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# Thermodynamics of crystallization of sodium sulfate decahydrate in $H_2O$–NaCl–$Na_2SO_4$: application to $Na_2SO_4\cdot10H_2O$-based latent heat storage materials

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## Abstract

In this paper, we present a methodology for the prediction of the crystallization enthalpy of mirabilite ($Na_2SO_4\cdot10H_2O$) from supersaturated $H_2O$–NaCl–$Na_2SO_4$ solutions. Required thermodynamic properties of $H_2O$–NaCl–$Na_2SO_4$ such as dissolution enthalpies, phase equilibria and heat of hydration of $Na_2SO_4$ are represented or determined using Pitzer's ion-interaction model. Measurements of crystallization enthalpies at various temperatures and concentrations were made in a SETARAM C80D calorimeter by mixing $H_2O$–$Na_2SO_4$ and $H_2O$–NaCl–$Na_2SO_4$ solutions supersaturated relatively to mirabilite with a *seed crystal* of $Na_2SO_4\cdot10H_2O$ once the thermal equilibrium was reached.

Good agreement was obtained between experimental and predicted values of crystallization enthalpies. Furthermore, we have studied the influence of NaCl used as an additive regarding the heat storage capacity of supersaturated $H_2O$–$Na_2SO_4$ solutions.

*Keywords:* Pitzer's model; Supersaturated solutions; Sodium sulfate decahydrate; Crystallization; Heat storage; Calorimetry

## Nomenclature

| | |
|---|---|
| $a_w$ | activity of water |
| $A_L$ | Debye–Hückel slope for enthalpy |
| $A_\phi$ | Debye–Hückel term associated with Pitzer's model for the osmotic coefficient |
| $b$ | universal parameter with the value 1.2 $kg^{1/2}$ $mol^{-1/2}$ |
| cal | calculated |
| $C^\phi$ | adjustable binary parameter for Pitzer's model |
| exp. | experimental |
| $\hat{G}^E$ | excess Gibbs energy of an electrolyte solution containing 1 kg of water |
| $h_i^*$ | molar enthalpy of species $i$ |
| $I$ | ionic strength in the molality scale |
| $Ks_i$ | solubility product of mineral 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 ($i$ distinct of $w$) |
| $m_w$ | mass of water in the liquid phase |
| $M_w$ | molar mass of water ($18.0153 \times 10^{-3}$ kg $mol^{-1}$) |
| $n_i$ | number of moles of species $i$ |

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| | |
|---|---|
| $P$ | pressure (Pa) |
| $R$ | gas constant (8.31451 J $mol^{-1}$ $K^{-1}$) |
| $T$ | temperature (K) |
| $T_0$ | reference temperature (298.15 K) |
| $z_i$ | number of charges on the ionic species $i$ |

*Greek letters*

| | |
|---|---|
| $\alpha$ | equal to 2.0 $kg^{1/2}$ $mol^{-1/2}$ for 1–1, 1–2 and 2–1 electrolytes |
| $\beta^0$ | adjustable binary parameter for Pitzer's model |
| $\beta^1$ | adjustable binary parameter for Pitzer's model |
| $\gamma_i$ | activity coefficient of species $i$ in the molality scale |
| $\Delta_{\mathrm{cryst}}H$ | crystallization enthalpy (kJ $kg^{-1}$) of initial solution |
| $\Delta_{\mathrm{hyd}}H$ | heat of hydration of $Na_2SO_4$ into $Na_2SO_4 \cdot 10H_2O$ |
| $\Delta_{\mathrm{sol}}\hat{H}$ | molal dissolution enthalpy |
| $\overline{\Delta_{\mathrm{sol}}H_i^{\infty}}$ | molar dissolution enthalpy of mineral species $i$ at infinite dilution |
| $\theta_{i,j}$ | adjustable parameter accounting for interactions between ions of like sign |
| $\psi_{i,j,k}$ | adjustable ternary parameter for Pitzer's model |

*Subscripts*

| | |
|---|---|
| w | water |
| 0 | NaCl |
| 1 | $Na_2SO_4$ |
| 2 | $Na_2SO_4 \cdot 10H_2O$ |

## 1. Introduction

Efficient and economical heat storage is the key to the effective and widespread utilization of solar energy for low temperature thermal applications [1]. Latent heat storage is particularly attractive because of its ability to provide a high energy storage density and its characteristic to store heat in a narrow range of temperature.

Sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), also known as mirabilite or Glauber's salt, has been the most investigated salt hydrate for use in latent thermal energy storage systems since the earliest works of Telkes [2], mostly because of its high latent heat storage density and its low cost. The major problem in using sodium sulfate decahydrate as phase change material is its incongruent melting [3]. To overcome this drawback or to modify the transition temperature several additives are often added to $Na_2SO_4 \cdot 10H_2O$, generally water [4] and salts such as NaCl, $NH_4Br$, etc.

Another consideration with $Na_2SO_4 \cdot 10H_2O$ is its poor nucleating properties resulting in supersaturation of the solution prior to crystallization. Solutions to this problem are numerous [5]; for example the addition of nucleating agents such as borax ($Na_2B_4O_7 \cdot 10H_2O$) [6] or the use of electrical means of nucleation [7]. In this last case, mirabilite is formed from supersaturated solutions containing dissolved sodium sulfate.

It is therefore of great interest for heat storage media selection to predict phase equilibria and thermal properties in aqueous electrolyte solutions containing $Na_2SO_4$. Pitzer's model [8,9] seems particularly adapted for such applications since it allows the simultaneous representation of activity coefficients and excess enthalpy in aqueous solutions of mixed electrolytes.

