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Phase diagram prediction of systems $Mn(NO_3)_2$-$M(NO_3)_n$-H_2O (M= Ca, Mg and Li) with modified BET-model①

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Abstract: BET-model parameters for the binary system $Mn(NO_3)_2$-H_2O were obtained by fitting experimental water activities at 298.15 K. The values obtained in this work were compared to those fitted previously for the systems $Ca(NO_3)_2$-H_2O and $Zn(NO_3)_2$-H_2O, showing reasonable agreement. With the model parameters fitted at 298 K, the vapor pressure of the saturated solution for the phases $Mn(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ were predicted and shows quite good agreement with the experimental values. The phase diagram of the $Mn(NO_3)_2$-H_2O system reproduced by the BET model shows smaller deviation from the experimental data than that by the extended UNIQUAC model. The ternary phase diagrams of the systems $Me(NO_3)_n$-$Mn(NO_3)_2$-H_2O (Me= Mg, Ca and Li) are predicted with the binary model parameter and compared with available experimental data. The predicted eutectic compositions were given as possible heat storage materials.

Key words: activity; thermodynamic model; solubility; manganous nitrate; heat storage materials
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1 INTRODUCTION

Molten salt hydrates have been extensively used as phase change materials (PCM) in many energy storage fields, especially in air-conditioning systems. For example, in those areas where the difference of temperature between daytime and night is large, one can use a molten salt hydrate as PCM to store the sonar energy in the daytime, and then reuse it in the cold midnight by automatically releasing of the heat energy from the PCM. Besides, imbalance of demand for energy between daytime and midnight makes the price of electricity much cheaper at midnight than in daytime. A good idea is to store the energy at midnight and reuse it in the daytime. To these purposes, a PCM with melting point between 288－298 K is highly desirable[1]. Unfortunately, up to now few molten salt hydrates melting in this temperature range have been found. On the other side, there are four concurrent points between 297 K and 310 K in the binary system $Mn(NO_3)_2$-H_2O, which makes $Mn(NO_3)_2$-based hydrated salt mixtures potential phase change materials for heat storage in air conditioning systems. In principle, the melting point of the $Mn(NO_3)_2$ hydrates can be decreased by adding some salts in the $Mn(NO_3)_2$ aqueous solution. But little experimental data is available for the Mn $(NO_3)_2$-$M(NO_3)_n$-H_2O ternary systems except some information revealed in patents[2-4]. Thereby, further finding new $Mn(NO_3)_2$-based hydrated salt mixtures is necessary. In our previous work[5], a series of new eutectic points of hydrated salt mixtures have been successfully predicted by using the modified BET model. In this work the same method will be applied in the prediction of phase diagram of the ternary systems $Me(NO_3)_n$-$Mn(NO_3)_2$-H_2O.

The modified BET model to be used in this work was developed by Ally et al[6]. For a ternary system A-B-H_2O, the component activities are related with the BET parameter according to Eqns. (1)－(5).

$$\frac{N_{A(M)}(N_{A(M)}+N_{B(M)})}{(r_A \cdot N_A - N_{A(M)})(N_H - N_{A(M)} - N_{B(M)})} = c_A = \exp(-\varepsilon_A/(RT)) \quad (1)$$

$$\frac{N_{B(M)}(N_{A(M)}+N_{B(M)})}{(r_B \cdot N_B - N_{B(M)})(N_H - N_{A(M)} - N_{B(M)})} = c_B = \exp(-\varepsilon_B/(RT)) \quad (2)$$

$$a_H = (N_H - N_{A(M)} - N_{B(M)})/N_H \quad (3)$$

$$a_A = \{N_A/(N_A+N_B)\}\{(r_A \cdot N_A - N_{A(M)})/(r_A \cdot N_A)\}^{r_A} \quad (4)$$

$$a_B = \{N_B/(N_A+N_B)\}\{(r_B \cdot N_B - N_{B(M)})/(r_B \cdot N_B)\}^{r_B} \quad (5)$$

where A, B and H denote salt A, salt B and water; N_A, N_B and N_H are molar number of salt A, B and water, respectively; $N_{A(M)}$, $N_{B(M)}$ are coordination number of water on the salt A and B, respectively; a_i is activity of the component i; R is gas constant.

