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Phase diagrams and thermochemical modeling of salt lake brine systems. II. NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O systems

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ABSTRACT

This study is part of a series of studies on the development of a multi-temperature thermodynamically consistent model for salt lake brine systems. Under the comprehensive thermodynamic framework proposed in our previous study, the thermodynamic properties of the binary systems (i.e., NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O) are simulated by the Pitzer–Simonson–Clegg (PSC) model. Various thermodynamic properties (i.e., water activity, osmotic coefficient, mean ionic activity coefficient, enthalpy of dilution and solution, relative apparent molar enthalpy, heat capacity of aqueous phase and solid phases) are collected and fitted to the model equations. The thermodynamic properties of these systems are reproduced or predicted by the obtained model parameters. Comparison to the experimental or model values in the literature suggests that the model parameters determined in this study can describe all of the thermodynamic and phase equilibria properties over wide temperature and concentration ranges. This modeling study of binary systems provides a solid basis for property predictions of salt lake brines under complicated conditions.

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1. Introduction

Phase diagram calculations are a useful approach for studying the natural brine evolution and designing chemical engineering process to extract valuable salts from salt lake brines by predicting their salt formation sequence. In a previous study [1], the Pitzer–Simonson–Clegg (PSC) model [2,3] was chosen to represent the properties (e.g., solid–liquid equilibria) of highly soluble salt–water systems (i.e., LiCl + H₂O). In the parameterization process, various types of thermodynamic data (i.e., water activity a_w , salt activity coefficients γ_{\pm} , heat capacity of solution and solid phases c_p , enthalpy of dilution $\Delta_{dil}H_m$, enthalpy of solution $\Delta_{sol}H_m$ and solubility) were used as constraint conditions to guarantee parameter reliability. Emphasis was placed on the key role of the heat capacity of the solid phases and the aqueous phase in the model parameterization under multi-temperature conditions. Under the new parameterization framework, the thermodynamic properties of the LiCl + H₂O system was simulated in a wide temperature range from 190 K to 400 K and a salt concentration range from a dilute solution to the solubility limit. Herein, the

modeling results for the NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O binary systems are reported. The modeling of the binary systems will provide a solid basis for property prediction of multi-component systems at various temperature and concentration conditions.

2. Thermodynamic framework and parameter regression method

The thermodynamic framework, parameter regression and data weighting method were performed according to our previous study [1]. For any species in an aqueous solution and any solid phase, its standard Gibbs energy as a function of temperature can be written as shown in Eq. (1)

$$G_i^{\circ}(t) = A(t - t \ln t) - Bt^2/2 - Ct^3/6 - Dt^4/12 - E/2t + F - Gt \quad (1)$$

with $t = (T/K)/1000$ and T is the absolute temperature in Kelvin.

Eq. (1) is slightly different from Eq. (18) in [1]. The latter has a typographical minor mistake.

The standard enthalpy and entropy as well as the heat capacity can be derived from the fundamental thermodynamic relationships in (Eqs. (2)–(4):

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Table 1Sources of experimental data used for parameterization of the NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O binary systems.

System	Data property ^a	Temperature range (K)	Concentration range (mol kg ⁻¹)	Reference
NaCl + H ₂ O	Activity	273.15–573.15	0.002–10.413	[8–25]
	Thermal	283.15–498.2	0.0002–6.078	[26–47]
	SLE	252.15–573.15	5.1401–10.413	[10,48,49,53–57]
KCl + H ₂ O	Activity	273.15–474	0.002–8.075	[11,61–75]
	Thermal	268.15–423.65	0.01–4.66	[32,34,35,40,46,76–80]
	SLE	262.49–573.15	3.299–14.67	[50,55–57,81–84]
MgCl ₂ + H ₂ O	Activity	298.15–524.12	0.001–12.094	[64,67,87–95]
	Thermal	278.15–423.65	0.002–5.7	[43,96–100]
	SLE	239.55–523.15	2.725–16.631	[101–108]
CaCl ₂ + H ₂ O	Activity	273.15–524.12	0.001–21.8803	[11,64,109–117]
	Thermal	283.15–526.25	0.0001–7.2589	[32,98,99,114,118–124]
	SLE	223.35–503	3.9–29.6	[102,107,125,126]

^a Activity stands for water activity, osmotic coefficient and mean ionic activity coefficient; thermal stands for enthalpy of dilution, enthalpy of solution, relative apparent molar enthalpy, specific heat and apparent molar heat capacity; SLE stands for solid–liquid equilibria data.

Table 2Assessed PSC model parameters for NaCl (aq), KCl (aq), MgCl₂ (aq) and CaCl₂ (aq).

Parameter ^a	$P(T) = a_0 + a_1T + a_2T \ln(T) + a_3T^2 + a_4T^3 + a_5/T$					
	a_0	a_1	a_2	a_3	a_4	a_5
$B_{\text{NaCl(aq)}}$	5.2673540876E+04	–1.2862655402E+03	2.1830667409E+02	–4.0147229213E–01	1.3816150751E–04	–2.3797399473E+06
$B_{\text{NaCl(aq)}}^1$	0	0	0	0	0	0
$W_{\text{NaCl(aq)}}$	–2.3830547835E+04	5.5315830040E+02	–9.2648756954E+01	1.5539677186E–01	–4.7473038278E–05	1.1116441567E+06
$U_{\text{NaCl(aq)}}$	–6.0948803248E+04	1.4186905570E+03	–2.3774274508E+02	3.9997134051E–01	–1.2255433850E–04	2.8362735721E+06
$V_{\text{NaCl(aq)}}$	4.1007318832E+04	–9.5409005339E+02	1.5989161291E+02	–2.6913638706E–01	8.2515153533E–05	–1.9138348495E+06
$B_{\text{KCl(aq)}}$	3.9560903013E+05	–9.8601244399E+03	1.6795521770E+03	–3.1489849139E+00	1.1015107342E–03	–1.7350430832E+07
$B_{\text{KCl(aq)}}^1$	0	0	0	0	0	0
$W_{\text{KCl(aq)}}$	1.2987116507E+05	–3.2812329495E+03	5.5990363228E+02	–1.0553567540E+00	3.6745900194E–04	–5.5544841742E+06
$U_{\text{KCl(aq)}}$	3.5398179757E+05	–8.8936745021E+03	1.5160440445E+03	–2.8419620324E+00	9.8508754040E–04	–1.5257774170E+07
$V_{\text{KCl(aq)}}$	–2.4684267843E+05	6.1767236620E+03	–1.0521318451E+03	1.9648394849E+00	–6.7918013932E–04	1.0700347556E+07
$B_{\text{MgCl2(aq)}}$	2.2160457529E+05	–5.4025180270E+03	9.2648218831E+02	–1.8891057047E+00	7.5897357565E–04	–1.0948508689E+07
$B_{\text{MgCl2(aq)}}^1$	4.4144567179E+04	–1.9634710700E+03	3.4416850971E+02	–5.8683267155E–01	9.3166963214E–05	1.8451297613E+06
$W_{\text{MgCl2(aq)}}$	–2.5343640484E+04	2.9584383323E+02	–4.2111517269E+01	1.5871842534E–02	3.9411692475E–07	2.1463072624E+06
$U_{\text{MgCl2(aq)}}$	–6.2496030510E+04	8.6367865923E+02	–1.2835374147E+02	7.8895849606E–02	2.7192072092E–06	4.7326089303E+06
$V_{\text{MgCl2(aq)}}$	3.2841791832E+04	–2.4398423230E+02	2.7438965042E+01	5.5543949322E–02	–2.8951196741E–05	–3.2296234097E+06
$B_{\text{CaCl2(aq)}}$	–1.7901762478E+05	4.3285790251E+03	–7.3203212295E+02	1.3109912940E+00	–4.3339436344E–04	8.0465966201E+06
$B_{\text{CaCl2(aq)}}^1$	1.4662428664E+04	–5.1819311781E+01	6.9522361789E–02	6.8777977139E–02	–2.8849305145E–05	–1.3465360612E+06
$W_{\text{CaCl2(aq)}}$	4.5781716418E+04	–9.2860227154E+02	1.5150146947E+02	–2.1818619126E–01	5.8451136180E–05	–2.5077303118E+06
$U_{\text{CaCl2(aq)}}$	1.0530013078E+05	–2.1314551169E+03	3.4745553913E+02	–4.9530470490E–01	1.2921813853E–04	–5.7743280731E+06
$V_{\text{CaCl2(aq)}}$	–6.1177829337E+04	1.1439533907E+03	–1.8296766791E+02	2.2678808074E–01	–4.8711058889E–05	3.5698842777E+06

