



Isopiestic measurement and solubility evaluation of the ternary system (CaCl₂ + SrCl₂ + H₂O) at T = 298.15 K

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ABSTRACT

Water activities in the ternary system (CaCl₂ + SrCl₂ + H₂O) and its sub-binary system (CaCl₂ + H₂O) at T = 298.15 K have been elaborately measured by an isopiestic method. The data of the measured water activity were used to justify the reliability of solubility isotherms reported in the literature by correlating them with a thermodynamic Pitzer–Simonson–Clegg (PSC) model. The model parameters for representing the thermodynamic properties of the (CaCl₂ + H₂O) system from (0 to 11) mol · kg^{−1} at T = 298.15 K were determined, and the experimental water activity data in the ternary system were compared with those predicted by the parameters determined in the binary systems. Their agreement indicates that the PSC model parameters can reliably represent the properties of the ternary system. Under the assumption that the equilibrium solid phases are the pure solid phases (SrCl₂ · 6H₂O and CaCl₂ · 6H₂O)_(s) or the ideal solid solution consisting of CaCl₂ · 6H₂O_(s) and SrCl₂ · 6H₂O_(s), the solubility isotherms were predicted and compared with experimental data from the literature. It was found that the predicted solubility isotherm agrees with experimental data over the entire concentration range at T = 298.15 K under the second assumption described above; however, it does not under the first assumption. The modeling results reveal that the solid phase in equilibrium with the aqueous solution in the ternary system is an ideal solid solution consisting of SrCl₂ · 6H₂O_(s) and CaCl₂ · 6H₂O_(s). Based on the theoretical calculation, the possibility of the co-saturated points between SrCl₂ · 6H₂O_(s) and the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) and between CaCl₂ · 6H₂O_(s) and the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s), which were reported by experimental researchers, has been discussed, and the Lippmann diagram of this system has been presented.

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1. Introduction

The thermodynamic properties of the (CaCl₂ + SrCl₂ + H₂O) system, including water activities and solubility isotherms, are instructive for extracting valuable resources from oilfield brines. Because of the high similarity of properties of the two types of cations, the solubility isotherms of the titled ternary system are difficult to determine. Up to now, only Bi *et al.* [1] and Assarsson and Balder [2] have reported the solubility data of the (CaCl₂ + SrCl₂ + H₂O) system at different temperatures, using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP) for the analysis of the cations' concentrations. Bi *et al.* [1] reported that there are three (solid + liquid) equilibrium branches in this system at T = 298.15 K, i.e., SrCl₂ · 6H₂O_(s), CaCl₂ · 6H₂O_(s) and the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) with two invariant points

between them. However, Assarsson and Balder [2] reported that the saturated solid solution is complete miscible on the entire concentration range of the system at (291 and 301) K. The former case means that the chemical potentials of the pure solid phases CaCl₂ · 6H₂O_(s) and SrCl₂ · 6H₂O_(s) are equal to their values in the solid solutions (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s), which are in equilibrium with the saturation solution of the invariant points. This is theoretically incomprehensible, if the solid solution is an ideal mixture.

Thermodynamic modeling provides an alternative approach to understand or justify the reliability of the experimental solubility isotherms. For the model parameterization, the water activities in the ternary system are a prerequisite. Currently, no experimental water activities have been reported for the titled ternary system. In this work, we elaborately measured the water activities of the ternary system (CaCl₂ + SrCl₂ + H₂O) and chose a Pitzer–Simonson–Clegg (PSC) model [3,4] to represent the properties (water activity and solubility) of the titled system. Based on a model calculation, the reliability of the experimental solubility data [1] was evaluated.

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TABLE 1

Compounds used for the preparation of stock solutions.

Compound	Grade	Source	Purification method	Final purity (%)	Impurity analysis method
NaCl	G. R.	Sinopharm Chemical Reagent Co., Ltd.	Recrystallization	99.99	ICP
CaCl ₂ · 2H ₂ O	A. R.	Sinopharm Chemical Reagent Co., Ltd.	Recrystallization	99.95	ICP
SrCl ₂ · 6H ₂ O	G. R.	Sinopharm Chemical Reagent Co., Ltd.	Recrystallization	99.99	ICP
H ₂ SO ₄	G. R.	Beijing Chemical Works	No further purification	99.99	No analysis

2. Experimental

2.1. Materials

All the chemical agents used in the experiment are shown in table 1, including the source of compounds, purification method, final purity, etc., and further detailed information are given as follows.