The objective of this paper is to propose a methodology for the prediction of the heat effect associated with the crystallization of $Na_2SO_4 \cdot 10H_2O$ from supersaturated $H_2O$–NaCl–$Na_2SO_4$ solutions at constant temperature.

## 2. Experimental

Stock solutions of supersaturated $H_2O$–$Na_2SO_4$ (resp. $H_2O$–NaCl–$Na_2SO_4$) were prepared at ambient temperature in clean vessels by adding progressively reduced amounts of anhydrous sodium sulfate in demineralized water (respectively in aqueous sodium chloride) and by shaking thoroughly. Despite their metastability, the stock solutions could be used during several weeks put in a warm place, furthermore only disposable sterile syringes were used to take samples.

Measurements of crystallization enthalpies at various temperatures and concentrations were then made in a SETARAM C80D calorimeter by mixing samples of supersaturated $H_2O$–$Na_2SO_4$ or $H_2O$–NaCl–$Na_2SO_4$ solutions with a *seed crystal* (about 0.5 mg) of $Na_2SO_4 \cdot 10H_2O$ in order to start the crystallization process. The experimental results can be found in Table 3.

## 3. Theoretical aspects

Given a solution made from $n_w$ moles of water, $n_0$ moles of NaCl and $n_1$ moles of $Na_2SO_4$ supersaturated relatively to decahydrate, a *seed crystal* of mirabilite containing $n_2$ moles of $Na_2SO_4{\cdot}10H_2O$ is added to the solution in order to start the crystallization which is clearly exothermic. At the end of the reaction, we obtain a saturated solution containing $n_0$ moles of dissolved NaCl, $n'_1$moles of dissolved $Na_2SO_4$ and $n'_w$ moles of water ($n'_1$ and $n'_w$ are, respectively, lower than $n_1$ and $n_w$ because of the formation of decahydrate). This saturated solution is in equilibrium with $n'_2$ moles of mirabilite.

Provided that the thermal properties and phase equilibria in $H_2O$–NaCl–$Na_2SO_4$ can be accurately represented, the heat effect accompanying the crystallization can be predicted by the following mass and heat balances.

### 3.1. Mass balance

Each mole of decahydrate is formed from 2 mol of $Na^+$, 1 mol of $SO_4^{2-}$ and from 10 mol of water, therefore,

$$n_w - n'_w = 10(n_1 - n'_1). \tag{1}$$

Prediction of phase equilibria is necessary for the resolution of the mass balance since the second equation required for the calculation of the final composition is given by the solid/liquid equilibrium between the solution and mirabilite ($Na_2SO_4{\cdot}10H_2O$):

$$\gamma_{Na^+}^2 \cdot m_{Na^+}^2 \cdot \gamma_{SO_4^{2-}} \cdot m_{SO_4^{2-}} \cdot a_w^{10} = Ks_{\text{Mirabilite}}(T), \tag{2}$$

in which $\gamma_i$ is the activity coefficient of the ionic species $i$ in the liquid solution, $a_w$ is the corresponding activity of water and $Ks_{\text{Mirabilite}}$ is the solubility product of mirabilite.

The molality of each ion in the saturated final solution can be expressed as

$$m_{Na^+} = m'_0 + 2m'_1 = \frac{1}{M_w}\frac{n_0}{n'_w} + 2\frac{1}{M_w}\frac{n'_1}{n'_w},$$

$$m_{Cl^-} = m'_0 = \frac{1}{M_w}\frac{n_0}{n'_w}, \quad m_{SO_4^{2-}} = m'_1 = \frac{1}{M_w}\frac{n'_1}{n'_w},$$

where $n'_1$ and $n'_w$ are obtained by solving Eqs. (1) and (2).

Table 1
Solubility products ($Ks$) of the mineral species (273.15 < $T$ <373.15 K): $\ln(Ks) = -1/RT(a_K - b_K T + c_K((T-T_0) - T\ln(T/T_0)))$ with $T_0 = 298.15$ K

| Mineral species | $a_K$ | $b_K$ | $c_K$ |
|---|---|---|---|
| Halite (NaCl) | 3392.79 | 41.7014 | −74.1643 |
| Mirabilite ($Na_2SO_4{\cdot}10H_2O$) | 80 875.3 | 247.852 | 11.3598 |
| Thenardite ($Na_2SO_4$) | −303.239 | −6.61418 | −357.626 |

#### 3.1.1. Phase equilibria in $H_2O$–NaCl–$Na_2SO_4$

Pitzer's equations for activity coefficients of ions and activity of water are presented in Appendix A (Eqs. (A3), (A4), (A5), (A6), (A7) and (A8)). Solubility products of NaCl, $Na_2SO_4$, $Na_2SO_4{\cdot}10H_2O$ (Table 1) and binary parameters for $H_2O$–NaCl and $H_2O$–$Na_2SO_4$ used with Pitzer's model were determined in a previous paper [10]. In this previous paper, the activity coefficients in the $H_2O$–NaCl–$Na_2SO_4$ system were represented using constant values for the ternary parameters of Pitzer's model determined using solubility data in the ternary system at 298.15 K [11]. The inclusion of the temperature-dependence of these parameters has no obvious influence on the prediction of the solubilities, however, it significantly improves the representation of the dissolution enthalpies in $H_2O$–NaCl–$Na_2SO_4$. For this reason, we have considered this temperature-dependence in the present paper. These parameters along with parameters relative to the binary systems are presented in Appendix A (Table 4).