^a All of the parameters can be found in Eqs. (1)–(6) in Ref. [1]; for NaCl(aq) and KCl(aq), $\alpha=13.0$, $\alpha_1=0.0$, and for MgCl₂ (aq) and CaCl₂ (aq), $\alpha=13.0$ and $\alpha_1=2.0$.

$$H_i^\ominus(t) = At + Bt^2/2 + Ct^3/3 + Dt^4/4 - E/t + F \quad (2)$$

$$S_i^\ominus(t) = A \ln t + Bt + Ct^2/2 + Dt^3/3 - E/2t^2 + G \quad (3)$$

$$C_{p,i}^\ominus(t) = A + Bt + Ct^2 + Dt^3 + E/t^2 \quad (4)$$

For any aqueous ion, its temperature coefficients (A , B , C , D and E) in (Eqs. (1)–(4)) are determined by fitting the individual isobaric heat capacity values calculated from the Helgeson–Kirkham–Flowers (HKF) equations of state (EOS) [4,5] that are incorporated into the CHNOSZ software package [6] over a temperature range of 273.15 K to 523.15 K. The F and G coefficients in (Eqs. (2) and (3)) are evaluated by substituting $H_{i,298.15}^\ominus$ and $S_{i,298.15}^\ominus$ in the equations. The enthalpy and entropy values at 298.15 K are available in the same software package [6].

For an anhydrous salt solid whose heat capacity as a function of temperature is known, its A , B , C , D and E parameters can be read out directly. For hydrated salt solids whose heat capacity data are unavailable, their heat capacity $C_{p,\text{MX} \cdot n\text{H}_2\text{O(s)}}^\ominus(t)$ can be estimated using group contribution approaches:

$$C_{p,\text{MX} \cdot n\text{H}_2\text{O(s)}}^\ominus(t) = C_{p,\text{MX(s)}}^\ominus(t) + nC_{p,\text{H}_2\text{O}}^\ominus \quad (5)$$

where $C_{p,\text{MX} \cdot n\text{H}_2\text{O(s)}}^\ominus(t)$ and $C_{p,\text{MX(s)}}^\ominus(t)$ are the heat capacity of the hydrated and anhydrous salt at temperature t , respectively, and $C_{p,\text{H}_2\text{O}}^\ominus$ is the group contribution of one crystal water molecule to the heat capacity of the hydrated salt independent of temperature and set to 43.5 J K⁻¹ mol⁻¹, as recommended by Archer [7].

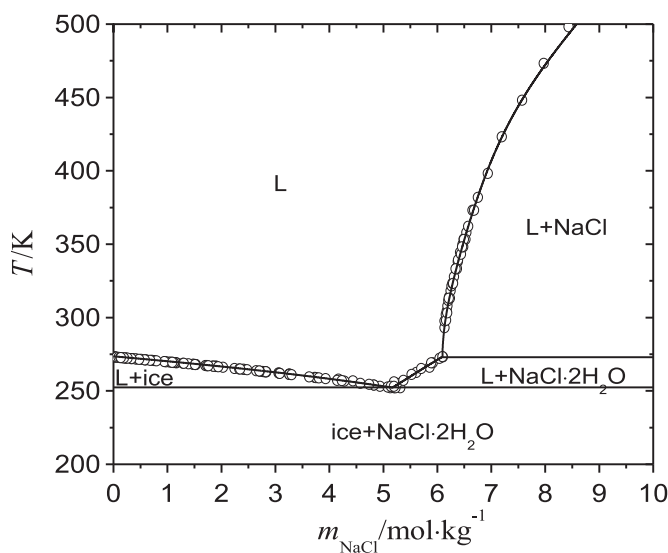
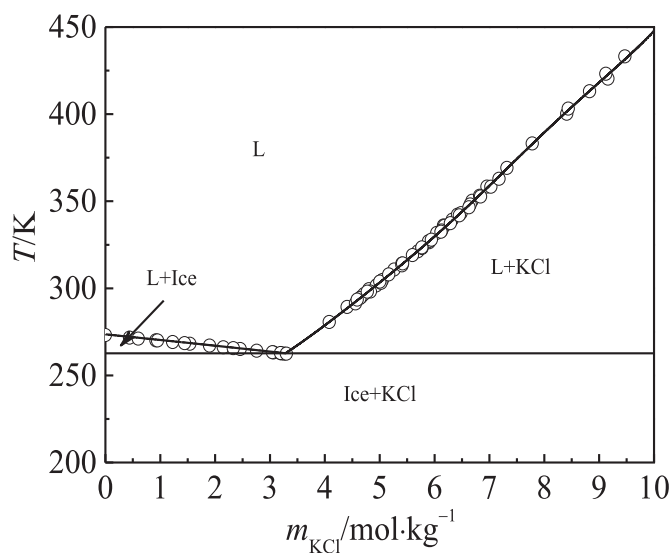
The rest parameters (F and G) of a solid phase will be evaluated by fitting to the solubility data at various temperatures.

For each binary system, the model parameters are also

Table 3

Gibbs free energy as a function of temperature for the studied solid and aqueous species involved at standard state.

