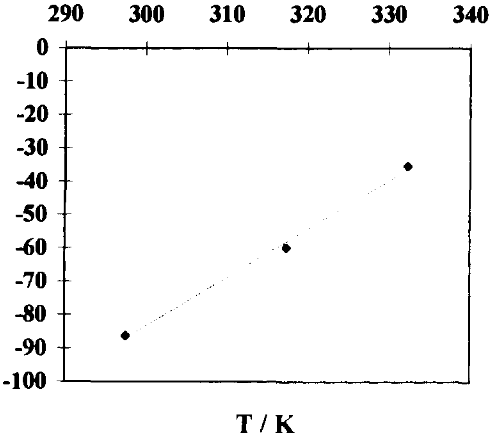

Fig. 4. Values of parameter C versus temperature T for the {H_2O–NaCl} system, with $C(T) = RT^2(\partial C^\phi/\partial T)_pC^\phi$ an adjustable parameter in the Pitzer model.

results. We have reported in Fig. 1 the values of each parameter versus temperature.

Values of $\overline{\Delta_{sol}H^\infty}(T)$ are well represented by a linear relationship in temperature:

$$\overline{\Delta_{sol}H^\infty}(T)\ (\mathrm{J\,mol^{-1}}) = A_1 + B_1(T/K),$$
$$\overline{\Delta_{sol}H^\infty}(T)\ (\mathrm{J\,mol^{-1}}) = 38211.53 - 115.26(T/K). \tag{26}$$

$\overline{\Delta_{sol}H^\infty}(T)$ has been experimentally determined by several authors at 25°C, and more scarcely at higher temperatures. We have represented in Fig. 5 the experimental values of Crises and Cobble [5], and of Nazarov and Charykov [6], at different temperatures and the estimated values of Clarke and Glew [7], as well as our experimental values and the values calculated using Eq. (26).

This representation shows that our values are in very good agreement with those of the literature, and that Eq. (26) may be used in the whole range of this study. Using this relation, we obtain, at t_0=25°C $\overline{\Delta_{sol}H^\infty} = 3847\ \mathrm{J\,mol^{-1}}$.

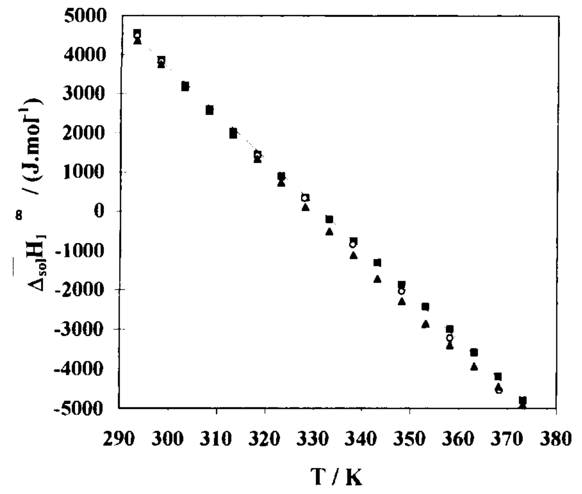

Fig. 5. Values of $\Delta_{sol}h_l^\infty(t)$ versus temperature T for the {H_2O–NaCl} system. (▲) Nazarov et al., (○) Criss and Cobble, (■) Clarke and Glew, (—) Eq. (26).

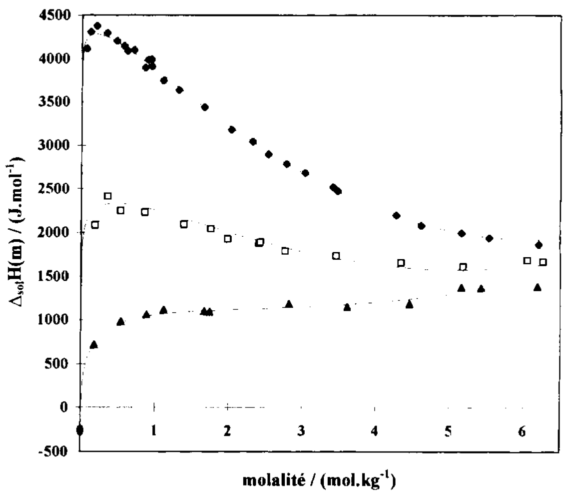

Fig. 6. Variations of $\Delta_{sol}H(m)$ versus composition for the {H_2O–NaCl} system. (◆) T=298.15, (□) T=317.45, (▲) T=332.35, (—) $\Delta_{sol}H(m)$ calculated.

This value may be compared with those of Clarke and Glew [7] 3858 J mol^{-1}, Parker [8] 3883 J mol^{-1}. Criss and Cobble [5] 3824 J mol^{-1}, Sanahuja and Cesari [9] 3867 J mol^{-1}, and Nazarov and Charykov [6] 3750 J mol^{-1}.