### 3.2. Heat balance

$\Delta H_{\text{exp}}$ (J), the heat effect accompanying the crystallization is equal to the enthalpy variation between the initial and final states of the experiment:

$$\Delta H_{\text{exp}} = H_{\text{final}} - H_{\text{initial}} = H(n'_w, n_0, n'_1) + n'_2 h_2^* - H(n_w, n_0, n_1) - n_2 h_2^*,$$

in which $h_2^*$ is the molar enthalpy of crystalline mirabilite, $H(n_w, n_0, n_1)$ the total enthalpy of a solution made from $n_w$ moles of water, $n_0$ the moles of NaCl and $n_1$ moles of $Na_2SO_4$.

The composition of the solution is usually expressed in the molality scale, $m_0 = n_0/n_w$ is the molality in sodium chloride and $m_1 = n_1/n_w$ is the molality in sodium sulfate. $m_w = n_w M_w$ is the mass of water (kg) contained in the liquid phase with $M_w$ being the molar mass of water (kg mol$^{-1}$).

Introducing $\Delta_{sol}\hat{H}(m_0, m_1)$ the variation of enthalpy accompanying the dissolution of $m_0$ moles of NaCl and $m_1$ moles of anhydrous $Na_2SO_4$ in 1 kg of water, the following relation can be written as

$$m_w\Delta_{sol}\hat{H}(m_0, m_1) = H(n_w, n_0, n_1) - n_w h_w^* - n_0 h_0^* - n_1 h_1^*,$$

where $h_w^*$ is the molar enthalpy of liquid water, $h_0^*$ the molar enthalpy of crystalline NaCl, and $h_1^*$ is the molar enthalpy of crystalline $Na_2SO_4$.

Subsequently,

$$\Delta H_{exp} = m'_w\Delta_{sol}\hat{H}(m'_0, m'_1) - m_w\Delta_{sol}\hat{H}(m_0, m_1) + (n'_w - n_w)h_w^* + (n'_0 - n_0)h_0^* + (n'_1 - n_1)h_1^* + (n'_2 - n_2)h_2^*.$$

If we consider the reaction of hydration of anhydrous sodium sulfate into decahydrate

$$Na_2SO_{4(cr)} + 10H_2O_{(liq)} = Na_2SO_4 \cdot 10H_2O_{(cr)}.$$

Then $h_2^* - h_1^* - 10h_w^* = \Delta_{hyd}H$ is the molar enthalpy of this reaction. Introducing $x$, the number of moles of decahydrate formed during the crystallization ($x = n_1 - n'_1$), we obtain

$$\Delta H_{exp} = m'_w\Delta_{sol}\hat{H}(m'_0, m'_1) - m_w\Delta_{sol}\hat{H}(m_0, m_1) + x\Delta_{hyd}H. \quad (3)$$

We have used Pitzer's model [8,9] to represent dissolution enthalpies and to determine the heat of hydration of anhydrous sodium sulfate which are necessary to predict the heat effect due to the crystallization of mirabilite from supersaturated $H_2O$–NaCl–$Na_2SO_4$ solutions.

### *3.2.1. Dissolution enthalpies of NaCl + $Na_2SO_4$ mixtures in water*

The molal dissolution enthalpy $\Delta_{sol}\hat{H}(m_0, m_1)$ is related to the molal excess enthalpy $\hat{L}(m_0, m_1)$ and to the molar dissolution enthalpies of NaCl and $Na_2SO_4$ at infinite dilution ($\overline{\Delta_{sol}H_0^\infty}$ and $\overline{\Delta_{sol}H_0^\infty}$) by the following relationship:

Table 2
Molar dissolution enthalpy at infinite dilution in J mol$^{-1}$ ($273.15 < T < 373.15$ K): $\overline{\Delta_{sol}H^\infty} = a_\infty + b_\infty(T - T_0)$ with $T_0 = 298.15$ K

| Solid species | $a_\infty$ | $b_\infty$ |
|---|---|---|
| NaCl | 3799.7 | −115.80 |
| $Na_2SO_4$ | −1380.4 | −302.09 |

$$\Delta_{sol}\hat{H}(m_0, m_1) = \hat{L}(m_0, m_1) + m_0\overline{\Delta_{sol}H_0^\infty} + m_1\overline{\Delta_{sol}H_1^\infty}. \quad (4)$$

Values of molar dissolution enthalpies of NaCl and $Na_2SO_4$ at infinite dilution are calculated from coefficients in Table 2. The molal excess enthalpy, $\hat{L}(m_0, m_1)$, is calculated with Pitzer's model from Eq. (A10) given in Appendix A.

The mean relative deviation between our experimental [12] and calculated values of molal dissolution enthalpies of NaCl and $Na_2SO_4$ mixtures in water is 5.8%.

### *3.2.2. Heat of hydration of $Na_2SO_4$ into $Na_2SO_4 \cdot 10H_2O$*

Values of heat of hydration of $Na_2SO_4$ into $Na_2SO_4 \cdot 10H_2O$ at different temperatures were evaluated from Table 3 using experimental results corresponding to supersaturated $H_2O$–$Na_2SO_4$ solutions ($m'_0 = m_0 = 0$). In this case, the following equation is used:

$$\Delta_{hyd}H = \frac{1}{x}[\Delta H_{exp} + m_w\Delta_{sol}\hat{H}(0, m_1) - m'_w\Delta_{sol}\hat{H}(0, m'_1)]. \quad (5)$$

The heat of hydration of $Na_2SO_4$ into $Na_2SO_4 \cdot 10H_2O$ is usually determined by dissolving the hydrate and the anhydrous salt in water to attain the same final concentration and by measuring the difference between the heats of solution [13,14]. As shown in Fig. 1 the two methods are in good agreement. We obtain a relatively good agreement from 291.15 to 303.15 K with Perman and Urry [13] and Rode [15]. Our value at 298.15 K (−81.556 kJ mol$^{-1}$) is in excellent agreement with Pitzer and Coulter [14] (−81.170 kJ mol$^{-1}$), Pickering [16] (−81.462 kJ mol$^{-1}$) and Thomsen [17] (−80.584 kJ mol$^{-1}$).