Provided that the binary BET parameter r_i and c_i are known, one can calculate the component activities a_i at the composition (N_A, N_B and N_H) and the temperature

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The binary parameters r_i and c_i are obtained by fitting experimental values of water activity a_H in Eqns. (6)-(8)[7].

$$\frac{(1-x_H)\cdot a_H}{x_H(1-a_H)} = \frac{1}{c_A \cdot r_A} + \frac{c_A - 1}{c_A \cdot r_A} a_H \quad (6)$$

$$c_A = \exp[(E_A - E_L)/RT] = \exp[(-\varepsilon_A)/(RT)] \quad (7)$$

$$x_H = N_H/(N_H + N_A) \quad (8)$$

where E_A and E_L denote the heat of adsorption on the salt A and the heat of condensation of pure water vapor, respectively.

2 BINARY SYSTEM $Mn(NO_3)_2$-H_2O

Prior to the prediction of the ternary systems, the BET parameters and liquidus for the binary $Mn(NO_3)_2$-H_2O system should be fitted and reproduced. At first, substitution of experimental data[8] of water activities and corresponding salt concentrations of the $Mn(NO_3)_2$ aqueous solution in Eqn. (6) yields a linear relationship between the terms $(1-x_H)\cdot a_H/(x_H(1-a_H))$ and a_H in concentrated salt solution, as shown in Fig. 1. The BET parameters obtained in this way at 298.15 K are $r_{Mn(NO_3)_2} = 5$, $\varepsilon_{Mn(NO_3)_2} = -7.16$ kJ/mol.

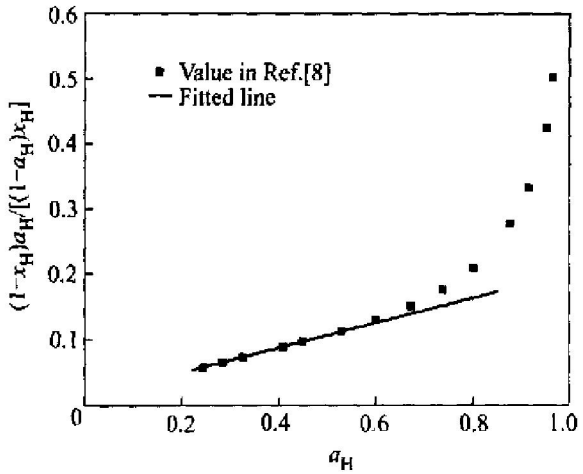

Fig. 1 Dependence of water activities a_H on salt concentrations $(1-x_H)$ for BET parameter fitting in binary $Mn(NO_3)_2$-H_2O system at 298.15 K

Caminiti, Cucca and Pintori[9] investigated the solution structure of the concentrated $Mn(NO_3)_2$ solution with X-ray and Raman spectroscope and confirmed the formation of a inner type complex between the cation Mn^{2+} and the anion NO_3^-, which was described as the formula $Mn(H_2O)_{6-z}^{-}(ONO_2)_z$. The average number z of the nitrate groups bound to each Mn^{2+} proved to be less than one. In this regard, the BET model parameter $r_{Mn(NO_3)_2} = 5$, namely the coordination sites of water molecule on each Mn^{2+}, should be reasonable.

A comparison of the BET parameters of this system with those of other systems is listed in Table 1. It can be seen that the BET energy parameters decrease regularly along the periodic table from the left side Ca to the right side Zn, which can be attributed to the decrease of ionic radius. This also agrees with the order of the hydration energy of cations as $Ca^{2+} > Mn^{2+} > Zn^{2+}$ in gas phase[10].

