

Use of Pitzer's model to calculate thermodynamic properties of aqueous electrolyte solutions of $\text{Na}_2\text{SO}_4 + \text{NaCl}$ between 273.15 and 373.15 K

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Abstract

Pitzer's model has been used to calculate various thermodynamic properties of $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$ system. A methodology taking into account enthalpy and solubility data has been proposed. This leads to the proposal of a unique set of parameters allowing simultaneous representation of dissolution enthalpies, activity coefficients and solubility data in binary and ternary systems. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous solutions of electrolytes; Pitzer's model; Enthalpy; Activity coefficient; Solid–liquid equilibria; $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$ system

1. Introduction

Phase equilibria and heat effect data in electrolyte solutions are of crucial importance in numerous industrial processes such as crystallisation, distillation, etc.

Generally, the required data concern complex mixtures (several electrolytes + water) in a large temperature range. Exhaustive experimental determination of such systems is impossible. Consequently, it is necessary to use an adequate thermodynamic model to calculate the properties of these systems. While most of them are appropriate for describing activities of single electrolyte solutions at 298.15 K, their extensions to mixed electrolytes, higher temperatures and to calculate excess enthalpy simultaneously are often unreliable, especially in the case of weak electrolytes.

Recently, Lu et al. [1] extended Lu and Maurer's model [2] to predict activity coefficients and enthalpy simultaneously. Thomsen et al. [3] presented a modification of the Extended UNIQUAC

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activity coefficient model by Sander [4] capable of describing solid–liquid equilibria and heat of mixing.

Pitzer's model is also capable of accurately predicting activity and enthalpy provided that the variation of the parameters with temperature is known. This variation has been determined for some electrolytes [5–7]. Without this information, Zemaitis et al. [8] suggested to admit the parameters to be constant and to consider the influence of temperature only on the Debye–Hückel term, A_ϕ . This gives satisfactory results for water activities but very bad results for solubilities and enthalpies at medium and high ionic strengths.

Pitzer's binary and ternary interaction parameters are fitted with data relative to binary and ternary systems. These parameters are usually adjusted in a large temperature range using several sources of experimental data such as electrochemical, calorimetric, solubility and liquid–vapour equilibrium measurements to take into account the strong influence of temperature.

In this paper, we present a methodology for the determination of Pitzer's binary and ternary parameters. The influence of temperature is taken into account using only mixing enthalpies and some data available at 298.15 K. This methodology is illustrated on the system NaCl–Na₂SO₄–H₂O.

Binary and ternary interaction parameters of Pitzer's model were respectively determined using dissolution enthalpies of solid NaCl and Na₂SO₄ in pure water and solubility data at 298.15 K in the ternary system.

The solubility product of halite (NaCl), thenardite (Na₂SO₄) and mirabilite (Na₂SO₄ · 10H₂O) were calculated from the solubility data in the NaCl–H₂O and Na₂SO₄–H₂O binary systems applying Pitzer's model with our parameters from 273.15 to 373.15 K.

Finally, we tested successfully our parameters by predicting the solubilities in the NaCl–Na₂SO₄–H₂O system from 273.15 to 373.15 K.

2. Theoretical aspects

Thermodynamic properties like activity, activity coefficients and enthalpies are derived from appropriate derivatives of the excess Gibbs energy. The chemical potential, μ_i , of an ionic species i can be expressed according to the following expression:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

in which μ_i^0 is the chemical potential of the solute in the hypothetical molal ideal solution (unsymmetrical convention). The activity, a_i , is related to the excess Gibbs energy as follows:

$$a_i = \gamma_i \cdot m_i$$

and:

$$RT \ln \gamma_i = \mu_i^E = \left(\frac{\partial \hat{G}^E}{\partial m_i} \right)_{T, P, m_j \neq i} \quad (1)$$

where γ_i is the activity coefficient of species i in the molality scale, m_i the molality of species i , μ_i^E is the partial molar excess Gibbs energy of specie i and \hat{G}^E is the excess Gibbs energy of the electrolyte solution containing 1 kg of water.

The chemical potential of the solvent (pure water) is given by the following expression:

$$\mu_w = \mu_w^0 + RT \ln a_w$$

where μ_w^0 is the chemical potential of pure liquid water (unsymmetrical convention) and a_w is the activity of water.