Aqueous species or minerals	$G_m^0(t) = A(t - t \ln t) - Bt^2/2 - Ct^3/6 - Dt^4/12 - E/2t + F - Gt^a$							
	A	B	C	D	E	F	G	T (K)
Na ⁺ (aq) ^b	8348.7	−42244.5	80859.5	−55349.6	−127.822	−1885.564	18932.935	273–523
K ⁺ (aq) ^b	5097.33	−25943.2	49804.1	−34187.3	−77.8793	−1252.516	11654.894	273–523
Mg ²⁺ (aq) ^b	6638.14	−37893.1	79861.3	−60195.6	−83.0268	−1625.991	15708.155	273–523
Ca ²⁺ (aq) ^b	14540.6	−77281.2	154173	−110453	−205.156	−3275.405	33550.695	273–523
Cl [−] (aq) ^b	29421.3	−157725	316626	−227316	−412.404	−5660.068	68302.467	273–523
H ₂ O (l) ^c	−90.0669	748.166	−1377.94	1055.31	3.26118	−271.203	−191.886	180–523
H ₂ O (cr, l) ^c	13.44	20.2535	371.643	−418.377	−0.0301987	−300.209	42.01	100–273
NaCl (cr) ^d	50.7239	6.6723	−2.5172	10.1593	−0.2007	−427.1923	130.6230	273–523
NaCl · 2H ₂ O (cr) ^e	137.7239	6.6723	−2.5172	10.1593	−0.2007	−1039.1109	328.1839	252–273
KCl (cr) ^d	35.4160	70.0347	−91.3823	52.5243	0.1535	−447.9278	112.3270	263–453
MgCl ₂ · 12H ₂ O (cr) ^e	600.3073	2.4359	6.8589	−1.7290	−0.7299	−4450.3476	1342.4456	240–256
MgCl ₂ · 8H ₂ O (cr, α) ^e	426.3073	2.4359	6.8589	−1.7290	−0.7299	−3224.3210	942.5040	255–268
MgCl ₂ · 6H ₂ O (cr) ^e	339.3073	2.4359	6.8589	−1.7290	−0.7299	−2605.7284	757.7598	268–388
MgCl ₂ · 4H ₂ O (cr) ^e	252.3073	2.4359	6.8589	−1.7290	−0.7299	−1987.9437	528.4763	388–455
MgCl ₂ · 2H ₂ O (cr) ^e	165.3073	2.4359	6.8589	−1.7290	−0.7299	−1342.4036	339.4832	455–550
CaCl ₂ · 6H ₂ O (cr) ^e	348.2958	−35.0764	44.1278	−9.8480	−0.6743	−2709.5430	786.9744	220–303
CaCl ₂ · 4H ₂ O (cr, α) ^e	261.2958	−35.0764	44.1278	−9.8480	−0.6743	−2086.0574	602.3704	300–318
CaCl ₂ · 4H ₂ O (cr, β) ^e	261.2958	−35.0764	44.1278	−9.8480	−0.6743	−2072.7674	643.6994	300–318
CaCl ₂ · 4H ₂ O (cr, γ) ^e	261.2958	−35.0764	44.1278	−9.8480	−0.6743	−2069.1854	654.9591	300–318
CaCl ₂ · 2H ₂ O (cr) ^e	174.2958	−35.0764	44.1278	−9.8480	−0.6743	−1459.6190	420.0734	325–450
CaCl ₂ · H ₂ O (cr) ^e	130.7958	−35.0764	44.1278	−9.8480	−0.6743	−1160.8232	277.1566	450–465
CaCl ₂ · 1/3H ₂ O (cr) ^e	101.7958	−35.0764	44.1278	−9.8480	−0.6743	−946.4439	213.8421	465–520

^a $t = (T/K)/1000$.^b Determined by fitting the thermodynamic values calculated from the HKF equation of state [4,5].^c According to our previous study [1].^d Parameters A, B, C, D and E were taken from the NIST WebBook [131], and F and G were determined by fitting to experimental solubility data.^e Parameters A, B, C, D and E were estimated using Eq. (5), and F and G were determined by fitting to experimental solubility data.**Fig. 1.** Phase diagram for the NaCl+H₂O system. Symbols: experimental data [10,48,49,53–57]. Lines: the model values in this study.**Fig. 2.** Phase diagram for the KCl+H₂O system. Symbols: experimental data [50,55–57,81–84]. Lines: current model results.

regressed with the PSCBREG program [1]. All of the collected experimental data are fitted using PSCBREG in one simultaneous regression process.

3. Determination of parameters

The model parameters for the NaCl+H₂O, KCl+H₂O, MgCl₂

+H₂O and CaCl₂+H₂O binary systems were determined using various types of thermodynamic data including the water activity a_w and osmotic coefficient ϕ , enthalpy of dilution $\Delta_{dil}H_m$ or solution $\Delta_{sol}H_m$, heat capacity c_p and solid–liquid equilibria data. All of the data were available in the literature [8–128] and collected in Table 1. Among these data, the smoothed or model correlated values in comprehensive reviews [7,58–60,86,126–130] and the solubility experiment data for ice or the freezing point are cited for

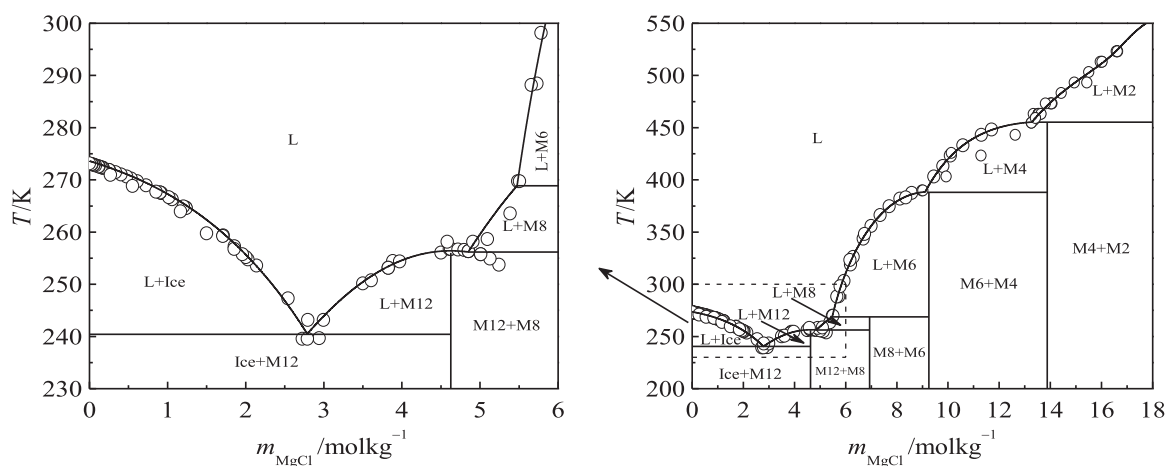


Fig. 3. Phase diagram for the $\text{MgCl}_2 + \text{H}_2\text{O}$ system. Symbols: experimental data [101–108]. Lines: the present model results.

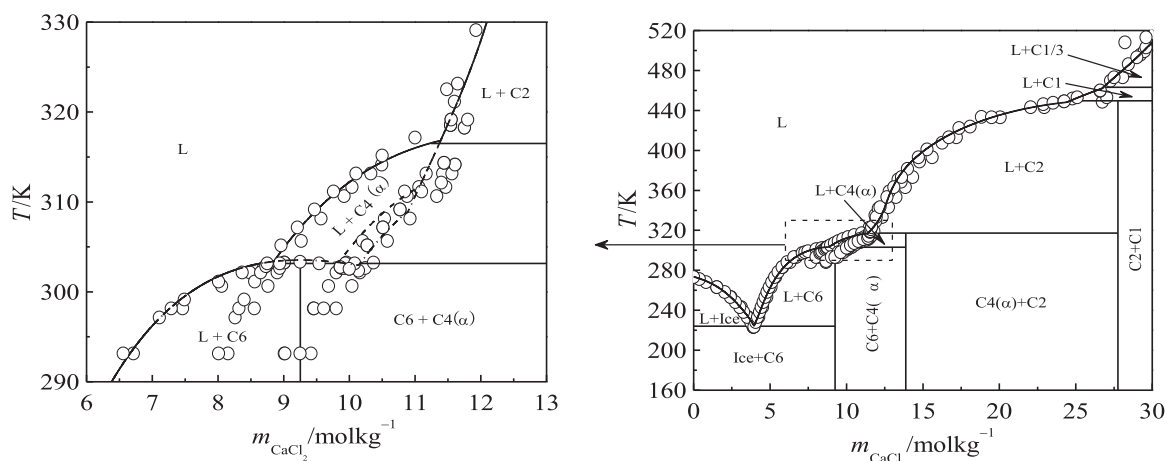


Fig. 4. Phase diagram for the $\text{CaCl}_2 + \text{H}_2\text{O}$ system. Symbols: experimental data [102,107,125,126]. Lines: current model results.

comparison to the data created by the current models rather than for determining the model parameters. These experimental data along with their assigned weight factors used for parameter determination are collected in Appendix A. The assessment procedure for the weight factors was described in our previous study [1].