The stock solutions of NaCl, H₂SO₄ and SrCl₂ used in the experiment were prepared through the procedure described in our previous work [5]. Water purified by deionization followed by double distillation (once with trace K₂MnO₄) with a conductance less than $1.5 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$ was used for all sample purifications, preparations, and dilutions in the experiment. The NaCl (G.R., Sinopharm Chemical Reagent Co., Ltd.) was purified by triple recrystallization, and the contents of each main impurity element (K, Ca, Mg and Fe) were detected to be less than 0.01%. The NaCl stock solution was prepared according to the procedure described previously [6]. H₂SO₄ (G.R., Beijing Chemical Works) was used as a stock solution without further purification, and its content was determined gravimetrically using BaCl₂. The largest relative deviation among three parallel samples was controlled below 0.05%. SrCl₂ · 6H₂O (G.R., Sinopharm Chemical Reagent Co., Ltd.) was purified by triple recrystallization, and the content of each main impurity element (Ca, Mg, K, Na, Fe and Ba) was less than 0.01%.

The analytical agent CaCl₂ · 2H₂O (Sinopharm Chemical Reagent Co., Ltd.) was purified by recrystallization, which was repeated four times, and the content of the main impurity elements (K, Na, Mg, Ba and Fe) were less than 0.01%. The salt contents of the SrCl₂ and CaCl₂ stock solutions were determined by precipitation with AgNO₃, and the largest relative deviations of the analytical results for three parallel samples could be controlled below 0.05%. The salt impurities were analyzed by ICP Emission Spectrometry (Thermo Electron Corporation, ICAP 6500 DUO).

2.2. Apparatus and experimental procedure

Isopiestic measurements of water activity for the (CaCl₂ + SrCl₂ + H₂O) system were carried out by the procedure described in our previous work [5]. In an isopiestic chamber, 8 sample cups were used, and the temperature accuracy was controlled within $\pm 0.01 \text{ K}$. NaCl and H₂SO₄ were used as reference systems for low and high sample concentrations, respectively.

The stock solutions with different Y_{CaCl_2} ($Y_{\text{CaCl}_2} = m_{\text{CaCl}_2} / (m_{\text{SrCl}_2} + m_{\text{CaCl}_2})$) were prepared by mixing the two pure stock solutions of CaCl₂ and SrCl₂. Before the first isopiestic measurement, the appropriate amounts of various stock solutions were added to each weighed cup and weighed; the difference was the solution mass. To accelerate the equilibrium process and shorten the equilibrium time needed, the solution concentration in each sample cup was adjusted in advance by adding water to or by evaporating the solutions in an oven below $T = 333 \text{ K}$ to maintain the water activity of each sample at approximately the same level. In each experimental run, duplicate samples for the reference solution and some of the mixture solutions were used to check the reliability of the experimental results. After all of the sample cups were placed in the isopiestic chamber, the chamber was closed and

slowly evacuated, and the solutions were carefully degassed. The equilibrium time was set to be (4 to 9) days. When equilibrium was reached, the sample cups were closed with the caps that were fixed previously in the capping device inside the isopiestic chamber. Then, the chamber was removed from the thermostat bath, and clean dry air was admitted to the chamber. All of the cap-sealed cups were moved into a desiccator for 30 min and then weighed. The isopiestic equilibrium molalities of the solutions were determined by the vacuum-corrected masses of the solutions and the mole amount of salt or acid of the added stock solutions. In the subsequent experiments, samples were roughly evaporated or diluted to another water activity level, and the same isopiestic measurement was repeated. All of the goal water activity levels of each sample cup were budgeted so that their equilibrium concentrations were below the solubility limit in each run of the isopiestic measurement.

3. Results and discussion

3.1. Experimental results

The osmotic coefficients, ϕ , as functions of the NaCl and H₂SO₄ concentrations were taken from the literature [7–9] and fitted in equation (1), whose parameters are given in table 2.

$$\phi = A + B \times (m/\text{mol} \cdot \text{kg}^{-1})^{0.5} + C \times (m/\text{mol} \cdot \text{kg}^{-1}) + D \times (m/\text{mol} \cdot \text{kg}^{-1})^{1.5} + E \times (m/\text{mol} \cdot \text{kg}^{-1})^2 + F \times (m/\text{mol} \cdot \text{kg}^{-1})^{2.5} + G \times (m/\text{mol} \cdot \text{kg}^{-1})^3 + H \times (m/\text{mol} \cdot \text{kg}^{-1})^{3.5}. \quad (1)$$

The water activities, a_w , of the reference solution were calculated using equation (2),

$$\ln a_w = \frac{-v \times M_w \times m \times \phi}{1000}, \quad (2)$$

where v is the number of ions for the complete dissociation of one molecule of NaCl or H₂SO₄. M_w is the molar mass of H₂O.