The activity of water, a_w , is usually expressed by the osmotic coefficient, ϕ :

$$\ln(a_w) = \ln(a_w^{\text{id}}) \cdot \phi = -\frac{M_w}{1000} \cdot \left(\sum_i m_i \right) \cdot \phi$$

in which a_w^{id} is the activity of water in the ideal solution, M_w is the molecular weight of water (18.0153 g mol⁻¹) and $\sum_i m_i$ is the sum of the molalities of all the solute species.

The osmotic coefficient is related to the excess Gibbs energy by the following relationship:

$$\phi - 1 = -\frac{1}{R \cdot T} \cdot \frac{1}{\sum_i m_i} \cdot \left[\hat{G}^E - \sum_i m_i \cdot \left(\frac{\partial \hat{G}^E}{\partial m_i} \right)_{T, P, m_j \neq i} \right] \quad (2)$$

Heat effect data (dissolution, dilution, mixing...) are related to the excess enthalpy. \hat{L} , the excess enthalpy of a solution containing 1 kg of water can be calculated from the excess Gibbs energy by:

$$\hat{L} = -R \cdot T^2 \cdot \left(\frac{\partial \left(\frac{\hat{G}^E}{R \cdot T} \right)}{\partial T} \right)_{P, m_i} \quad (3)$$

Pitzer [6] has proposed a general equation for the excess Gibbs energy of aqueous electrolyte solutions. The general expressions of \hat{G}^E , of activity coefficients of anions and cations and of osmotic coefficients are given in Appendix A.

3. Binary systems: NaCl–H₂O and Na₂SO₄–H₂O

3.1. Dissolution enthalpies

The dissolution enthalpy of sodium chloride and sodium sulfate in pure water was measured up to saturation at 297.55 K, 317.45 K and 332.35 K using a SETARAM C80D differential calorimeter [9–11]. The molar dissolution enthalpy, $\Delta_{\text{sol}} H(m)$, is the variation of enthalpy accompanying the dissolution of 1 mole of salt in enough water to make a solution of molality m . It is related to the excess enthalpy, \hat{L} and to the molar dissolution enthalpy at infinite dilution, $\Delta_{\text{sol}} H^\infty$, by the following relationship [9]:

$$\Delta_{\text{sol}} H(m) = \frac{\hat{L}(m)}{m} + \overline{\Delta_{\text{sol}} H^\infty} = \phi L + \Delta_{\text{sol}} H^\infty \quad (4)$$

It can be calculated using Pitzer's expression for \hat{G}^E given in Appendix A (Eq. (A1)) and from Eq. (3). In the case of a 1–1, a 1–2 or a 2–1 single electrolyte, the following simplified expression is obtained:

$$\Delta_{\text{sol}}H = \Delta_{\text{sol}}H^\infty + \frac{A_H}{b} \cdot \frac{z_c \cdot z_a}{2} \cdot (\nu_c + \nu_a) \cdot \ln(1 + b \cdot \sqrt{I}) - 2 \cdot \nu_c \cdot \nu_a \cdot m \cdot \left[R \cdot T^2 \frac{\partial B_{\text{ca}}}{\partial T} + \nu_c \cdot z_c \cdot m \cdot R \cdot T^2 \frac{\partial C_{\text{ca}}}{\partial T} \right] \quad (5)$$

with $A_H = 4 \cdot R \cdot T^2 \cdot \frac{\partial A_\phi}{\partial T}$. In the last equation, $\frac{\partial B_{\text{ca}}}{\partial T}$, $\frac{\partial C_{\text{ca}}}{\partial T}$ represent the derivatives of binary interaction parameter defined in Appendix A (Eqs. (A4) and (A5)). Their values depend on the temperature function considered for expressing the Pitzer's parameters, β_{ca}^0 , β_{ca}^1 , C_{ca}^ϕ .

The apparent molar enthalpy $^\phi L$ is usually used to determine temperature dependence of parameters. Moreover, dissolution enthalpy data allowed us to propose values of molar dissolution enthalpy at infinite dilution [9,11], which are difficult to measure experimentally. In our calculation, $\Delta_{\text{sol}}H^\infty$, $R \cdot T^2 \frac{\partial \beta_{\text{ca}}^0}{\partial T}$, $R \cdot T^2 \frac{\partial \beta_{\text{ca}}^1}{\partial T}$ and $R \cdot T^2 \frac{\partial C_{\text{ca}}^\phi}{\partial T}$ were considered as adjustable parameters at each temperature. We found them to be linear with T between 297.55 K and 332.35 K [9,11] and, by integration, the following function was obtained:

$$\text{parameter} = a_H + b_H \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right) + c_H \cdot \ln \left(\frac{T}{T_0} \right) \quad (6)$$

in which T_0 is the reference temperature (298.15 K) and 'parameter' is respectively equal to β_{ca}^0 , β_{ca}^1 and C_{ca}^ϕ ; a_H is the value of the parameter at 298.15 K which can be found in the literature [6] or can be fitted with osmotic coefficient or e.m.f data at 298.15 K. b_H and c_H are determined by fitting enthalpy data as explained above.