The determined model parameters for these four binary systems are listed in Tables 2 and 3. Table 2 lists the Pitzer–Simonson–Clegg (PSC) model [2,3] parameters as a function of temperature. Table 3 shows the standard state properties and parameters of the Helgeson–Kirkham–Flowers (HKF) [4,5] equations of state (EOS) for water and all ions and solid species that were included in the current models. All of the parameters for the ions were fitted to the values calculated from the HKF equations that were incorporated in the CHNOSZ software package [6].

4. Results and discussion

4.1. Phase diagrams and invariant points

The calculated phase diagrams of the $\text{NaCl} + \text{H}_2\text{O}$, $\text{KCl} + \text{H}_2\text{O}$, $\text{MgCl}_2 + \text{H}_2\text{O}$ and $\text{CaCl}_2 + \text{H}_2\text{O}$ systems compared to the experimental

solubility data [10,49,50,58–62,81–84,101–108,126] are shown in Figs. 1–4. The predicted invariant points for the $\text{NaCl} + \text{H}_2\text{O}$, $\text{KCl} + \text{H}_2\text{O}$, $\text{MgCl}_2 + \text{H}_2\text{O}$ and $\text{CaCl}_2 + \text{H}_2\text{O}$ systems are listed in Table 4 and compared to the literature values [7,86,107,125,132]. As shown in Figs. 1–4 and Table 4, the solid–liquid equilibria data (i.e., the points on the solubility curve and the invariant points) are reproduced well by the current models. The ice solubility data for all of these systems were accurately predicted even though they were not used to regress the model parameters.

4.2. Component activity in the aqueous phases

Fig. 5 shows the deviations of the experimental water activities a_w from the model values in this work. Most deviations are less than 0.005 for all of the studied systems.

The a_w of the NaCl (aq) solution has been extensively and accurately studied. All of the data in literature and in this study are in good agreement.

The a_w of KCl (aq) that were converted from the vapor pressure data measured by Patil et al. [69] are remarkably overestimated, comparing with the data in literature and in this work, as shown in Fig. 5B. The most large relative deviations fall on the data at low temperature (303.15 K) for the low vapor pressure. Similar case of

Table 4Comparison of invariant points in the NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O systems.

Invariant point	Property ^a	Trans. temp. (K)	Comp. (wt%)	Ref.
Ice + NaCl · 2H ₂ O	E	251.95 252.15 252.29	23.3 23.1 23.2	[107] [7] This work
NaCl · 2H ₂ O + NaCl	P	273.25 273.28 273.31	26.3 26.27 26.26	[107] [7] This work
Ice + KCl	E	262.35 262.57 262.71	19.87 19.44 19.68	[107] [86] This work
Ice + MgCl ₂ · 12H ₂ O	E	239.55 239.10 240.48	21.0 21.17 20.97	[107] [132] This work
MgCl ₂ · 12H ₂ O	M	256.75 256.70 256.40	30.6 30.6 30.6	[107] [132] This work
MgCl ₂ · 12H ₂ O + MgCl ₂ · 8H ₂ O	E	256.35 256.40 256.19	31.6 31.57 31.58	[107] [132] This work
MgCl ₂ · 8H ₂ O + MgCl ₂ · 6H ₂ O	P	269.75 271.50 268.85	34.4 34.38 34.26	[107] [132] This work
MgCl ₂ · 6H ₂ O + MgCl ₂ · 4H ₂ O	P	389.85 389.00 388.63	46.2 46.03 46.4	[107] [132] This work
MgCl ₂ · 4H ₂ O + MgCl ₂ · 2H ₂ O	P	454.65 456.00 456.18	55.8 54.93 55.87	[107] [132] This work
Ice + CaCl ₂ · 6H ₂ O	E	223.35 223.45 224.58	30.22 30.5 30.5	[107] [125] This work
CaCl ₂ · 6H ₂ O + CaCl ₂ · 4H ₂ O (α)	P	303.25 302.85 303.35	50 49.21 49.55	[107] [125] This work
CaCl ₂ · 4H ₂ O(α) + CaCl ₂ · 2H ₂ O	P	318.25 318.55 316.82	56.6 56.15 55.82	[107] [125] This work
CaCl ₂ · 2H ₂ O + CaCl ₂ · H ₂ O	P	448.65 449.00 448.19	74.8 72.91 73.04	[107] [125] This work

Table 4 (continued)

Invariant point	Property ^a	Trans. temp. (K)	Comp. (wt%)	Ref.
CaCl ₂ · H ₂ O + CaCl ₂ · 1/3H ₂ O	P	460.00 462.05	74.7 74.78	[125] This work

^a E: eutectic point; P: peritectic point; M: melting point.

the data for LiCl (aq) was also observed in our previous work [1].

In comparison to the other three systems, the a_w of MgCl₂ (aq) from different sources [64,67,87–95] are very scattered (see Fig. 5C). Fortunately, most of the data in the literature and from this model agree with each other within an error range of ± 0.005 for a_w , which is acceptable for such large concentration and temperature ranges.

Fig. 5D shows the deviations of the a_w of CaCl₂ (aq) between the current model and literature data [11,64,109–115]. Most of the experimental data differed within ± 0.005 of the results from the current model. The a_w converted from vapor pressure measurements by Duckett [111], Jakli [112] and Sako [115] differed from that of the current model, and the maximum absolute derivation of a_w was approximately 0.02. The insufficient precision of these data was previously discussed by Gruszkiewicz and Simonson [113]. The previously determined water activities [11,64,109,110,113,114] are in good agreement with those from the current model, and the maximum absolute derivation was less than 0.005.

Comparisons of the model values in this study and those from the literature for MgCl₂(aq) are shown in Figs. 6 and 7. The model values for the water activity and mean ionic activity coefficient in this study are in good agreement with the model values reported by Holmes and Mesmer [91] and Wang et al. [128]. Both our model and the model reported by Wang et al. are valid to the saturation concentration. However, the model reported by Holmes and Mesmer was only valid to approximately 4 mol kg⁻¹.