Table 1 Comparison of BET parameters of various binary salt-water systems at 298.15 K

Binary system	r	ε/(kJ·mol^{-1})	Ionic radius of cation/pm
$Ca(NO_3)_2$[5]	3.78	−5.64	99
$Mn(NO_3)_2$*	5.0	−7.16	80
$Zn(NO_3)_2$[5]	5.23	−10.25	74

* —Calculated in this work

The Gibbs energy $\mu^0_{Mn(NO_3)_2\cdot nH_2O}$ of the solid phase $Mn(NO_3)_2\cdot nH_2O$ as a function of temperature and pressure can be obtained by calculating the activities of salt and water at binary liquidus points according to Eqn. (9), when the BET parameters r_i and c_i (or ε_i) are known.

$$Mn(NO_3)_2\cdot nH_2O_{(s)} = Mn(NO_3)_{2(l)} + nH_2O_{(l)} \quad (9)$$

$$\begin{aligned}\mu^0_{Mn(NO_3)_2\cdot nH_2O} &= \mu_{Mn(NO_3)_2} + n\mu_{H_2O} \\ &= \mu^0_{Mn(NO_3)_2} + RT\ln a_{Mn(NO_3)_{2(l)}} + n\mu^0_{H_2O} + nRT\ln a_{H_2O(l)} \\ &= RT\ln(a_{Mn(NO_3)_{2(l)}}\cdot a^n_{H_2O(l)}) \\ &= RT\ln k_{Mn(NO_3)_2\cdot nH_2O} \quad (10)\end{aligned}$$

where the values of μ^0_{Salt} and $\mu^0_{H_2O}$ are set to be zero at any temperature in this paper.

The values of $\ln k_i$ obtained in a binary system at different temperatures are fitted as: $\ln k_i = A + B/T + C/T^2$. The parameters A, B and C obtained for all relevant solid phases are listed in Table 2, as well as the Latent warm of the solid phase $Mn(NO_3)_2\cdot 6H_2O$ and $Mn(NO_3)_2\cdot 4H_2O$ derived from the BET-model parameters (see the Appendix for details). The predicted enthalpy of fusion of the phase $Mn(NO_3)_2\cdot 6H_2O$ in this model agrees with that reported by Riesenfeld and Milchsack[11].

Fig. 2 shows the binary phase diagram of the system recalculated with all parameters fitted in this work. The agreement seems quite good. Meanwhile, the vapor pressures of the saturated solution are also predicted and coincide with the experimental data very well (Fig. 3). Although the BET model parameters are fitted only to the experimental water activities at 298.15 K

Table 2 Fitted logarithm of activity production and predicted latent warm of solid phase

Phase	*A*	*B*	*C*
$Mn(NO_3)_2 \cdot 6H_2O$	38.845	− 25 924	2 672 400
$Mn(NO_3)_2 \cdot 4H_2O$	6.480	− 6 434.7	0
$Mn(NO_3)_2 \cdot 2H_2O$	2.637	− 3 618.1	0
$Mn(NO_3)_2 \cdot H_2O$	− 0.469	− 1 719.6	0

Phase	Enthalpy of fusion/ ($kJ \cdot mol^{-1}$)		
	Predicted in this work	Literature values	
$Mn(NO_3)_2 \cdot 6H_2O$	35.5	34.53[11]	40.16[12]
$Mn(NO_3)_2 \cdot 4H_2O$	28.8		

$\ln k_{Mn(NO_3)_2 \cdot nH_2O} = A + B/T + C/T^2$

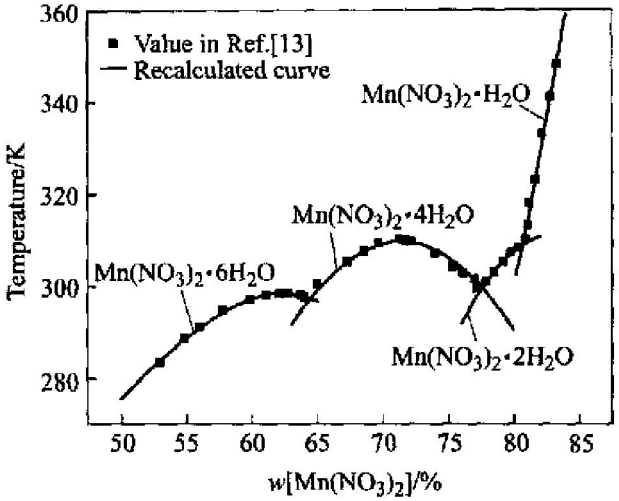

Fig. 2 Curves of recalculated $Mn(NO_3)_2$-H_2O binary system compared with experimental data from Ref. [13]