Values of a_H , b_H and c_H obtained in the case of the NaCl–H₂O and Na₂SO₄–H₂O system are presented in Table 1. Eq. (6) used in this work are simpler than the complex and empirical functions proposed by Pitzer [6]. However, in our case, they are only applicable from 273.15 K to 373.15 K.

With this set of binary parameters, Mean Relative Deviations (MRD) between our experimental and calculated values of dissolution enthalpies of NaCl and Na₂SO₄ in water are respectively of 1.98 and 1.69%. This good agreement is illustrated in Fig. 1a and b.

Table 1

Pitzer's parameters (273.15 < T < 373.15 K), parameter = $a_H + b_H \cdot (1/T - 1/T_0) + c_H \cdot \ln(T/T_0)$ with $T_0 = 298.15$ K

Parameter	a_H	b_H	c_H
β_{NaCl}^0	0.0765	−440.1328	−1.248891
β_{NaCl}^1	0.2664	518.3828	1.911939
C_{NaCl}^ϕ	0.00127	61.07728	0.171046
$\beta_{\text{Na}_2\text{SO}_4}^0$	0.018675	−790.0071	−2.071428
$\beta_{\text{Na}_2\text{SO}_4}^1$	1.0995	−4870.511	−13.11122
$C_{\text{Na}_2\text{SO}_4}^\phi$	0.005549	121.5825	0.305269
$\theta_{\text{Cl},\text{SO}_4}$	0.068166	0	0
$\psi_{\text{Na,Cl,SO}_4}$	−0.009454	0	0

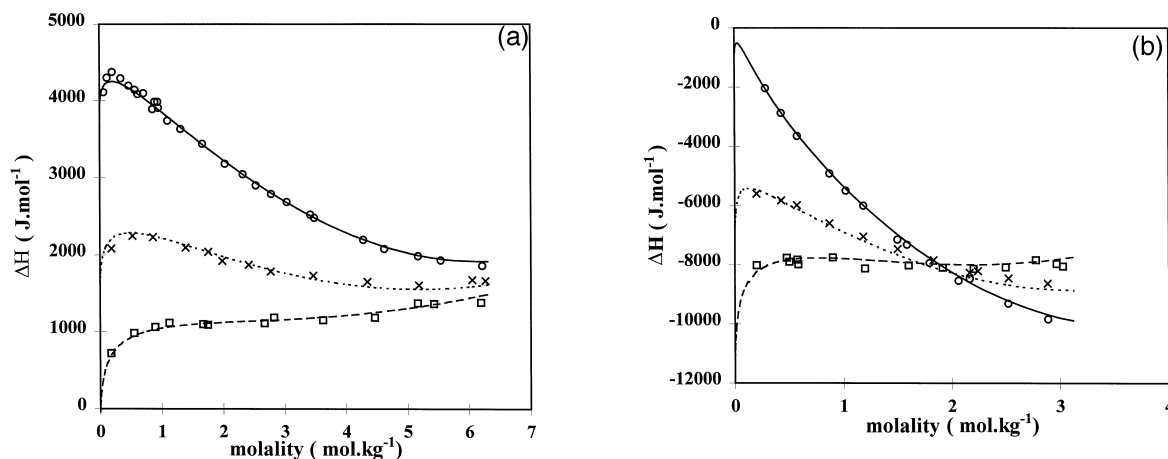


Fig. 1. (a) Molar dissolution enthalpy of sodium chloride in water vs. composition. \circ Experimental data at 297.75 K [9]; — model at 297.75 K; \times experimental data at 317.45 K [9]; ... model at 317.45 K; \square experimental data at 332.35 K [9]; - - - model at 332.35 K. (b) Molar dissolution enthalpy of sodium sulfate in water vs. composition. \circ Experimental data at 297.55 K [10], — model at 297.55 K; \times experimental data at 317.45 K [10]; ... model at 317.45 K; \square experimental data at 332.35 K [11], - - - model at 332.35 K.