Fig. 8 shows a comparison of the vapor pressure of a saturated MgCl₂(aq) solution that was predicted by the current model and reported in literature [133–135]. The PSC model using the current model parameters can simultaneously describe the solubility (Fig. 3) and the vapor pressure (Fig. 8) of saturation solutions. Therefore, the self-consistency of the current model was verified. Morillon et al. [133] reported the vapor pressure of a saturated MgCl₂(aq) solution but the corresponding solid phases were not reported. Because all of their data agree with the values predicted in this study for MgCl₂ · 6H₂O(s) in a temperature range from 248 K to 283 K, the equilibrium solid phase in the experiments should be MgCl₂ · 6H₂O(s) at temperatures less than 269 K. An analogous case was observed in the LiCl + H₂O system, as discussed in our previous study [1].

The model value comparisons of the water activities and mean ionic activity coefficients of CaCl₂(aq) are shown in Figs. 9 and 10, respectively. Although the model values from the literature [113,125,136] were not used for the current parameterization, they are in good agreement with the current model values.

Fig. 11 shows the vapor pressure of saturated CaCl₂(aq) solutions. The values predicted from the model are also in good agreement with the previously reported experimental data.

4.3. Thermal properties of aqueous phases

The standard deviations of the model for the thermal properties of the NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O systems are listed in Table 5. For MgCl₂(aq), the remarkably large deviation of the apparent molal heat capacities are due to the

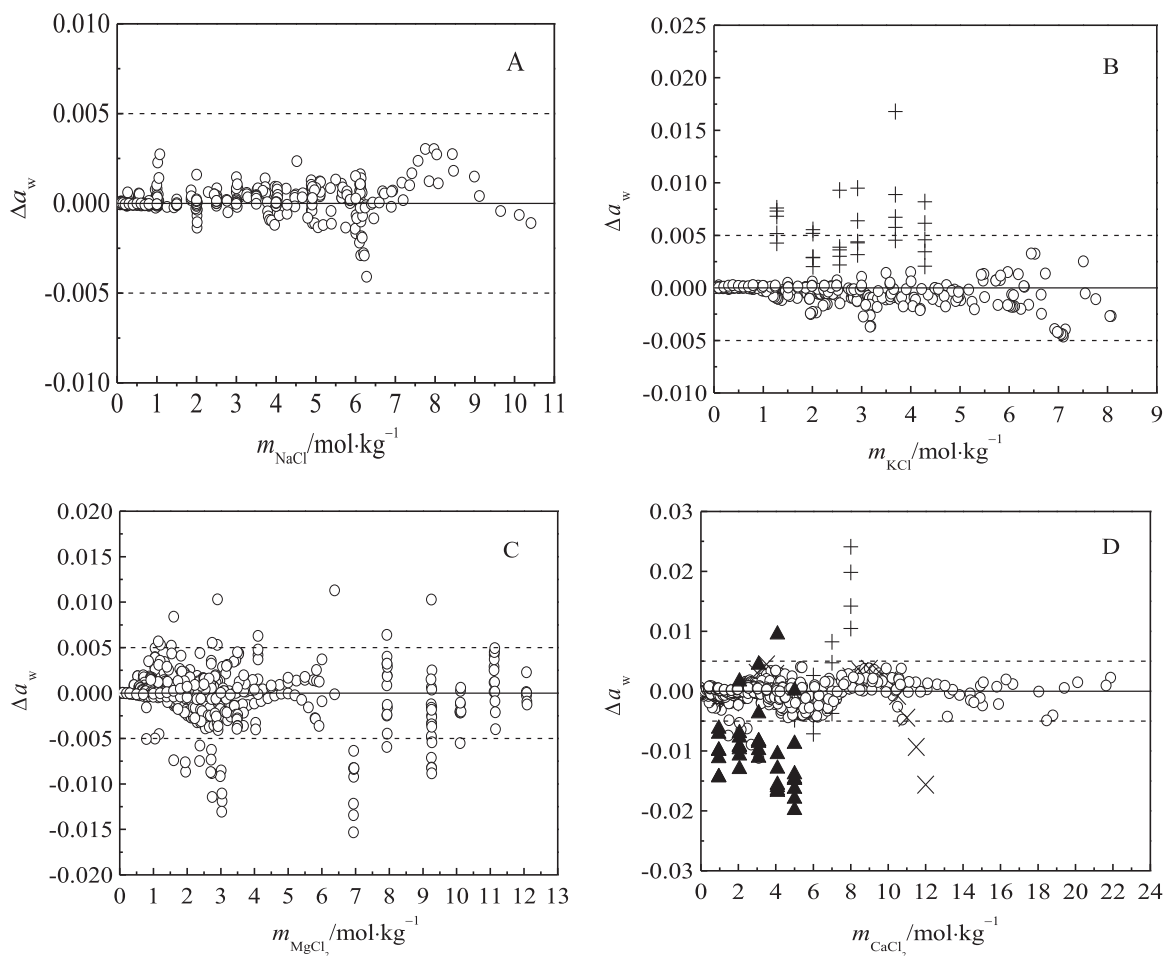


Fig. 5. Differences ($\Delta a_w = a_w(\text{exp.}) - a_w(\text{calc.})$) between the experimental water activities $a_w(\text{exp.})$ in the literature and the model values $a_w(\text{calc.})$ in this study. A: NaCl (aq), \circ [8–19]; B: KCl (aq), \circ [11,61–68,70–72], + [69]; C: MgCl_2 (aq), \circ [64,67,87–95]; D: CaCl_2 (aq), \circ [11,64,109–115], \times [111], + [112], \blacktriangle [115].

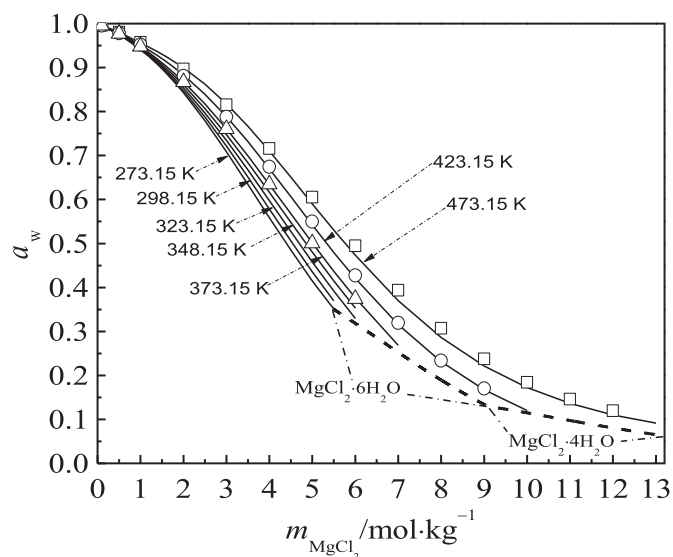


Fig. 6. Temperature and concentration dependence of the water activity a_w in a $\text{MgCl}_2(\text{aq})$ solution. — Calculated isotherms of a_w in this study and --- calculated a_w at the solubility limits. All of the symbols represent the model values that have been reported in the literature [128]: \square (473.15 K), \circ (423.15 K) and \triangle (373.15 K).