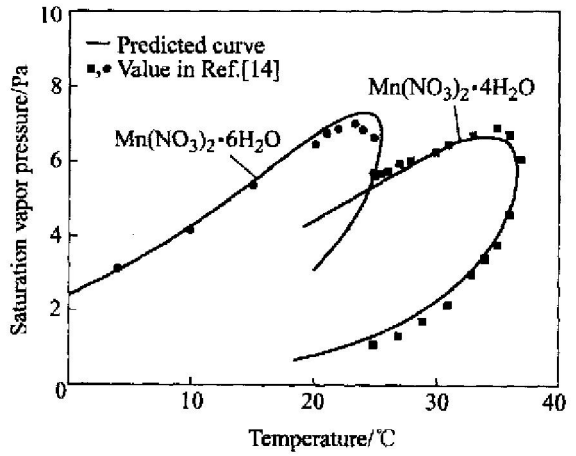

Fig. 3 Curves of predicted vapor pressures of saturated solution of manganous nitrate compared with experimental values in Ref. [14]

in the salt concentration up to 64% (mass fraction), the model can predict the properties of the binary salt-water solution up to 75% $Mn(NO_3)_2$ and in the temperature range of 277 − 310 K.

3 PREDICTION OF TERNARY SYSTEMS

In our previous works the binary systems $Mg(NO_3)_2$-H_2O, $Ca(NO_3)_2$-H_2O and $LiNO_3$-H_2O were treated with the BET model and their BET parameters are already known[5]. With the BET parameters of the $Mn(NO_3)_2$-H_2O system being fitted in this work, the phase diagrams of the ternary $Mn(NO_3)_2$-$M(NO_3)_n$-H_2O (M= Ca, Mg and Li) systems are calculated directly using Eqn. (1). The results are shown in Figs. 4, 5 and 6, respectively.

Based on our prediction, there are three eutectics (e1, e2 and E1 in Fig. 4) in the ternary system $Mn(NO_3)_2$-$Ca(NO_3)_2$-H_2O. Unfortunately, because of the formation of solid solution at 293 K, the two theoretical eutectics E1 and e2 do not exist any more. At 293 K the predicted isotherm of the phase $Ca(NO_3)_2 \cdot 4H_2O$ agrees with the experimental data very well, while that for $Mn(NO_3)_2 \cdot 6H_2O$ doesn't fit. Experimental data shows that the solubility of $Ca(NO_3)_2$ in the solid phase $Mn(NO_3)_2 \cdot 6H_2O_{(s)}$ is around 3% (mass fraction, the same below)[15], this may change the chemical potential of $Mn(NO_3)_2 \cdot 6H_2O$, leading to the shift of liquidus. According to our calculation, there should be an eutectic point e1 melting at 288 K at the composition of 42.1% $Mn(NO_3)_2$, 22.9% $Ca(NO_3)_2$ and 34.9% H_2O (see Table 3), provided that the liquidus of the solid solution keeps invariable as it does at 293 K. In order to test the accuracy of the prediction, further experiments are needed.

Different experimental isotherms at 293 K in the system $Mg(NO_3)_2$-$Mn(NO_3)_2$-H_2O were reported by several authors[16, 17]. Our prediction determines that the invariant point at 293 K lies close on the $Mn(NO_3)_2$-riched side, which agrees with the result of Zdanovskii et al[16] quite well and is different from Ref. [17]. In this ternary system three eutectics are predicted and their melting points and compositions are listed in Table 3.

Four eutectics are predicted in the system $LiNO_3$-$Mn(NO_3)_2$-H_2O, as shown in Fig. 6 and Table 3. Up to date, no exact experimental data of solubility are reported for this ternary system, except a patent information states[3] that a composition containing 23.5% − 62.8% $Mn(NO_3)_2 \cdot 6H_2O$, 19.4% − 39.8% $LiNO_3 \cdot 3H_2O$ melts at 286.7 13 − 289.4 K. Note that the predicted eutectic point e1 (Fig. 6) containing 76.5% $Mn(NO_3)_2 \cdot 6H_2O$ and 23.5 % $LiNO_3 \cdot 3H_2O$ melts at 284.4 K, both results agree approximately with each other's.