3.2. Activity coefficients

The activity coefficients of the cation of the anion and the osmotic coefficient for a single electrolyte in water can be calculated from the general expressions Eqs. (A2), (A3) and (A4) with our set of parameters presented in Table 1. Mean activity coefficients of sodium chloride in water at 298.15 and 373.15 K and sodium sulfate in water at 298.15 K and 353.15 K [8] can be restituted with a good accuracy (M.R.D. of 0.23 and of 1.29%).

Extrapolations toward higher temperatures than 373 K can be made successfully up to 423.15 K as it is illustrated in the Fig. 2a and b which represent the mean activity coefficients of $\text{NaCl-H}_2\text{O}$ at 403.15, 423.15 and 443.15 K [12] and $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ systems at 398.15, 423.15 and 448.15 K [13,14].

3.3. Solubility products of solid species

When a salt precipitates from an aqueous solution, the molalities of ionic species in the liquid phase are determined from the corresponding solubility product, K_s .

For the halite (NaCl):

$$K_{s_{\text{Halite}}} = \gamma_{\text{Na}^+} \cdot m_{\text{Na}^+} \cdot \gamma_{\text{Cl}^-} \cdot m_{\text{Cl}^-}$$

For the thenardite (Na_2SO_4):

$$K_{s_{\text{Thenardite}}} = \gamma_{\text{Na}^+}^2 \cdot m_{\text{Na}^+}^2 \cdot \gamma_{\text{SO}_4^{2-}} \cdot m_{\text{SO}_4^{2-}}$$

For the mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$):

$$K_{s_{\text{Mirabilite}}} = \gamma_{\text{Na}^+}^2 \cdot m_{\text{Na}^+}^2 \cdot \gamma_{\text{SO}_4^{2-}} \cdot m_{\text{SO}_4^{2-}} \cdot a_{\text{H}_2\text{O}}^{10}$$

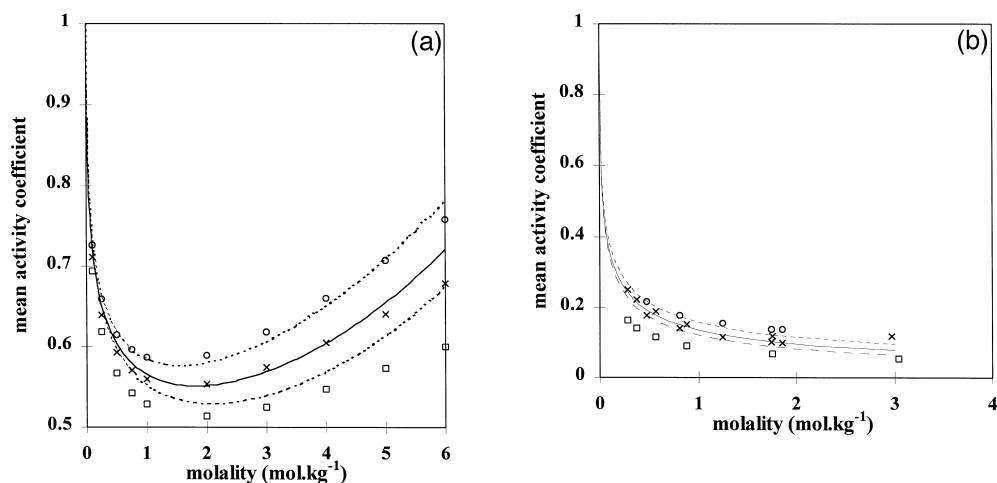


Fig. 2. (a) Mean activity coefficient of sodium chloride in water vs. composition. ○ Experimental data at 403.15 K [12]; ... model at 403.15 K; x experimental data at 423.15 K [12]; — model at 423.15 K; □ experimental data at 443.15 K [12]; - - - model at 443.15 K. (b) Mean activity coefficient of sodium sulfate in water vs. composition. ○ Experimental data at 398.15 K [13]; ... model at 398.15 K; x experimental data at 423.15 K [13,14]; — model at 423.15 K; □ experimental data at 448.15 K [14]; - - - model at 448.15 K.