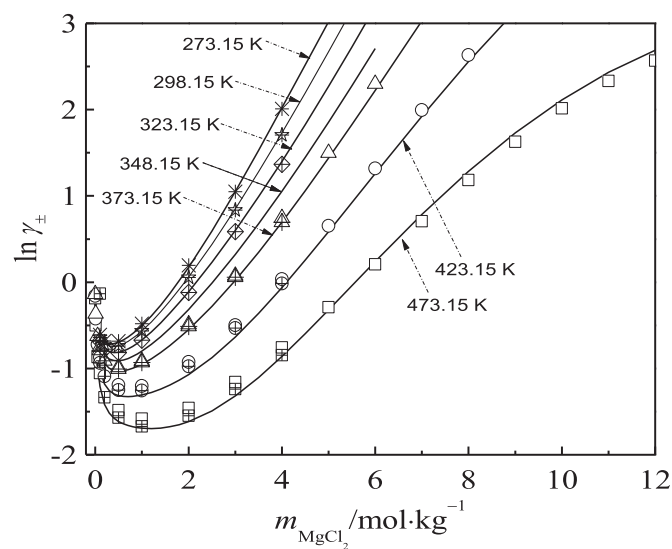


Fig. 7. Temperature and concentration dependence of the mean ionic activity coefficient γ_{\pm} in a $\text{MgCl}_2(\text{aq})$ solution. — Calculated isotherms of $\ln \gamma_{\pm}$ in this study. All of the symbols are model values that have been reported in the literature: \triangle (373.15 K) [128], \circ (423.15 K) [128], \square (473.15 K) [128], $*$ (273.15 K) [91], \otimes (298.15 K) [91], \boxtimes (323.15 K) [91], \boxtriangle (373.15 K) [91], \boxtimes (423.15 K) [91] and \boxtimes (473.15 K) [91].

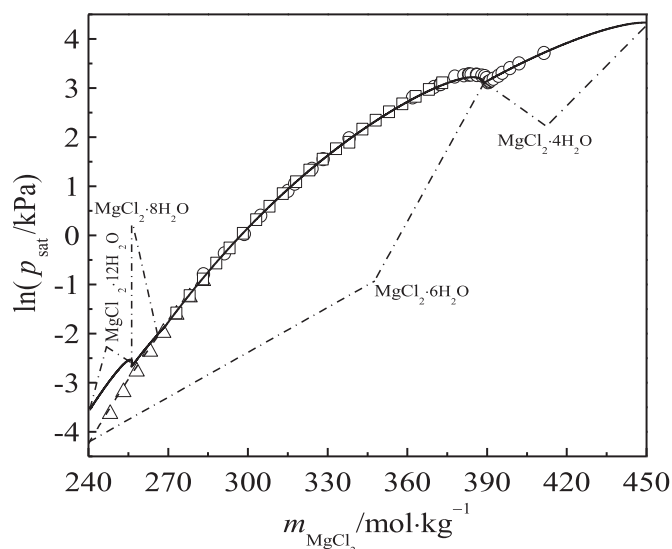


Fig. 8. Water vapor pressure p_{sat} of a saturated $\text{MgCl}_2(\text{aq})$ solution. All of the lines are model values in this study: — stable equilibrium and --- metastable equilibrium. The symbols are experimental values that have been reported in the literature: Δ [133], \square [134] and \circ [135].

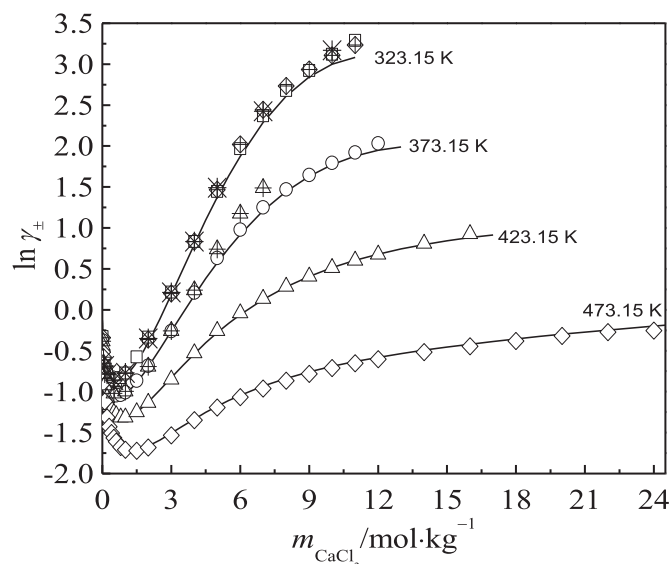


Fig. 10. Temperature and concentration dependence of the mean ionic activity coefficient γ_{\pm} in a $\text{CaCl}_2(\text{aq})$ solution. — Calculated isotherms of $\ln \gamma_{\pm}$. All of the symbols are model or smoothed values that have been reported in the literature: \square (323.15 K) [113], \circ (373.15 K) [113], Δ (423.15 K) [113], \diamond (473.15 K) [113], $*$ (323.15 K) [125], \boxtimes (323.15 K) [136] and \otimes (373.15 K) [136].

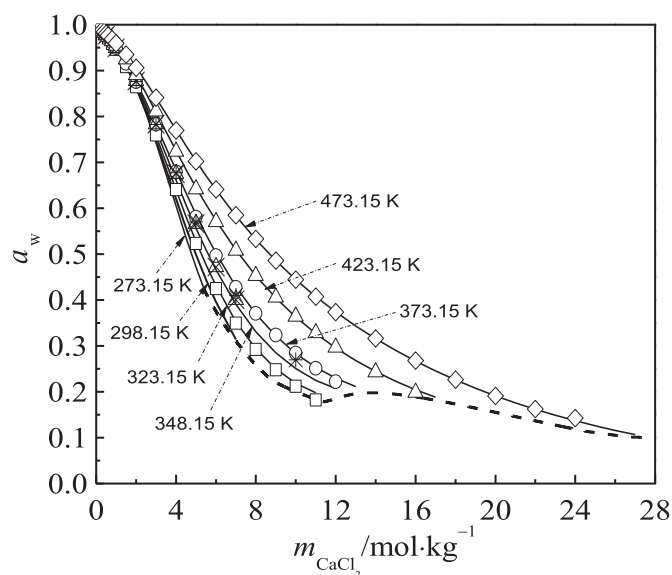


Fig. 9. Temperature and concentration dependence of the water activity a_w in a $\text{CaCl}_2(\text{aq})$ solution. — Calculated isotherms of a_w in this study and --- calculated a_w at the solubility limits in this study. All of the symbols are model or smoothed values that have been reported in the literature: \square (323.15 K) [113], \circ (373.15 K) [113], Δ (423.15 K) [113], \diamond (473.15 K) [113], $*$ (373.15 K) [125] and \otimes (373.15 K) [136].

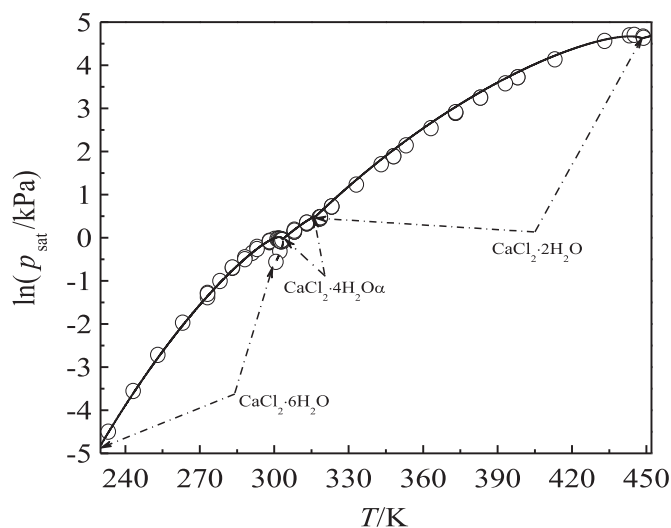


Fig. 11. Water vapor pressure p_{sat} of a saturated $\text{CaCl}_2(\text{aq})$ solution. Solid line: model values in this study. Symbols: previously reported experimental values [133,137–140].

experimental values measured by Call et al. [100] being for very dilute MgCl_2 solution.