Parameters A, B and C are also well represented by a linear relationship with temperature:

$$A(T) = A_2 + B_2(T/K),$$
$$B(T) = A_3 + B_3(T/K),$$
$$C(T) = A_4 + B_4(T/K),$$

where

$$A_2 = 7435.77, \quad B_2 = -21.10,$$
$$A_3 = -4668.91, \quad B_3 = 17.17,$$
$$A_4 = -520.41, \quad B_4 = 1.457.$$

We have calculated the isothermal variations of $\Delta_{sol}H(m)$ versus composition, using Eq. (24) and the eight constants $A_1, A_2, A_3, \ldots, B_1, \ldots, B_4$. Representations are given in Fig. 6. We observe that this simulation leads to a good representation of the molar enthalpies of dissolution. The average relative error is about 2%.The variations of the Pitzer parameters with temperature can be found using previous coefficients given by calorimetric measurements.

We have from relation Eq. (25):

$$\beta^{(0)\mathrm{L}} = \left(\frac{\partial\beta^{(0)}}{\partial T}\right)_P = \frac{A_2}{2R}\frac{1}{T^2} + \frac{B_2}{2R}\frac{1}{T},$$
$$\beta^{(1)\mathrm{L}} = \left(\frac{\partial\beta^{(1)}}{\partial T}\right)_P = \frac{A_3}{R}\frac{1}{T^2} + \frac{B_3}{R}\frac{1}{T},$$
$$C^{\mathrm{L}} = \left(\frac{\partial C^{\phi}}{\partial T}\right)_P = \frac{A_4}{R}\frac{1}{T^2} + \frac{B_4}{R}\frac{1}{T}.$$

Integration of expressions in Eq. (27) between T_0 and T leads to an analytical representation of $\beta^{(0)}(T)$, ${}^{(1)}(T)$ and $C^{\phi}(T)$:

$$\beta^{(0)}(T) = \beta^{(0)}(T_0) - \frac{A_2}{2R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{B_2}{2R}\ln\left(\frac{T}{T_0}\right),$$
$$\beta^{(1)}(T) = \beta^{(1)}(T_0) - \frac{A_3}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{B_3}{R}\ln\left(\frac{T}{T_0}\right),$$
$$C^{\phi}(T) = C^{\phi}(T_0) - \frac{A_4}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{B_4}{R}\ln\left(\frac{T}{T_0}\right).$$

It appears easy to determine the constants $\beta^{(0)}(T_0)$, ${}^{(1)}(T_0)$ and $C^{\phi}(T_0)$ from experimental values at 25°C, which are usually accurate and numerous.

We have used the molal osmotic coefficient value proposed by Clarke and Glew [7], at 25°C, to determine these constants.

Table 4
Comparison between experimental activity of water a_w (exp.), and those calculated a_w (calc.) and the corresponding relative deviation for m=4.086 mol kg^{-1}

T/K	a_w (exp.)	a_w (calc.)	$\lvert\Delta a_w/a_w\rvert$
294.42	0.8465	0.8481	0.1878
299.30	0.8474	0.8475	0.143
304.10	0.8472	0.8471	0.0158
308.94	0.8461	0.8467	0.0716
313.81	0.8455	0.8464	0.1111
318.67	0.8454	0.8463	0.1020
323.54	0.8452	0.8462	0.1150
328.41	0.8454	0.8462	0.0902
333.28	0.8456	0.8462	0.0746
338.25	0.8457	0.8464	0.0800
343.09	0.8459	0.8466	0.0815
348.07	0.8464	0.8469	0.0565
352.94	0.8470	0.8472	0.0266
357.81	0.8476	0.8476	0.0041
362.79	0.8483	0.8481	0.0220
367.93	0.8482	0.8487	0.0555

We have obtained:

$$\beta^0(T_0) = 0.0791, \quad \beta^1(T_0) = 0.2628,$$
$$C^\phi(T_0) = 0.0007.$$

The authenticity of this representation is verified by calculating the activity of water using Eqs. (13) and (23), which were then compared to our experimental values [10]: a nonisothermal static apparatus allowing the measurements of vapour pressures has been constructed. We have obtained the activity of water of the binary system {H_2O–NaCl} for temperatures from 293.15 to 363.15 K and for salt molalities from 1 to 5.5 mol kg^{-1} of water corresponding to 133 values.

Calculated values of water activity using the latter coefficients are very close to our experimental values (the average relative deviation is of about 0.1%). As an example, Table 4 presents experimental and calculated values of activity of water for molality m=4.086 mol kg^{-1}.

5. Conclusion

The calorimetric measurements allow the determination of the molar dissolution enthalpy at infinite dilution of NaCl in water between 25°C and 100°C.

The calorimetric measurements, combined with available data at 25°C, allow a complete thermodynamical treatment of the {N_2O–NaCl} system with Pitzer's model. Particularly, it seems possible to represent simultaneously liquid–vapour and calorimetric data using the same set of parameters.

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