The solubility product is related to the standard Gibbs energy ($\Delta_r G^0$) of dissociation by the following formula:

$$\Delta_r G^0 = -R \cdot T \cdot \ln(K_s)$$

The standard Gibbs energy ($\Delta_r G^0$) of dissociation of halite (NaCl), thenardite (Na₂SO₄) and mirabilite (Na₂SO₄ · 10H₂O) were calculated from the solubility data in the NaCl–H₂O [15] and Na₂SO₄–H₂O binary systems [15–17] applying Pitzer's model with parameters taken from Table 1. Values obtained were represented by the following expression:

$$\Delta_r G^0 = a_G - b_G \cdot T + c_G \cdot \left((T - T_0) - T \cdot \ln \left(\frac{T}{T_0} \right) \right) \quad (6')$$

with a_G , b_G and c_G given in Table 2 for each solid species.

Values at 298.15 K are reported in Table 3 and are compared with those proposed by NBS [18] and USGS (U.S Geological Survey) [19] Tables. A very good agreement is obtained in the case of halite for which RMD is less than 1%. For mirabilite and thenardite, the difference between NBS and USGS

Table 2

Standard Gibbs energies ($\Delta_r G^0$) of dissociation in kJ mol⁻¹ (273.15 < T < 373.15 K), $\Delta_r G^0 = a_G - b_G \cdot ((T - T_0) - T \cdot \ln(T/T_0))$ with $T_0 = 298.15$ K

Solid species	a_G	b_G	c_G
Halite (NaCl)	3392.79	41.7014	-74.1643
Mirabilite (Na ₂ SO ₄ · 10H ₂ O)	80875.3	247.852	11.3598
Thenardite (Na ₂ SO ₄)	-303.239	-6.61418	-357.626

Table 3

Standard Gibbs energies ($\Delta_r G^0$) of dissociation at 298.15 K. Comparison between our calculated, NBS and USGS values

Solid species	Halite (NaCl)	Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)	Thenardite (Na_2SO_4)
Our work (kJ mol^{-1})	−9.036	+6.967	+1.664
NBS tables (kJ mol^{-1})	−8.995	+7.220	+1.820
(Cal–NBS)/NBS	−0.5%	−3.5%	−8.6%
USGS tables (kJ mol^{-1})	−8.958	+6.700	+1.555
(Cal–USGS)/USGS	−0.9%	+4.0%	+7.0%

values is significative (respectively 7 and 15% of RMD) and, by comparison, our values are situated just between those of USGS and NBS Tables.

With these parameters, the solubility data of NaCl [15] in water and of Na_2SO_4 [15–17] from 273.15 K to 373.15 K in water are very well-represented, with an accuracy of 0.1 and 1.1%, respectively.

4. Ternary system: NaCl – Na_2SO_4 – H_2O

The activity coefficients of the Na^+ cation, of the Cl^- and SO_4^{2-} anions and the osmotic coefficient for NaCl – Na_2SO_4 mixtures in water are related to the binary and ternary Pitzer's parameters, according to Eqs. (A2) and (A3). In these equations, binary parameters previously determined are used together with parameters, $\theta_{\text{Cl}^-, \text{SO}_4^{2-}}$ and $\Psi_{\text{Na}^+, \text{Cl}^-, \text{SO}_4^{2-}}$, which must be fitted to experimental data. In Pitzer's model [6], terms relative to SO_4^{2-} and Cl^- interactions, $(\Phi_{\text{Cl}^-, \text{SO}_4^{2-}}, \Phi'_{\text{Cl}^-, \text{SO}_4^{2-}}, \Phi^\phi_{\text{Cl}^-, \text{SO}_4^{2-}})$ are expressed with unsymmetrical mixing functions, ${}^E\theta(I)$ and its derivative with respect the ionic strength, ${}^E\theta'(I)$, according to the following expressions:

$$\Phi_{\text{Cl}^-, \text{SO}_4^{2-}} = \theta_{\text{Cl}^-, \text{SO}_4^{2-}} + {}^E\theta(I)$$

$$\Phi'_{\text{Cl}^-, \text{SO}_4^{2-}} = {}^E\theta'(I)$$

$$\text{and } \Phi^\phi_{\text{Cl}^-, \text{SO}_4^{2-}} = \theta_{\text{Cl}^-, \text{SO}_4^{2-}} + {}^E\theta(I) + I {}^E\theta'(I)$$

The unsymmetrical mixing functions depend only on the electrolyte pair type and ionic strength. Integrals defining these terms are given by Pitzer [6].