Figs. 12 and 13 show the relative apparent molar enthalpies and specific heat capacities, respectively, of $\text{CaCl}_2(\text{aq})$ at various temperatures. The relative apparent molar enthalpies of $\text{CaCl}_2(\text{aq})$ in this study are consistent with previously reported data [113,125] even though the latter were not used for model parameterization

in this study. The specific heat capacities of $\text{CaCl}_2(\text{aq})$ at 298.15 K to 373.15 K, which were calculated from the current model, are in good agreement with previously reported experimental data [99,124].

4.4. Standard state properties of solid phases

The evaluated thermodynamic values of the solid phases in the four binary systems at standard state and 298.15 K are

summarized in Table 6.

The thermodynamic values ($\Delta_f G_m^\ominus$, $\Delta_f H_m^\ominus$, S_m^\ominus and $C_{p,m}$) of NaCl(cr), NaCl·2H₂O(cr) and KCl(cr), which were calculated by the current model, are in good agreement with the literature values. The deviations between the results from this study and those in the literature for the MgCl₂·12H₂O(cr), MgCl₂·8H₂O(cr), MgCl₂·6H₂O(cr), MgCl₂·4H₂O(cr), CaCl₂·6H₂O(cr), CaCl₂·4H₂O(cr, α), CaCl₂·4H₂O(cr, β) and CaCl₂·4H₂O(cr, γ) solid phases are acceptable. However, the differences for the MgCl₂·2H₂O(cr), CaCl₂·2H₂O(cr), CaCl₂·H₂O(cr) and CaCl₂·1/3H₂O(cr) solid phases are significant. It is difficult to determine which results are more reliable at the present states. In fact, the heat capacities of most hydrated salts are difficult to measure at an acceptable accuracy. The group contribution approach for the heat capacity evaluation is compromised one.

4.5. Dissociation pressures of hydrated salts

Figs. 14 and 15 show a comparison of the dissociation water vapor pressure for reactions (6A), (6B), (7A) and (7B). The experimental data in Figs. 14 and 15 were not used for parameterization.

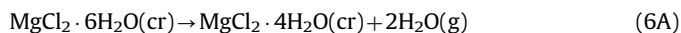


Table 5

Standard deviations of the model for the thermal properties of the NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O systems.

System	Standard deviation		
	Enthalpies of dilution (kJ mol ⁻¹)	Enthalpies of solution (kJ mol ⁻¹)	Apparent molal heat capacities (J K ⁻¹ mol ⁻¹)
NaCl + H ₂ O	0.185	0.181	7.52
KCl + H ₂ O	0.177	0.140	6.38
MgCl ₂ + H ₂ O	0.272	—	29.6
CaCl ₂ + H ₂ O	2.64	1.30	6.68

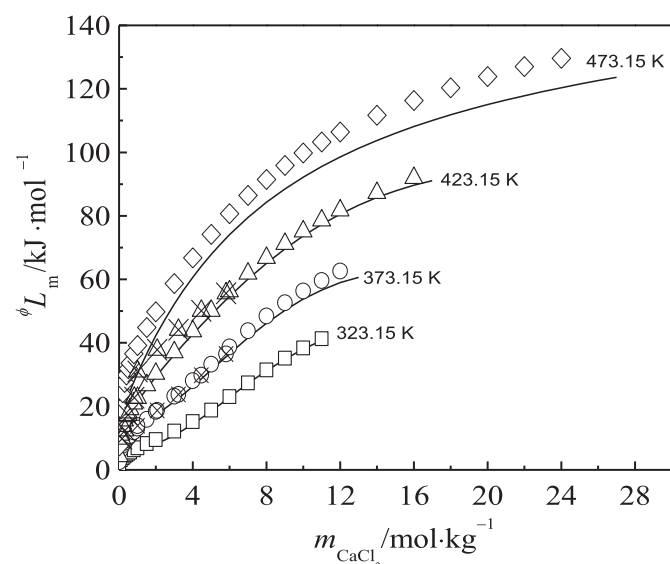


Fig. 12. Temperature and concentration dependence of the apparent relative molar enthalpy of the solute ϕL_m in a CaCl₂(aq) solution. — current model results. All of the symbols represent the previously reported model values: □ (323.15 K) [113], ○ (373.15 K) [113], △ (423.15 K) [113], ◇ (473.15 K) [113], ⊗ (373.15 K) [125] and ⊠ (423.15 K) [125].

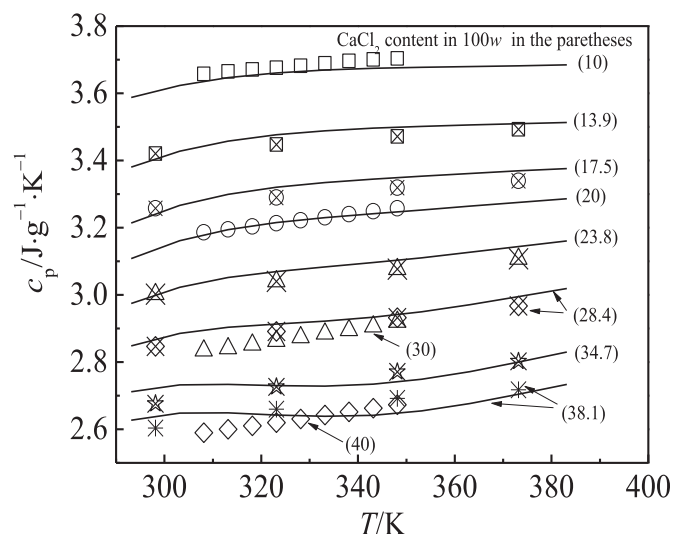
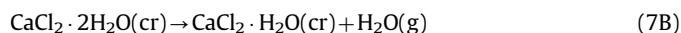
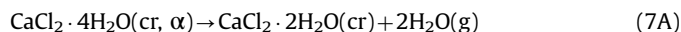
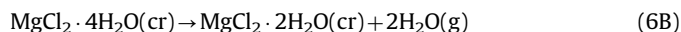


Fig. 13. Specific heat capacity c_p of CaCl₂(aq) as a function of temperature. The lines are model values at various CaCl₂ contents in 100w, and the symbols represent the experimental results from the literature: crossed symbols [99] and open symbols [124].



The results in Fig. 14 indicate that both of the values predicted in this study are in good agreement with those reported in the literature [132] for reaction (6A) [108,143]. In comparison to our thermodynamic model, the model reported by Steiger et al. [132] provides a less accurate prediction of the vapor pressure for reaction (6B).

As shown in Fig. 15, the thermodynamic model for CaCl₂ + H₂O in this study also provides a reliable prediction for the dissociation pressure of calcium chloride hydrates, and the accuracy of this model is superior to that in our previous study [129] for the prediction of the equilibrium water vapor partial pressure of reaction (7A).