The heat of hydration of $Na_2SO_4$ into $Na_2SO_4 \cdot 10H_2O$, calculated using Eq. (5), is represented

Table 3

Experimental and calculated values of crystallization enthalpies of $Na_2SO_4 \cdot 10H_2O$ from supersaturated $H_2O$–NaCl–$Na_2SO_4$ at various temperatures (crystallization enthalpies are expressed in kJ kg$^{-1}$ of initial solution (heat storage capacity))

| Temp. (K) | $m_0$ (mol kg$^{-1}$) | $m_1$ (mol kg$^{-1}$) | $m_{\mathrm{w}}$ (g) | Initial solution mass (g) | $m'_0$ (mol kg$^{-1}$) | $m'_1$ (mol kg$^{-1}$) | $m'_{\mathrm{w}}$ (g) | $x/n_1$ (%) | $\Delta_{\mathrm{hyd}}H$ (kJ mol$^{-1}$) | $\Delta_{\mathrm{cryst}}H$ (exp) (kJ kg$^{-1}$) | $\Delta_{\mathrm{cryst}}H$ (cal) (kJ kg$^{-1}$) | Deviation (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 290.75 | 0 | 2.2183 | 0.6250 | 0.8219 | 0 | 1.1239 | 0.4705 | 61.9 | −77.220 | −69.315 | −68.526 | −1.14 |
| 293.75 | 0 | 1.9479 | 0.7067 | 0.9022 | 0 | 1.4076 | 0.6145 | 37.2 | −78.780 | −38.583 | −38.440 | −0.37 |
| 293.75 | 0 | 2.2183 | 0.5585 | 0.7345 | 0 | 1.4076 | 0.4492 | 49.0 | −79.045 | −56.209 | −55.782 | −0.76 |
| 293.75 | 0 | 2.5500 | 0.4811 | 0.6553 | 0 | 1.4076 | 0.3484 | 60.0 | −77.797 | −74.823 | −75.645 | 1.10 |
| 297.75 | 0 | 2.5500 | 0.4645 | 0.6328 | 0 | 1.8992 | 0.3817 | 38.8 | −80.496 | −50.138 | −50.888 | 1.50 |
| 297.75 | 0 | 3.4509 | 0.4093 | 0.6099 | 0 | 1.8992 | 0.2354 | 68.4 | −80.246 | −110.03 | −111.28 | 1.14 |
| 302.75 | 0 | 3.3560 | 0.4533 | 0.6694 | 0 | 2.7828 | 0.3594 | 34.3 | −85.006 | −58.062 | −57.841 | −0.38 |
| 302.75 | 0 | 3.4509 | 0.4749 | 0.7077 | 0 | 2.7828 | 0.3603 | 38.8 | −85.315 | −67.407 | −66.874 | −0.79 |
| 304.65 | 0 | 3.4509 | 0.4696 | 0.6998 | 0 | 3.2590 | 0.4303 | 13.5 | −86.176 | −23.794 | −23.747 | −0.20 |
| 294.75 | 0.2999 | 2.9998 | 0.4853 | 0.7005 | 0.4961 | 1.3305 | 0.2934 | 73.2 | NA[a] | −103.02 | −103.36 | 0.33 |
| 297.75 | 0.2999 | 2.9995 | 0.4345 | 0.6272 | 0.4483 | 1.7367 | 0.2906 | 61.3 | NA | −87.802 | −89.149 | 1.53 |
| 298.75 | 0.2999 | 2.9998 | 0.4471 | 0.6454 | 0.4296 | 1.8964 | 0.3121 | 55.9 | NA | −81.802 | −82.062 | 0.86 |
| 302.65 | 0.2999 | 2.9995 | 1.2320 | 1.7785 | 0.3378 | 2.6772 | 1.0938 | 20.8 | NA | −32.614 | −31.148 | −4.50 |

[a] Non-applicable.

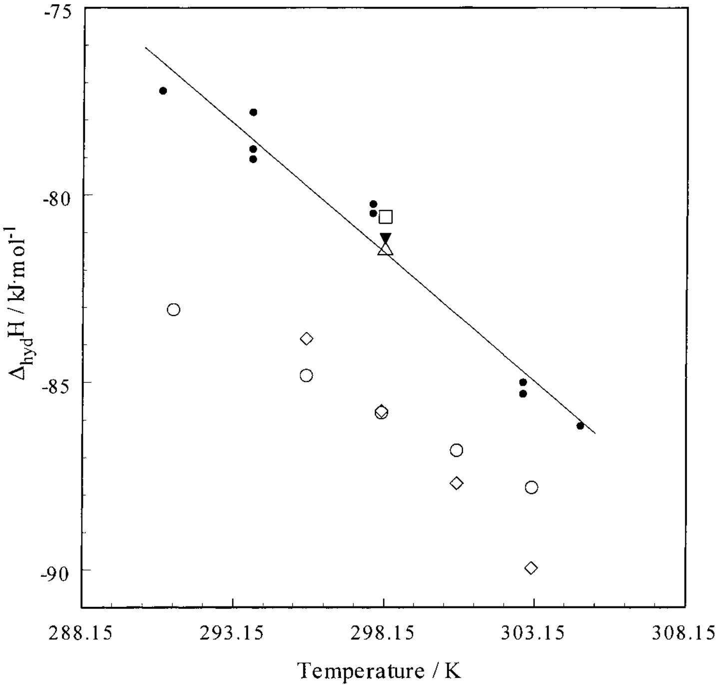

Fig. 1. Heat of hydration of $Na_2SO_4$ into $Na_2SO_4·10H_2O$: (●) our work (exp. data); (◇) Perman and Urry [13]; (▼) Pitzer and Coulter [14]; (○) Rode [15]; (Δ) Pickering [16]; (□) Thomsen [17]; (—) our work (linear regression).