The dissolution enthalpy of sodium chloride and sodium sulfate mixtures was measured up to saturation at 297.75 K, 317.45 K and 332.35 K using a SETARAM C80D differential calorimeter [20]. These data showed little influence of temperature on the Pitzer's parameters $\theta_{\text{Cl}^-, \text{SO}_4^{2-}}$ and $\Psi_{\text{Na}^+, \text{Cl}^-, \text{SO}_4^{2-}}$ in the temperature range considered. Then, they were taken constant between 273.15 and 373.15 K and fitted at 298.15 K using solubility data in the ternary NaCl – Na_2SO_4 – H_2O system [15].

4.1. Fitting of the ternary parameters using solubility data

In mixed electrolyte solutions saturated with respect to salt MX, the solubility product of the salt is equal to that of the pure MX saturated solution at the same temperature.

At 298.15 K, three solid species (halite, mirabilite and thenardite) exist in three distinct concentration domains.

$\theta_{\text{Cl}^-, \text{SO}_4^{2-}}$ and $\Psi_{\text{Na}^+, \text{Cl}^-, \text{SO}_4^{2-}}$ ternary parameters were fitted by minimizing the following objective function, F_{obj} :

$$F_{\text{obj}} = F_1 + F_2 + F_3$$

with:

$$F_1 = \frac{1}{N_{\text{exp}_1}} \cdot \sum_{\text{exp}_1} \left[\frac{\ln(\gamma_{\text{Na}^+} \cdot m_{\text{Na}^+} \cdot \gamma_{\text{Cl}^-} \cdot m_{\text{Cl}^-}) - \ln(\text{Ks}_{\text{Halite}}(\text{To}))}{\ln(\text{Ks}_{\text{Halite}}(\text{To}))} \right]^2$$

$$F_2 = \frac{1}{N_{\text{exp}_2}} \cdot \sum_{\text{exp}_2} \left[\frac{\ln(\gamma_{\text{Na}^+}^2 \cdot m_{\text{Na}^+}^2 \cdot \gamma_{\text{SO}_4^{2-}} \cdot m_{\text{SO}_4^{2-}}) - \ln(\text{Ks}_{\text{Thenardite}}(\text{To}))}{\ln(\text{Ks}_{\text{Thenardite}}(\text{To}))} \right]^2$$

$$F_3 = \frac{1}{N_{\text{exp}_3}} \cdot \sum_{\text{exp}_3} \left[\frac{\ln(\gamma_{\text{Na}^+}^2 \cdot m_{\text{Na}^+}^2 \cdot \gamma_{\text{SO}_4^{2-}} \cdot m_{\text{SO}_4^{2-}} \cdot a_{\text{H}_2\text{O}}^{10}) - \ln(\text{Ks}_{\text{Mirabilite}}(\text{To}))}{\ln(\text{Ks}_{\text{Mirabilite}}(\text{To}))} \right]^2$$

in which exp_i is relative to experimental solubility data in halite-solution ($i = 1$), thenardite-solution ($i = 2$) and mirabilite-solution ($i = 3$) coexistence domains. N_{exp_i} is the number of data of exp_i . The ternary parameters obtained are presented in Table 1.

Deviations between experimental [15,21] and calculated values of solubilities are presented in Table 4. The absolute mean deviation is defined as follows:

$$\text{A.M.D.} = \frac{1}{N} \cdot \sum_{\text{exp}} |m_{\text{Na}_2\text{SO}_4}^{\text{calc}} - m_{\text{Na}_2\text{SO}_4}^{\text{exp}}|$$

in which $m_{\text{Na}_2\text{SO}_4}$ is the molality of Na_2SO_4 when the solid precipitates.

Table 4

Comparison between experimental and calculated values of solubilities in the NaCl – Na_2SO_4 – H_2O system at different temperatures

T (K)	N	A.M.D.	Ref.
273.15	5	0.021	[15,21]
283.15	12	0.021	[15]
288.15	11	0.033	[15]
293.15	13	0.028	[15,21]
298.15	41	0.050	[15]
303.15	23	0.079	[15]
311.15	20	0.048	[15]
323.15	7	0.032	[15]
348.15	7	0.057	[15]
373.15	7	0.063	[15]
overall	146	0.048	

$$\text{A.M.D.} = \frac{1}{N} \cdot \sum_{\text{exp}} |m_{\text{Na}_2\text{SO}_4}^{\text{calc}} - m_{\text{Na}_2\text{SO}_4}^{\text{exp}}|$$

$m_{\text{Na}_2\text{SO}_4}$ is the molality of Na_2SO_4 when the solid precipitates.