5. Conclusions

The thermodynamic properties of the binary systems NaCl + H₂O, KCl + H₂O, MgCl₂ + H₂O and CaCl₂ + H₂O were simulated using the Pitzer–Simonson–Clegg (PSC) model under a comprehensive thermodynamic framework. Various thermodynamic properties (i.e., water activity, osmotic coefficient, mean ionic activity coefficient, enthalpy of dilution and solution, relative apparent molar enthalpy, heat capacity of aqueous phase and solid phases) were collected and employed to fit the model parameters. It is shown that the PSC model in the present thermodynamic framework can represent the properties of these binary systems in various aspects over a wide temperature and concentration ranges. Moreover, some experimentally undetermined properties can be deduced by the modeling and the consistence of the experimental or model data in literature can be verified by the present

Table 6

Standard state thermodynamic values of solid phases at 298.15 K.

Solids	$\Delta_f C_m^\ominus$ (kJ mol ⁻¹)	$\Delta_f H_m^\ominus$ (kJ mol ⁻¹)	S_m^\ominus (J mol ⁻¹ K ⁻¹)	$C_{p,m}$ (J mol ⁻¹ K ⁻¹)	Ref.
NaCl(cr)	-384.13 -348.14 -384.28 -384.32	-411.10 -411.15 -411.27 -	69.97 72.13 72.27 70.76	50.50 50.50 50.16 48.35	This work [141] [7] [130]
NaCl · 2H ₂ O(cr)	-858.53 -858.75 -858.84	-997.08 -997.24 -	162.24 162.51 164.61	137.50 137.0 130.12	This work [7] [130]
KCl(cr)	-408.56 -409.14 -408.55	-435.47 -436.74 -	83.35 82.29 80.59	51.29 51.30 47.81	This work [141] [130]
MgCl ₂ · 12H ₂ O(cr)	-3543.18 -3545.85	-4268.75 -	613.19 645.68	593.39 546.02	This work [130]
MgCl ₂ · 8H ₂ O(cr)	-2590.75 -2593.45	-3094.60 -	423.82 466.91	419.39 387.02	This work [130]
MgCl ₂ · 6H ₂ O(cr)	-2113.50 -2114.65 -2115.67	-2501.95 -2499.02 -	344.36 366.10 371.48	332.39 315.06 241.75	This work [141] [130]
MgCl ₂ · 4H ₂ O(cr)	-1623.77 -1623.29 -1627.54	-1910.10 -1898.99 -	220.36 241.42 249.41	245.39 241.42 187.57	This work [141] [130]
MgCl ₂ · 2H ₂ O(cr)	-1118.30 -1118.0 -1127.94	-1290.50 -1279.72 -	136.65 179.90 146.39	158.39 159.20 125.14	This work [141] [130]
CaCl ₂ · 6H ₂ O(cr)	-2216.04 - -2215.59 -2215.66 -2216.93	-2604.63 -2607.90 -2606.10 -2609.94 -	355.07 - 354.33 341.79 371.48	333.91 - - - 311.67	This work [141] [125] [142] [130]
CaCl ₂ · 4H ₂ O(cr, α)	-1733.94 - -1733.24 -1733.60 -1734.73	-2007.08 -2009.60 -2009.17 -2009.60 -	275.75 - 272.21 271.87 268.95	246.91 - - - 245.10	This work [141] [125] [142] [130]
CaCl ₂ · 4H ₂ O(cr, β)	-1732.97 -1732.48	-1993.79 -	317.08 -	246.91 -	This work [125]
CaCl ₂ · 4H ₂ O(cr, γ)	-1732.75 -1732.28	-1990.21 -	328.33 -	246.91 -	This work [125]
CaCl ₂ · 2H ₂ O(cr)	-1249.57 - -1244.15 -1247.40 -1248.90	-1406.58 -1402.90 -1404.03 -1403.97 -	198.73 - 194.93 206.19 212.38	159.91 - - - 176.45	This work [141] [125] [142] [130]
CaCl ₂ · H ₂ O(cr)	-1006.37 - -1007.58 -1002.7 -995.78	-1120.75 -1109.20 -1110.82 - -	108.46 - 151.65 134.69 190.17	116.41 - - - 107.95	This work [141] [125] [136] [130]
CaCl ₂ · 1/3H ₂ O(cr)	-838.59 - -833.80 -830.22	-915.02 -901.07 - -	80.24 - 116.40 149.7211	87.41 - - 83.68	This work [125] [136] [130]

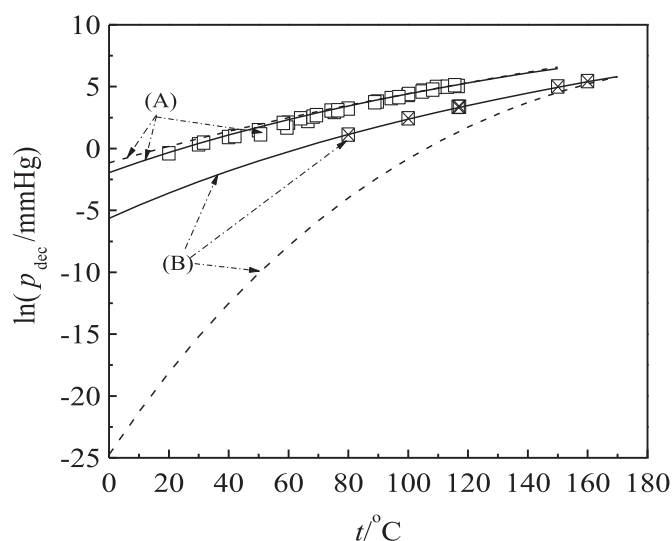


Fig. 14. Equilibrium water vapor partial pressure p_{dec} of reactions (6A) and (6B). — predicted by the current model and --- predicted by the model reported by Steiger et al. [132]. The symbols represent the previously reported experimental values [108,143].

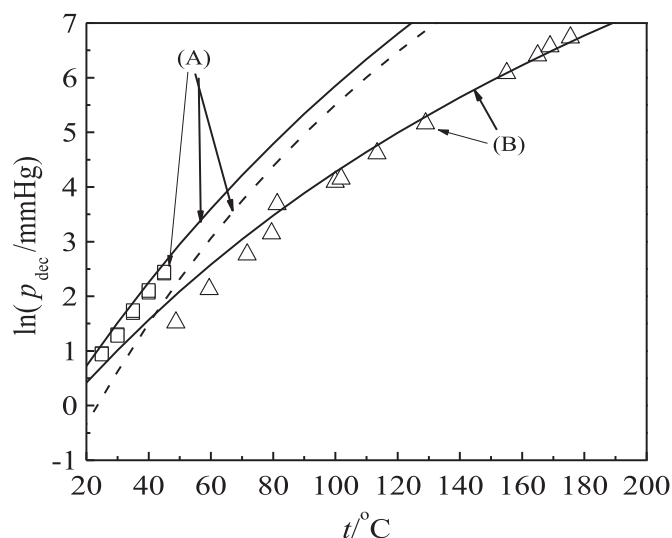


Fig. 15. Equilibrium water vapor partial pressure p_{dec} of reactions (7A) and (7B). — predicted by the current model and --- predicted by the model reported by Zeng et al. [129]. The symbols represent the previously reported experimental values [136,137].

modeling. The present work on the binary systems provides a solid basis for the prediction of properties of multi-component systems of salt lakes in the future.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.calphad.2016.03.007>.

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