between 291.15 and 305.15 K by the following equation:

$$\Delta_{hyd}H(T) = \Delta_{hyd}H(T_0) + \Delta_{hyd}C_p(T-T_0), \quad (6)$$

in which $\Delta_{hyd}H(T_0)$ is the heat of hydration of $Na_2SO_4$ at 298.15 K and $\Delta_{hyd}C_p$ is the mean heat capacity of hydration of $Na_2SO_4$. In Eq. (6), $\Delta_{hyd}H(T_0) = -81\,556$ J mol$^{-1}$ and $\Delta_{hyd}C_p = -687.91$ J mol$^{-1}$ K$^{-1}$.

Furthermore, the relative error between our calculated value of heat of hydration of $Na_2SO_4$ at 298.15 K and the value calculated from the NBS tables [18] (−81.88 kJ mol$^{-1}$) is −0.40 %.

## 4. Results and discussion

Glauber's salt ($Na_2SO_4·10H_2O$) melts incongruently causing sedimentation of anhydrous $Na_2SO_4$. It is then impossible to dissolve this anhydrous salt sediment and the heat storage capacity of the material decreases markedly with successive freeze/thaw cycles [3]. One of the solutions consists in adding enough liquid water to the decahydrate to avoid sedimentation during operation (*extra water principle*). Biswas [4] suggested to use a mixture containing 3 mol of $Na_2SO_4$ per kilogram of water. We have studied experimentally the addition of 1 mol of NaCl for 10 mol of $Na_2SO_4$ to this mixture ($m_0 = m_1/10 \approx$ 0.3 mol kg$^{-1}$).

The experimental results along with the calculated values of the heat of crystallization of mirabilite from supersaturated $H_2O$–$Na_2SO_4$ or $H_2O$–NaCl–$Na_2SO_4$ solutions are given in Table 3. Values at saturation $m_0'$ and $m_1'$ are determined by solving Eqs. (1) and (2) and $\Delta_{cryst}H$(cal) is calculated using Eq. (3) and expressed in kJ kg$^{-1}$ of initial solution (heat storage capacity). Calculated and experimental values are in very good agreement as shown in Fig. 2a.

Fig. 2a and b illustrates the influence of NaCl on the phase equilibria and the heat released at different temperatures by a kilogram (heat storage capacity) of the mixture proposed originally by Biswas ($m_0 = 0$, $m_1 \approx 3.0$ mol kg$^{-1}$) and the mixture containing sodium chloride ($m_0 = m_1/10 \approx 0.3$ mol kg$^{-1}$).