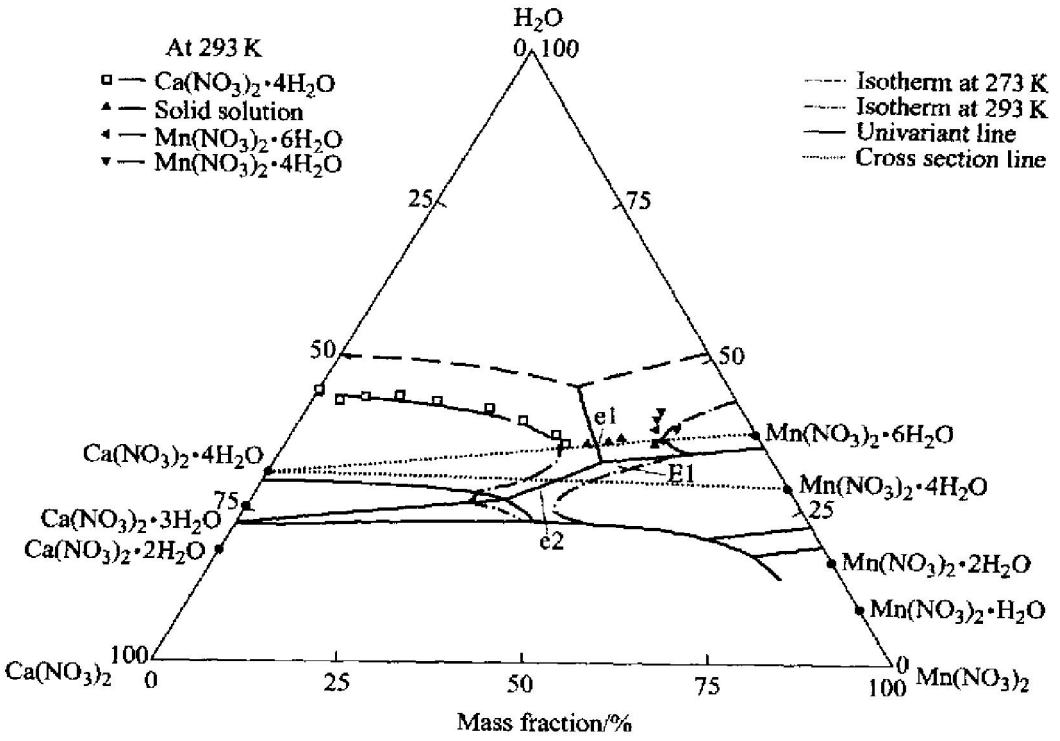

Fig. 4 Predicted phase diagram of ternary system $Mn(NO_3)_2$-$Ca(NO_3)_2$-H_2O compared with experimental data from Ref. [15]