The measured results are tabulated in table 3. In each record of the isopiestic experimental runs, the concentration and water activities of the reference solutions were tabulated in the first line, and the following data were the isopiestic concentrations of the

TABLE 2

Fitted parameters in equation (1) for the NaCl and H₂SO₄ reference solutions.

Parameters	NaCl ^a	H ₂ SO ₄ ^b
<i>a</i>	0.99538	0.78187
<i>b</i>	−0.333722	−0.579417
<i>c</i>	0.566836	1.011164
<i>d</i>	−0.5278638	−0.8809713
<i>e</i>	0.3361724	0.5308231
<i>f</i>	−0.1248621	−0.1713412
<i>g</i>	0.02604260	0.02704254
<i>h</i>	−0.00239629	−0.00166244
σ^c	$3.1328 \cdot 10^{-5}$	$1.1937 \cdot 10^{-3}$

^a Parameters obtained by fitting the osmotic coefficients of NaCl in the literature [7].

^b Parameters obtained by fitting the osmotic coefficients of H₂SO₄ in the literature [9].

^c Standard deviation, $\sigma = \left(\frac{\sum_{i=1}^n (\phi_i(\text{exp}) - \phi_i(\text{calc}))^2}{n-1} \right)^{1/2}$.

TABLE 3Isopiestic molalities and water activities of the ternary system (CaCl₂ + SrCl₂ + H₂O) with NaCl (aq) and H₂SO₄ (aq) as reference at $T = 298.15 \text{ K}^a$.