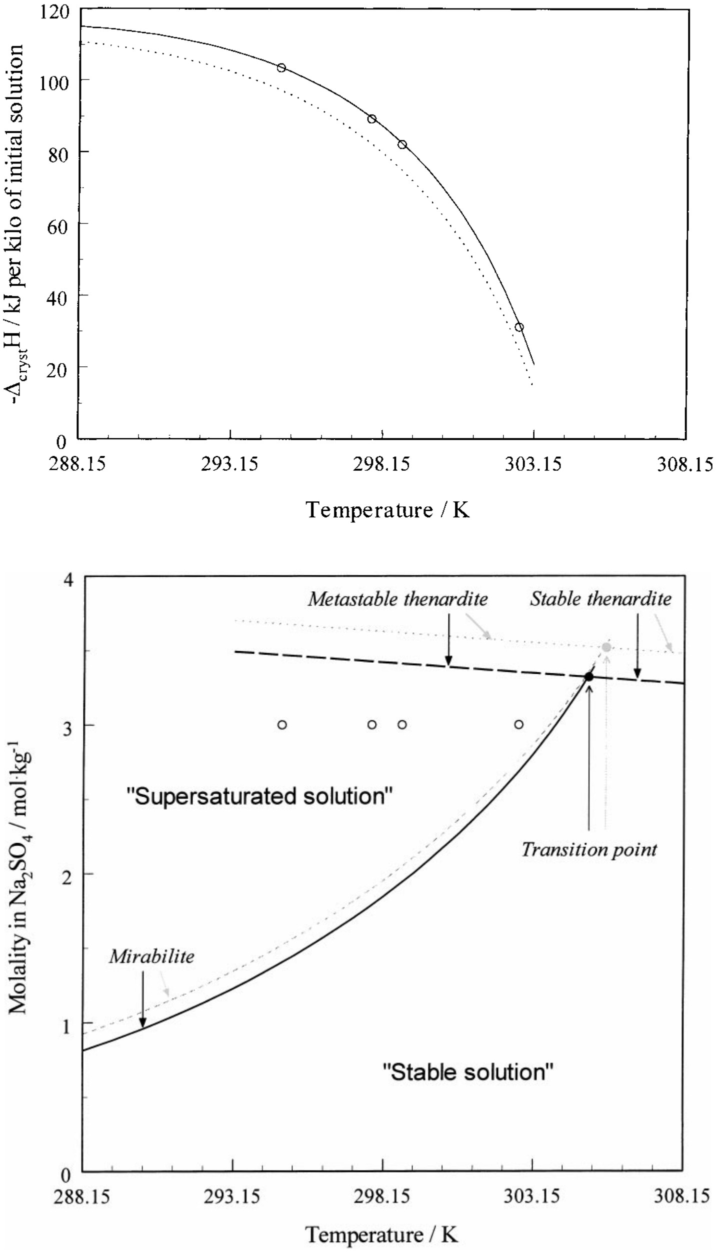

Fig. 2. (a) Heat storage capacity of the supersaturated solution: (—) $m_0 = 0.3$, $m_1 = 3$ mol kg$^{-1}$ (model); (···) $m_0 = 0.0$, $m_1 = 3$ mol kg$^{-1}$ (model); (○) $m_0 = 0.3$, $m_1 = 3$ mol kg$^{-1}$ (exp. data) and (b) *supersaturation diagram*: (– – – –) solubility of mirabilite in pure water; (—) solubility of mirabilite in $m_0 = 0.3$ mol kg$^{-1}$; (···) solubility of thenardite in pure water; (– –) solubility of thenardite in $m_0 = 0.3$ mol kg$^{-1}$; (○) exp. conditions ($m_0 = 0.3$, $m_1 = 3$ mol kg$^{-1}$).

The addition of NaCl decreases the solubility of mirabilite by *common ion effect* and, therefore, increases the supersaturation of the solution (Fig. 2b), the heat released during crystallization is then higher (Fig. 2a) since more $Na_2SO_4{\cdot}10H_2O$ precipitates.

Fig. 2b shows the supersaturation of the $H_2O$–NaCl–$Na_2SO_4$ solution before crystallization but cannot indicate the composition of the final solution. Indeed, since water is consumed during crystallization of the hydrate, the liquid solution at the end of the experiment is richer in NaCl (see column $m_0'$ in Table 3) and then slightly poorer in $Na_2SO_4$.

However, as shown in Fig. 2b, the addition of NaCl decreases even more the solubility of thenardite (anhydrous $Na_2SO_4$). The amount of NaCl that can be used as an additive in a given supersaturated $H_2O$–$Na_2SO_4$ solution is therefore limited.

## 5. Conclusion

We have used Pitzer's ion-interaction approach to represent dissolution enthalpies and phase equilibria in the $H_2O$–NaCl–$Na_2SO_4$ system. Besides, measurements of crystallization enthalpies of mirabilite from supersaturated $H_2O$–$Na_2SO_4$ solutions led us to values of heat of hydration of anhydrous sodium sulfate into decahydrate. These values are in good agreement with values of the literature [13,14] which were obtained by a completely different method.

These thermodynamic properties allow the accurate prediction of the heat effect associated with the crystallization of $Na_2SO_4{\cdot}10H_2O$ from supersaturated $H_2O$–NaCl–$Na_2SO_4$ solutions rich in sodium sulfate.

We have also discussed the effect of NaCl in the mixture recommended by Biswas [4] and found that the addition of limited amounts of NaCl is advantageous regarding the heat storage capacity. Nevertheless, the heat of crystallization is only one of the numerous criteria for the selection of salt hydrate-based latent heat storage systems [1,3] and the choice of additives results from a global optimization.

The proposed methodology could be generalized to more complex systems ($H_2O + Na_2SO_4 + NaCl +$ other salts, etc.) and is therefore of great interest for the selection of salt additives in $Na_2SO_4{\cdot}10H_2O$-based latent thermal energy storage systems.

## Appendix A. Equations of Pitzer's model

Pitzer [8,9] has proposed a general equation for $\hat{G}^{E}$, the excess Gibbs energy of an aqueous electrolyte solution containing 1 kg of water. In this approach, the excess Gibbs energy of the solution can be considered as the sum of a Debye–Hückel type term which express the effect of long-range interactions between ions and of a second term accounting for the short-range interactions between solute species.

### A.1. Excess Gibbs energy

In the particular case of an aqueous solution of molality $m_0$ in NaCl and $m_1$ in $Na_2SO_4$, $\hat{G}^{E}$ is represented by the following expression:

$$\frac{\hat{G}^{E}}{RT} = \left[\begin{array}{c} -A_{\phi}(4I/b)\ln(1+b(I)^{1/2}) \\ +2m_{Na^+}\cdot m_{Cl^-}(B_{NaCl}+ZC_{NaCl}) \\ +2m_{Na^+}\cdot m_{SO_4^{2-}}(B_{Na_2SO_4}+ZC_{Na_2SO_4}) \\ +2m_{Cl^-}\cdot m_{SO_4^{2-}}\left(\Phi_{Cl^-,SO_4^{2-}}+m_{Na^+}\cdot\dfrac{\Psi_{Na^+,Cl^-,SO_4^{2-}}}{2}\right). \end{array}\right], \qquad \text{(A1)}$$

with $b = 1.2$.

$A_{\phi}$ is the Debye–Hückel term associated with Pitzer's model for the osmotic coefficient, tabulated values can be found in [19].