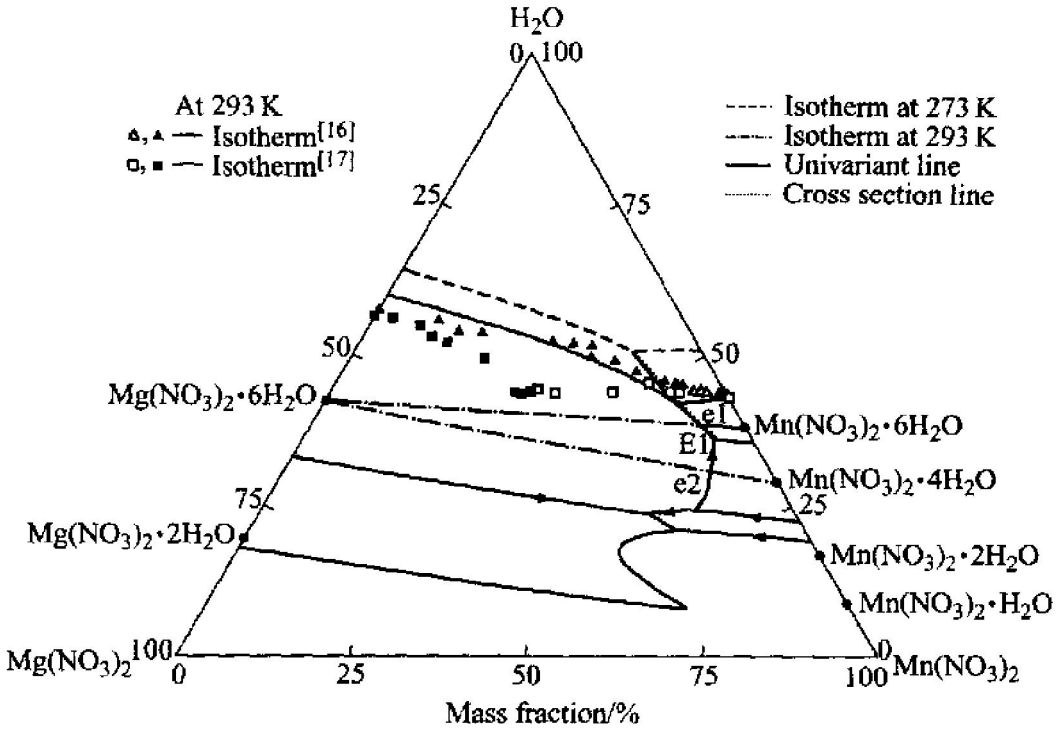

Fig. 5 Predicted phase diagram of ternary system $Mg(NO_3)_2$-$Mn(NO_3)_2$-H_2O compared with experimental data

4 DISCUSSION

As shown above, the BET-model can satisfactorily reproduce the activity properties of components and phase diagrams of salt-water systems with only two parameters. In a limited temperature range, the values of the parameters, namely, the number of adsorption sites and the adsorption energy of water on salt, can be treated as constants. Therefore, the parameters fitted at a specific temperature can be used for the property description of a system at other temperatures. This makes the BET-model especially useful for the phase diagram prediction of those systems of limited experimental data. Besides, a series of thermodynamic models has been developed for the de-

Table 3 Predicted melting points and compositions in $Mn(NO_3)_2$-$Me(NO_3)_n$-H_2O ternary systems

System	Property	Melting point/K	Mass fraction/%
$Ca(NO_3)_2 \cdot 4H_2O$-$Mn(NO_3)_2 \cdot 6H_2O$	e1	288.1	$Ca(NO_3)_2$ 22.9, $Mn(NO_3)_2$ 42.1
$Mg(NO_3)_2 \cdot 6H_2O$-$Mn(NO_3)_2 \cdot 6H_2O$	e1	295.6	$Mg(NO_3)_2$ 6.0, $Mn(NO_3)_2$ 55.9
$Mg(NO_3)_2 \cdot 6H_2O$-$Mn(NO_3)_2 \cdot 4H_2O$	e2	305.1	$Mg(NO_3)_2$ 8.5, $Mn(NO_3)_2$ 60.9
$Mg(NO_3)_2 \cdot 6H_2O$-$Mn(NO_3)_2 \cdot 6H_2O$-$Mn(NO_3)_2 \cdot 4H_2O$	E1	295.1	$Mg(NO_3)_2$ 5.2, $Mn(NO_3)_2$ 58.8
$LiNO_3 \cdot 3H_2O$-$Mn(NO_3)_2 \cdot 6H_2O$	e1	286.4	$LiNO_3$ 13.2, $Mn(NO_3)_2$ 48.0
$LiNO_3 \cdot 3H_2O$-$Mn(NO_3)_2 \cdot 4H_2O$	e2	286	$LiNO_3$ 19.3, $Mn(NO_3)_2$ 47.2
$LiNO_3$-$Mn(NO_3)_2 \cdot 4H_2O$	e3	303	$LiNO_3$ 7.4, $Mn(NO_3)_2$ 66.3
$LiNO_3 \cdot 3H_2O$-$Mn(NO_3)_2 \cdot 4H_2O$-$Mn(NO_3)_2 \cdot 6H_2O$	E1	284.1	$LiNO_3$ 14.2, $Mn(NO_3)_2$ 50.2

E—Ternary eutectic point; e—Binary eutectic point.