No.	$m_{\text{SrCl}_2}/(\text{mol} \cdot \text{kg}^{-1})$	$m_{\text{CaCl}_2}/(\text{mol} \cdot \text{kg}^{-1})$	No.	$m_{\text{SrCl}_2}/(\text{mol} \cdot \text{kg}^{-1})$	$m_{\text{CaCl}_2}/(\text{mol} \cdot \text{kg}^{-1})$
1	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 0.3125 \pm 0.0003, a_w = 0.9897$ 0	0.2229 ± 0.0002	16	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 4.2754 \pm 0.0043, a_w = 0.8395$ 0	2.2169 ± 0.0022
2	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 0.5363 \pm 0.0005, a_w = 0.9823$ 0	0.3709 ± 0.0004	17	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 4.5402 \pm 0.0045, a_w = 0.8277$ 1.6838 ± 0.0017 1.1921 ± 0.0012	0.7213 ± 0.0007 1.1925 ± 0.0012
3	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 0.7817 \pm 0.0008, a_w = 0.9742$ 0.3730 ± 0.0004 0.2654 ± 0.0003 0.1592 ± 0.0002 0.0529 ± 0.0001	0.1598 ± 0.0002 0.2655 ± 0.0003 0.3704 ± 0.0004 0.4734 ± 0.0004		0.7104 ± 0.0007 0.2360 ± 0.0002 0	1.6532 ± 0.0017 2.1121 ± 0.0021 2.3381 ± 0.0023
4	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 1.0054 \pm 0.0010, a_w = 0.9667$ 0	0.6548 ± 0.0007	18	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 5.0528 \pm 0.0051, a_w = 0.8044$ 0	2.5405 ± 0.0025
5	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 1.3303 \pm 0.0013, a_w = 0.9555$ 0	0.8413 ± 0.0008	19	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 3.7070 \pm 0.0037, a_w = 0.8019$ 1.8554 ± 0.0018	0.7948 ± 0.0008
6	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 1.4574 \pm 0.0015, a_w = 0.9511$ 0.6494 ± 0.0006 0.4615 ± 0.0005 0.2764 ± 0.0003 0.0916 ± 0.0001	0.2782 ± 0.0003 0.4616 ± 0.0005 0.6433 ± 0.0006 0.8200 ± 0.0008		1.3119 ± 0.0013 0.7816 ± 0.0008 0.2589 ± 0.0003 0.0519 ± 0.0001	1.3123 ± 0.0013 1.8190 ± 0.0018 2.3168 ± 0.0023 2.5172 ± 0.0025
7	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 1.4993 \pm 0.0015, a_w = 0.9496$ 0	0.9307 ± 0.0009	20	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 5.5098 \pm 0.0055, a_w = 0.7831$ 0	2.7238 ± 0.0027
8	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 2.1769 \pm 0.0022, a_w = 0.9250$ 0	1.2538 ± 0.0001	21	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 6.0348 \pm 0.0060, a_w = 0.7583$ 2.1128 ± 0.0021 1.4940 ± 0.0015 0.8889 ± 0.0009	0.9051 ± 0.0009 1.4945 ± 0.0015 2.0686 ± 0.0021
9	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 2.4491 \pm 0.0024, a_w = 0.9147$ 0	1.4089 ± 0.0001		0.2951 ± 0.0002 0	2.6407 ± 0.0026 2.9217 ± 0.0029
10	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 2.6540 \pm 0.0026, a_w = 0.9068$ 1.0811 ± 0.0011 0.7666 ± 0.0008 0.4575 ± 0.0005 0.1521 ± 0.0002 0	0.4632 ± 0.0005 0.7669 ± 0.0008 1.0647 ± 0.0011 1.3612 ± 0.0014 1.5085 ± 0.0015	22	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 4.9208 \pm 0.0049, a_w = 0.7094$ 2.4255 ± 0.0024 1.7113 ± 0.0017	1.0391 ± 0.0010 1.7119 ± 0.0017
11	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 2.9055 \pm 0.0029, a_w = 0.8969$ 0	1.6217 ± 0.0016		1.0180 ± 0.0010 0.3366 ± 0.0003 0.0675 ± 0.0001	2.3690 ± 0.0024 3.0127 ± 0.0030 3.2714 ± 0.0032
12	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 3.0046 \pm 0.0030, a_w = 0.8930$ 0	1.6625 ± 0.0017	23	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 6.3142 \pm 0.0063, a_w = 0.6020$ 1.2802 ± 0.0013 0.4226 ± 0.0004 0.0844 ± 0.0001	2.9792 ± 0.0030 3.7825 ± 0.0038 4.0938 ± 0.0041
13	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 3.2494 \pm 0.0032, a_w = 0.8831$ 0	1.7772 ± 0.0018	24	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 7.3079 \pm 0.0073, a_w = 0.5290$ 0.4819 ± 0.0005 0.0961 ± 0.0001	4.3131 ± 0.0043 4.6620 ± 0.0046
14	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 3.9108 \pm 0.0039, a_w = 0.8553$ 1.4893 ± 0.0015 1.0550 ± 0.0011 0.6289 ± 0.0006 0.2090 ± 0.0002 0	0.6380 ± 0.0006 1.0554 ± 0.0011 1.4636 ± 0.0015 1.8702 ± 0.0019 2.0707 ± 0.0021	25	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 8.7852 \pm 0.0088, a_w = 0.4306$ 0.1135 ± 0.0001	5.5049 ± 0.0055
15	$m_{\text{NaCl}}/(\text{mol} \cdot \text{kg}^{-1}) = 4.1915 \pm 0.0042, a_w = 0.8431$ 0	2.1865 ± 0.0022	26	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 10.4649 \pm 0.0105, a_w = 0.3366$ 0.1350 ± 0.0001	6.5495 ± 0.0065
			27	$m_{\text{H}_2\text{SO}_4}/(\text{mol} \cdot \text{kg}^{-1}) = 11.3007 \pm 0.0113, a_w = 0.2970$ 0.1469 ± 0.0001	7.1235 ± 0.0071

^a Water activities, a_w , for NaCl and H₂SO₄ are calculated according to equations (1) and (2), using the parameters in table 2; the experiments were carried out in Xining, China with atmosphere pressure of about 77.5 kPa.

salts in the mixture or pure solutions with the uncertainties resulting from impurities and weighing errors. The water activities of all of the solutions in each set of the isopiestic measurements were equal to the water activity of the reference at isopiestic equilibrium. In each run of the isopiestic measurements, the largest relative concentration difference of two duplicated samples was ±0.3%, which can be attributed to the errors in weighing, equilibrium time, water transportation in the isopiestic chamber, and

temperature difference between every two cups. Combining the uncertainty of 0.1% from impurities with the uncertainty of 0.3% reported above, we can reasonably evaluate that the total uncertainty of the measured salt concentration should be less than 0.4%, corresponding to the largest deviation of water activities, ±0.0026.