$I$ is the ionic strength of the solution in the molality scale.

$$Z = m_{Na^+}|z_{Na^+}| = m_{Cl^-}|z_{Cl^-}| + m_{SO_4^{2-}}\left|z_{SO_4^{2-}}\right|.$$

The molality of each ion in the solution can be calculated from $m_0$ and $m_1$:

$$m_{Na^+} = m_0 + 2m_1, \quad m_{Cl^-} = m_0, \quad m_{SO_4^{2-}} = m_1,$$

$$B_{NaCl} = \beta^0_{NaCl} + \beta^1_{NaCl}\cdot g(\alpha(I)^{1/2}),$$

$$B_{Na_2SO_4} = \beta^0_{Na_2SO_4} + \beta^1_{Na_2SO_4}\cdot g(\alpha(I)^{1/2}),$$

with $g(x) = (2(1-(1+x)e^{-x}))/x^2$,

$$C_{NaCl} = \frac{C^{\phi}_{NaCl}}{2(|z_{Na^+}z_{Cl^-}|)^{1/2}} \quad \text{and}$$

$$C_{Na_2SO_4} = \frac{C^{\phi}_{Na_2SO_4}}{2\left(\left|z_{Na^+}z_{SO_4^{2-}}\right|\right)^{1/2}},$$

where $\beta^0_{NaCl}$, $\beta^1_{NaCl}$, $C^{\phi}_{NaCl}$, $\beta^0_{Na_2SO_4}$, $\beta^1_{Na_2SO_4}$ and $C^{\phi}_{Na_2SO_4}$ are adjustable parameters fitted with data relative to $H_2O$–NaCl or $H_2O$–$Na_2SO_4$ binary solutions. Their values are presented in Table 4.

Table 4
Pitzer's adjustable interaction parameters ($273.15 < T < 373.15$ K): parameter $= a + b(1/T - 1/T_0) + c\ln(T/T_0)$ with $T_0 = 298.15$ K

| Parameter | *a* | *b* | *c* |
|---|---|---|---|
| $\beta^0_{NaCl}$ | 0.0765 | −440.1328 | −1.248891 |
| $\beta^1_{NaCl}$ | 0.2664 | 518.3828 | 1.911939 |
| $C^{\phi}_{NaCl}$ | 0.00127 | 61.07728 | 0.171046 |
| $\beta^0_{Na_2SO_4}$ | 0.018675 | −790.0071 | −2.071428 |
| $\beta^1_{Na_2SO_4}$ | 1.0995 | −4870.511 | −13.11122 |
| $C^{\phi}_{Na_2SO_4}$ | 0.005549 | 121.5825 | 0.305269 |
| $\theta_{Cl^-,SO_4^{2-}}$ | 0.068121 | 459.1685 | 1.458400 |
| $\Psi_{Na^+,Cl^-,SO_4^{2-}}$ | −0.010756 | −44.56551 | −0.180337 |

$\Phi_{Cl^-,SO_4^{2-}}$ is relative to $SO_4^{2-}$ and $C1^-$ interactions in $\hat{G}^E$, it is composed of two terms:

$$\Phi_{Cl^-,SO_4^{2-}} = \theta_{Cl^-,SO_4^{2-}} + {}^{E}\theta_{Cl^-,SO_4^{2-}}(I), \tag{A2}$$

where ${}^{E}\theta_{Cl^-,SO_4^{2-}}(I)$ is a term accounting for unsymmetrical mixing, integrals defining it are given by Pitzer [8,20]. The unsymmetrical mixing terms depend only on the electrolyte pair type and ionic strength.

$\theta_{Cl^-,SO_4^{2-}}$ and $\Psi_{Na^+,Cl^-,SO_4^{2-}}$ are adjustable parameters fitted with data relative to the $H_2O$–NaCl–$Na_2SO_4$ ternary solution. Their values are given in Table 4.

The expressions for activity coefficients of ions, osmotic coefficient and excess enthalpy are obtained from appropriate derivatives of $\hat{G}^E$.

### A.2. Activity coefficients of ions

$$\begin{aligned}\ln\gamma_{Na^+} = {} & z^2_{Na^+}\cdot F + 2m_{Cl^-}(B_{NaCl} + ZC_{NaCl}) \\ & + 2m_{SO_4^{2-}}(B_{Na_2SO_4} + ZC_{Na_2SO_4}) \\ & + m_{Cl^-}\cdot m_{SO_4^{2-}}\cdot \Psi_{Na^+,Cl^-,SO_4^{2-}} \\ & + |z_{Na^+}|(m_{Na^+}\cdot m_{Cl^-}\cdot C_{NaCl} \\ & + m_{Na^+}\cdot m_{SO_4^{2-}}\cdot C_{Na_2SO_4}), \\ \ln\gamma_{Cl^-} = {} & z^2_{Cl^-}\cdot F + 2m_{Na^+}(B_{NaCl} + ZC_{NaCl}) \\ & + 2m_{SO_4^{2-}}\cdot \Phi_{Cl^-,SO_4^{2-}} + m_{SO_4^{2-}}\cdot m_{Na^+} \\ & \cdot \Psi_{Na^+,Cl^-,SO_4^{2-}} + |z_{Cl^-}|(m_{Na^+}\cdot m_{Cl^-} \\ & \cdot C_{NaCl} + m_{Na^+}\cdot m_{SO_4^{2-}}\cdot C_{Na_2SO_4}),\end{aligned} \tag{A4}$$

$$\begin{aligned}\ln\gamma_{SO_4^{2-}} = {} & z^2_{SO_4^{2-}}\cdot F + 2m_{Na^+}(B_{Na_2SO_4} + ZC_{Na_2SO_4}) \\ & + 2m_{Cl^-}\cdot \Phi_{Cl^-,SO_4^{2-}} + m_{Cl^-}\cdot m_{Na^+} \\ & \cdot \Psi_{Na^+,Cl^-,SO_4^{2-}} + \left|z_{SO_4^{2-}}\right|^2(m_{Na^+}\cdot m_{Cl^-} \\ & \cdot C_{NaCl} + m_{Na^+}\cdot m_{SO_4^{2-}}\cdot C_{Na_2SO_4}).\end{aligned} \tag{A5}$$