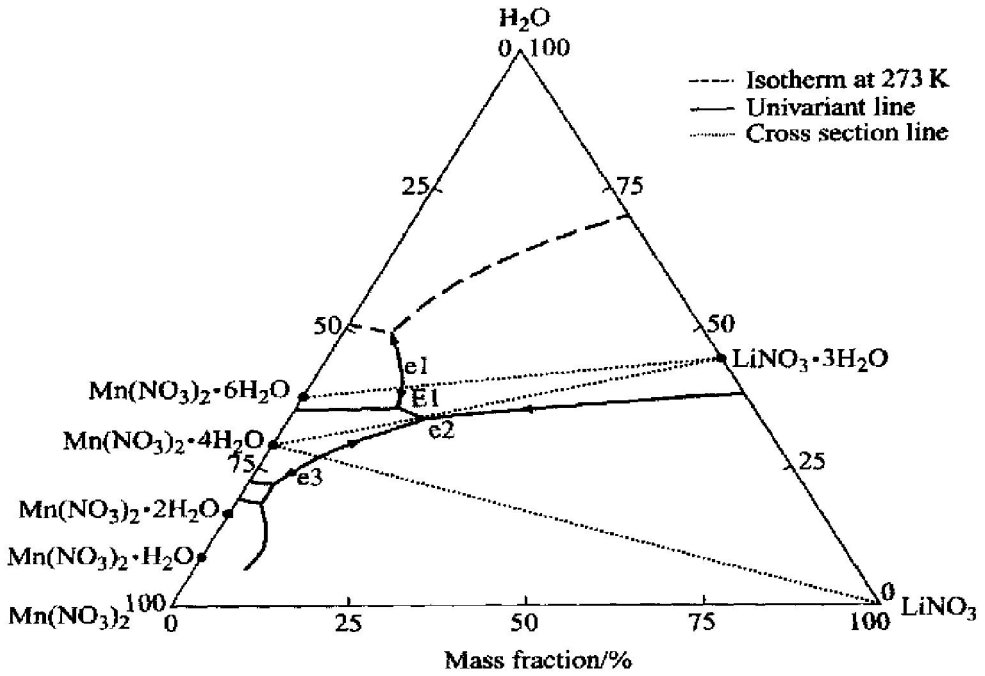

Fig. 6 Predicted phase diagram of ternary system $Mn(NO_3)_2$-$Li(NO_3)_2$-H_2O

scription of the properties of binary or multi-component salt-water systems, such as Pitzer ionic interaction model[18, 19], extended NRTL[20] and UNIQUAC[21] models et al.

The Pitzer ionic interaction model can accurately describe the activity properties of components in over 260 binary electrolyte systems with salt concentration lower than 6 mol/L. Over that limit the model is subject to a large uncertainty[20]. All the same, many researchers have tried to use this model to represent the solubility properties of some aqueous salt systems[22-24]. Because of the uncertainty of the model parameters, the experimental data of component activity at more than one temperatures are necessary for the determination of the temperature coefficients of the Pitzer-parameters. So, as Renon once described[25], the Pitzer model has no predictive value for one-salt aqueous solution.

Accounting for the short range interaction between ions and solvent with the NRTL model method[26] and the long range interaction between ions with the Deby-Hückel equation proposed by Pitzer[18], Chen et al[27] proposed a extended NRTL model for electrolyte systems. In comparison to the Pitzer model with 4 parameters for a binary electrolyte system, the Chen-model needs only two parameters, as those in the NRTL model. Later, Chen et al[20] extended the description range of their model to saturation electrolyte solution by treating some dissociated ion M^{Z+} as hydrated ion $M(H_2O)_n^{Z+}$ and the solute as partially dissociated one through a flexible fraction of dissociation. Their new model has five parameters. Like the Pitzer

model, the determination of the temperature coefficients of the parameters needs experimental data at more than one temperature.