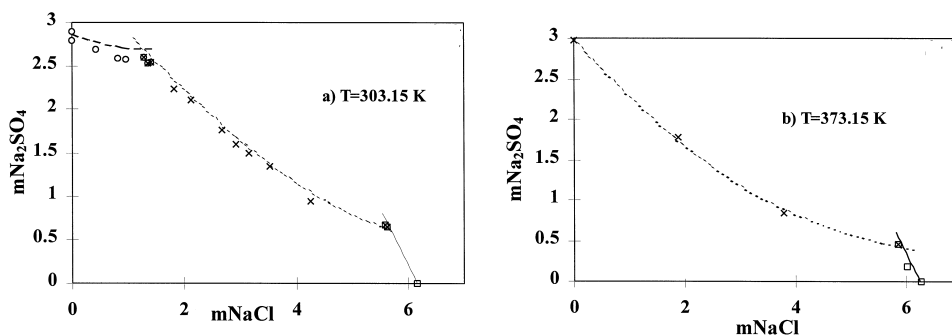


Fig. 3. (a) Solubility in the NaCl–Na₂SO₄–H₂O ternary system at 303.15 K. ○ Mirabilite (experimental data [15]); - - - mirabilite (model); x thenardite (experimental data [15]); ... thenardite (model); □ halite (experimental data [15]); — halite (model). (b) Solubility in the NaCl–Na₂SO₄–H₂O ternary system at 373.15 K. x Thenardite (experimental data [15]); ... thenardite; □ halite (experimental data [15]); — halite (model).

With our set of Pitzer's parameters and solubility products (Tables 1 and 2), we were able to predict solubilities in the ternary system NaCl–Na₂SO₄–H₂O from 273.15 to 373.15 K. We obtained an overall A.M.D. of 0.048. The good agreement between experimental and calculated solubility data is illustrated in Fig. 3. Maximal deviations are obtained for mirabilite precipitation at $T = 303.15$ K (Fig. 3a), in this case, other experimental data [22] could be used as it was previously reported by Moller [23].

Pitzer [24] has recommended omitting the unsymmetrical mixing terms in all but the most unsymmetrical mixtures, therefore, we experienced the same approach without considering these terms. The results were not as good as above, especially at temperatures below 298.15 K.

This can be solved by fitting the ternary parameters $\theta_{\text{Cl}^-, \text{SO}_4^{2-}}$ and $\Psi_{\text{Na}^+, \text{Cl}^-, \text{SO}_4^{2-}}$ at each temperature from 273.15 to 373.15 K.

These mixing terms are very helpful for the modelisation of 2–1 unsymmetrical mixtures, although not necessary. Harvie and Weare [25] also found that the inclusion of unsymmetrical mixing terms significantly improves the modelisation of electrolyte mixtures.

5. Conclusion

Enthalpy of mixing data at several temperatures in aqueous electrolyte solutions allow the determination of the variation of binary and ternary Pitzer's parameters with respect to temperature.

The methodology used allows to predict various thermodynamic properties and solid–liquid equilibria of aqueous mixed electrolyte systems from 273.15 to 373.15 K.

Prediction of enthalpy data is a rigorous test of the temperature dependence of parameters of excess Gibbs energy models.

6. Nomenclature

a_i	activity of species i
A_H	Debye–Hückel slope for enthalpy

A_ϕ	Debye–Hückel term associated with Pitzer's model for the osmotic coefficient
b	universal parameter with the value $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$
cal	calculated
C^ϕ	adjustable binary parameter for Pitzer's model
\hat{G}_E	excess Gibbs energy of an electrolyte solution containing 1 kg of water
I	ionic strength in the molality scale
K_{s_i}	solubility product of solid species i
\hat{L}	excess enthalpy of a solution containing 1 kg of water
m_i	molality of solute species i in an electrolyte solution
M_w	molecular weight of water ($18.0153 \text{ g.mol}^{-1}$)
P	pressure, Pa
R	Gas constant ($8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	temperature, K
To	reference temperature (298.15 K)
z_i	number of charges on the ionic species i
<i>Greek letters</i>	
α	equal to $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ for 1–1, 1–2 and 2–1 electrolytes
β^0	adjustable binary parameter for Pitzer's model
β^1	adjustable binary parameter for Pitzer's model
γ_i	activity coefficient of specie i in the molality scale
$\Delta_r G_i^0$	standard Gibbs energy of dissociation of solid species i
$\Delta_{\text{sol}} H$	molar dissolution enthalpy
$\Delta_{\text{sol}} H^\infty$	molar dissolution enthalpy at infinite dilution
$\theta_{i,j}$	adjustable parameter accounting for interactions between ions of like sign
μ_i	chemical potential of species i
ν_i	stoichiometric number of ionic species i
ϕ	osmotic coefficient of the solution
$\psi_{i,j,k}$	adjustable ternary parameter
<i>Subscripts</i>	
a	anion
c	cation
i	species i
j	species j
k	species k
w	water