In Eqs. (A3), (A4) and (A5), $F$ is given by the following equation:

$$\begin{aligned}F = {} & -A^{\phi}\left(\frac{(I)^{1/2}}{1 + b(I)^{1/2}} + \frac{2}{b}\ln(1 + b(I)^{1/2})\right) \\ & + m_{Na^+}\cdot m_{Cl^-}\cdot B'_{NaCl} + m_{Na^+}\cdot m_{SO_4^{2-}}\cdot B'_{Na_2SO_4} \\ & + m_{Cl^-}\cdot m_{SO_4^{2-}}\cdot \Phi''_{Cl^-,SO_4^{2-}} \\ B'_{NaCl} = {} & \beta^1_{NaCl}\frac{g'(\alpha(I)^{1/2})}{I}, \\ B'_{Na_2SO_4} = {} & \beta^1_{Na_2SO_4}\frac{g'(\alpha(I)^{1/2})}{I},\end{aligned}$$

with $g'(x) = -2(1 - (1 + x + (x^2/2))e^{-x})/x^2$.

$$\Phi'_{Cl^-,SO_4^{2-}} = {}^{E}\theta'_{Cl^-,SO_4^{2-}}(I), \tag{A6}$$

where ${}^{E}\theta'_{Cl^-,SO_4^{2-}}(I)$ is the derivative of ${}^{E}\theta_{Cl^-,SO_4^{2-}}(I)$ (see Eq. (A2)) with respect to the ionic strength. Integrals defining this term of unsymmetrical mixing are given by Pitzer [8,20].

### A.3. Osmotic coefficient and activity of water

The activity of water, $a_w$, is usually expressed by the osmotic coefficient, $\phi$:

$$\begin{aligned}\ln(a_w) & = -\frac{18.0153}{1000}\left(\sum_i m_i\right)\phi \\ & = -\frac{18.0153}{1000}\left(m_{Na^+} + m_{Cl^-} + m_{SO_4^{2-}}\right)\phi,\end{aligned} \tag{A7}$$

where 18.0153 is the molar mass of water in g mol$^{-1}$.

$\phi$ is calculated from the following equation:

$$(\phi-1)=\frac{2}{m_{\mathrm{Na}^+}+m_{\mathrm{Cl}^-}+m_{\mathrm{SO}_4^{2-}}}\times\left\{\begin{array}{c}-\frac{A_\phi I^{3/2}}{1+b(I)^{1/2}}\\ +m_{\mathrm{Na}^+}\cdot m_{\mathrm{Cl}^-}(B^{\phi}_{\mathrm{NaCl}}+2ZC_{\mathrm{NaCl}})\\ +m_{\mathrm{Na}^+}\cdot m_{\mathrm{SO}_4^{2-}}(B^{\phi}_{\mathrm{Na_2SO_4}}+2ZC_{\mathrm{Na_2SO_4}})\\ +m_{\mathrm{Cl}^-}\cdot m_{\mathrm{SO}_4^{2-}}\cdot\Phi^{\phi}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}\\ +m_{\mathrm{Cl}^-}\cdot m_{\mathrm{SO}_4^{2-}}\cdot m_{\mathrm{Na}^+}\cdot\Psi_{\mathrm{Na}^+,\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}\end{array}\right\}, \tag{A8}$$

$$\begin{aligned}\beta^{\phi}_{\mathrm{NaCl}}&=\beta^{0}_{\mathrm{NaCl}}+\beta^{1}_{\mathrm{NaCl}}\exp\left(-\alpha(I)^{1/2}\right),\\ B^{\phi}_{\mathrm{Na_2SO_4}}&=\beta^{0}_{\mathrm{Na_2SO_4}}+\beta^{1}_{\mathrm{Na_2SO_4}}\exp\left(-\alpha(I)^{1/2}\right),\\ \Phi^{\phi}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}&=\theta_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}+{}^{\mathrm{E}}\theta_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}\cdot(I)\\ &\quad+I\cdot{}^{\mathrm{E}}\theta'_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}(I).\end{aligned} \tag{A9}$$

### *A.4. Excess enthalpy*

$\hat{L}$, the excess enthalpy of a $H_2O$–NaCl–$Na_2SO_4$ solution containing 1 kg of water is given by the following expression:

$$\hat{L}=\left\{\begin{array}{c}\frac{A_L I}{b}\ln(1+b(I)^{1/2})-2RT^2\cdot m_{\mathrm{Na}^+}\cdot m_{\mathrm{Cl}^-}[B^{L}_{\mathrm{NaCl}}+ZC^{L}_{\mathrm{NaCl}}]\\ -2RT^2\cdot m_{\mathrm{Na}^+}\cdot m_{\mathrm{SO}_4^{2-}}[B^{L}_{\mathrm{Na_2SO_4}}+ZC^{L}_{\mathrm{Na_2SO_4}}]\\ -RT^2\cdot m_{\mathrm{Cl}^-}\cdot m_{\mathrm{SO}_4^{2-}}[\Phi^{L}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}+m_{\mathrm{Na}^+}\frac{\mathrm{Na}^+,\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}{2}]\end{array}\right\}, \tag{A10}$$

where $A_L=4RT^2(\partial A_\phi/\partial T)_P$ is the Debye–Hückel slope for enthalpy, tabulated values can be found in [19].

$X^L$ is the temperature derivative of $X$.

$$\Phi^{L}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}=\theta^{L}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}+{}^{\mathrm{E}}\theta^{L}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}(I), \tag{A11}$$

where ${}^{\mathrm{E}}\theta^{\mathrm{L}}_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}(I)$ is the temperature derivative of the unsymmetrical mixing term ${}^{\mathrm{E}}\theta_{\mathrm{Cl}^-,\mathrm{SO}_4^{2-}}(I)$ and is calculated from formulas given by Pitzer [21].

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