Using extended UNIQUAC model, Iliuta, Thomsen and Rasmussen[21] have represented a series of heavy salt solubility, including the system $Mn(NO_3)_2$-H_2O. In the model they expressed the short range interaction between ions and the solvent water in the UNIQUAC method and the long range interaction in a Deby-Hückel term. Totally, six parameters including their temperature coefficients were used for each binary systems and their values were obtained by fitting to the experimental osmotic coefficients and solubilities. For the system $Mn(NO_3)_2$-H_2O they only fitted the parameters values to the solubility data. So, they got the correct parameters for the binary system which is doubtful. Table 4 lists the deviation of the reproduced results by different models against the experimental solubility data. With only two parameters, the BET model presents better result than the extended UNIQUAC model. The reproduces of other $Mn(NO_3)_2$ containing ternary solubility systems with the extended UNIQUAC model, such as KNO_3-$Mn(NO_3)_2$-H_2O and $MnCl_2$-$Mn(NO_3)_2$-H_2O, show also large absolute deviations (over 10%)[21].

Table 4 Deviation of solubility data in binary system $Mn(NO_3)_2$-H_2O reproduced by different models against experimental values

Number of data points	Average absolute deviation in mass/ %		Reference of experimental solubility data
	Extended UNIQUAC model[21]	This work (BET Model)	
31	1.1	0.26	[31]
1	3.1	0.75	[28]

5 CONCLUSION

Phase diagram of the binary system $Mn(NO_3)_2$-H_2O has been reproduced with the BET model. The model parameter (ε) decreases with the decrease of the ionic radius in the order $Ca^{2+} \rightarrow Mn^{2+} \rightarrow Zn^{2+}$, showing reasonable agreement. Meanwhile, the BET-model with fewer numbers of parameters presents better result than the extended UNIQUAC model in the reproduce of the solubility of the binary system $Mn(NO_3)_2$-H_2O. With the parameters fitted previously for other three binary systems, the $Mn(NO_3)_2$-$M(NO_3)_n$-H_2O (M= Ca, Mg and Li) ternary phase diagrams are predicted and compared with available experimental data. Eight new eutectics are predicted, provided no solid solution is formed. With the melting points ranging from 284 to 296.5 K, the predicted eutectic composition may be used as heat storage materials for the air-conditioning application.

Appendix

The evaluation of the enthalpy of fusion of the solid phase $Mn(NO_3)_2 \cdot 6H_2O$ can be carried out though calculating the enthalpies of the following reactions:

$$Mn(NO_3)_{2(l)} + 6H_2O_{(l)} = Mn(NO_3)_2 \cdot 6H_2O_{(s)} \quad (1')$$

$$Mn(NO_3)_{2(l)} + 6H_2O_{(l)} = [Mn(NO_3)_2 + 6H_2O]_{aq} \quad (2')$$

The subscripts (l), (s) and (aq) denote the pure liquid phase of the components, the solid phase and the salt aqueous solution, respectively. The enthalpy of the reaction (2′) can be obtained according to

$$H^0 = G^0 - T\frac{\partial G^0}{\partial T} \quad (3')$$

$$G^0 = RT\ln k \quad (4')$$

Substituting the value of $\ln k$ for the phase $Mn(NO_3)_2 \cdot 6H_2O$ in Table 2 into Eqns. (3) and (4), we have $\Delta H_{(1A)} = -65.6\ kJ \cdot mol^{-1}$.

The enthalpy of the reaction (2′) describes essentially the enthalpy of mixing of the pure water and the hypothetical supercooled molten salt $Mn(NO_3)_2$. In the meaning of the BET model, this term equals the difference of the adsorption energy of water molecule on the salt "molecule" and the condensation energy of water (ε, $kJ \cdot mol^{-1}$). At the mixture $[Mn(NO_3)_2 + 6H_2O]$ the real adsorption number $N_{A(M)}$ of water molecule on 1 mol salt A is calculated to be $0.725\ 7 \times 6 = 4.354\ 2$mol. Thus, we obtain the warm of mixing $\Delta H_{(2A)} = \varepsilon N_{A(M)} = -7.16 \times 4.354\ 2 = -31.17$ kJ and the enthalpy of fusion of the solid phase $Mn(NO_3)_2 \cdot 6H_2O$: $\Delta H_{(2A)} - \Delta H_{(1A)} = 35.5$ kJ/ mol.

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