Appendix A. Equations of Pitzer's model

Pitzer [6] has proposed a general equation for the excess Gibbs energy of aqueous electrolyte solutions. In this approach, the excess Gibbs energy of the solution can be considered as the sum of the Debye–Hückel term which expresses the effect of long-range interactions between ions and of a second term accounting for the short-range interactions between solute species. In the case of a

multicomponent system, the general expression for cations and anions activity coefficients and osmotic coefficient is as follows:

$$\frac{\hat{G}^E}{RT} = \left[\begin{aligned} & f(I) + 2 \sum_c \sum_a m_c m_a \left(B_{ca} + \left(\sum_c m_c |z_c| \right) C_{ca} \right) \\ & + \sum_c \sum_{c'} m_c m_{c'} \left(\Phi_{cc'} + \frac{\sum_a m_a \Psi_{cc'a}}{2} \right) \\ & + \sum_a \sum_{a'} m_a m_{a'} \left(\Phi_{aa'} + \frac{\sum_c m_c \Psi_{caa'}}{2} \right) \end{aligned} \right] \quad (A1)$$

with $f(I) = -A_\phi \left(\frac{4I}{b} \right) [\ln(1 + bI^{1/2})]$;

$$\begin{aligned} \ln \gamma_C = & z_C^2 F + \sum_a m_a (2B_{Ca} + ZC_{Ca}) + \sum_c m_c \left(2\Phi_{Cc} + \sum_a m_a \Psi_{Cca} \right) \\ & + \sum_a \sum_{a'} m_a m_{a'} \Psi_{aa'C} + |z_C| \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (A2)$$

$$\begin{aligned} \ln \gamma_A = & z_A^2 F + \sum_c m_c (2B_{cA} + ZC_{cA}) + \sum_a m_a \left(2\Phi_{Aa} + \sum_c m_c \Psi_{Ca\hat{A}} \right) \\ & + \sum_c \sum_{c'} m_c m_{c'} \Psi_{cc'A} + |z_A| \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (A3)$$

with:

$$\begin{aligned} F = & -A_\phi \left(\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2I^{1/2}) \right) + \sum_c \sum_a m_c m_a B'_{ca} \\ & + \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_a \sum_{a'} m_a m_{a'} \Phi_{aa'} \\ C_{CA} = & C_{CA}^\phi / 2 |z_C z_A|^{1/2} \end{aligned} \quad (A4)$$

$$Z = \sum_c |z_c| \cdot m_c + \sum_a |z_a| \cdot m_a;$$

$$\begin{aligned} B_{CA}^\phi &= \beta_{CA}^{(0)} + \beta_{CA}^{(1)} e^{-\alpha_{CA}\sqrt{I}} \\ B_{CA} &= \beta_{CA}^{(0)} + \beta_{CA}^{(1)} g(\alpha_{CA}\sqrt{I}) \\ B'_{CA} &= \beta_{CA}^{(1)} g'(\alpha_{CA}\sqrt{I})/I \end{aligned} \quad (A5)$$

The functions, g and g' , are defined by the equations:

$$\begin{aligned} g(x) &= 2(1 - (1+x)e^{-x})/x^2 \\ g'(x) &= -2 \left(1 - \left(1+x + \frac{x^2}{2} \right) e^{-x} \right) / x^2 \end{aligned}$$

with $x = \alpha\sqrt{I}$, $\alpha = 2$.

$$(\phi - 1) = \frac{2}{\sum_i m_i} \left\{ \begin{aligned} & - \frac{A_\phi I^{3/2}}{1 + 1.2 I^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \\ & + \sum_{c < c'} \sum m_c m_{c'} \left(\Phi_{cc'}^\phi + \sum_a m_a \Psi_{cc'a} \right) \\ & + \sum_{a < a'} \sum m_a m_{a'} \left(\Phi_{aa'}^\phi + \sum_c m_c \Psi_{aa'c} \right) \end{aligned} \right\} \quad (\text{A6})$$

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