Our measured water activities in the (CaCl₂ + H₂O) binary system agree well with the literature data [10], as shown in figure

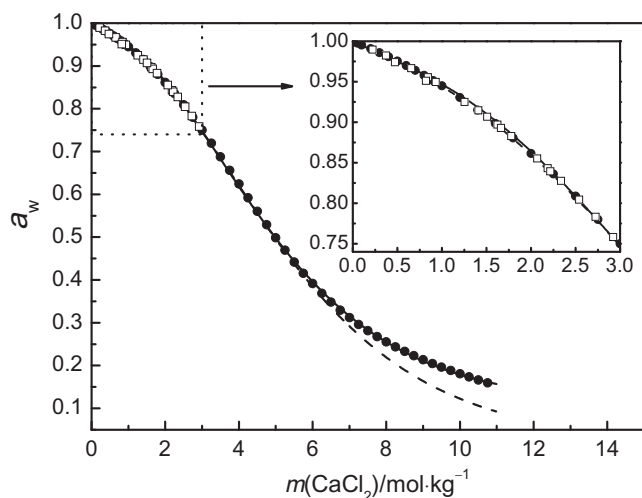


FIGURE 1. Measured water activities of the system ($\text{CaCl}_2 + \text{H}_2\text{O}$) at $T = 298.15$ K and their comparison with literature values: ●, [10]; □, this work; —, model values calculated by parameters given by Clegg [4]; —, model values by the parameters in table 4 determined in this work.

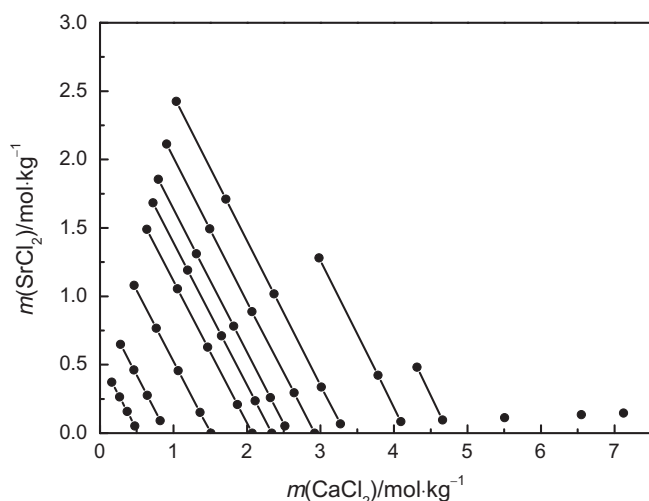


FIGURE 2. Experimental isopiestic compositions in the system ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) at $T = 298.15$ K.

1. The experimentally measured isopiestic points and equal-water activity lines of the ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) ternary system at $T = 298.15$ K are shown in figure 2.

3.2. Modeling

As described in our previous work [5], one can give a reasonable judgment on the reliability of the solubility isotherm data for a ter-

nary system by correlating the water activities and solubility data with a thermodynamic model. This strategy is briefly described as follows: first, a suitable thermodynamic model is selected for this purpose; second, the binary model parameters are determined by fitting to the water activity in each binary system; third, the solubility products $\ln K$ (equation (4)) for each solid phase are determined by calculating the activities of each component at saturation points using the model; fourth, the solubility isotherms for each solid phase in the ternary system are predicted using the obtained binary parameters and $\ln K$. If the experimental solubility isotherms and water activity data in the ternary system agree with the ones predicted with binary model parameters, the experimental solubility data can be judged to be reliable, and the interaction between the salts can be understood as “weak” in the framework of the selected thermodynamic model. Otherwise, the model parameters of mixing should be determined by fitting to ternary experimental water activity data, and the solubility isotherms should be predicted again. If the solubility isotherms predicted by the binary and ternary parameters agree with experimental solubility data, the latter can be judged to be reliable.

$$v_M X_M \cdot v_0 \text{H}_2\text{O}_{(s)} = v_M M_{(aq)}^{z_M} + v_X X_{(aq)}^{z_X} + v_0 \text{H}_2\text{O}_{(aq)}, \quad (3)$$

$$\ln K = v_M \ln(m_M \times \gamma_M) + v_X \ln(m_X \times \gamma_X) + v_0 \ln a_w. \quad (4)$$

Generally, the original Pitzer ion-interaction model [11] is appropriate to represent properties of an electrolyte solution with a salt concentration up to $6 \text{ mol} \cdot \text{kg}^{-1}$. An extended Pitzer model [12] can represent the properties of electrolyte solutions up to fairly high concentrations, although with many more parameters [10,13,14]. By systematically comparing the prediction ability of various thermodynamic models [15], we found that the PSC model [3,4] is suitable to represent and predict the properties of the electrolyte solution at both dilute and extremely concentrated concentrations. This model has been used for other purposes in our previous work [5,16–19].

Clegg and Pitzer [4] have given the binary model parameters (see table 4) for $\text{CaCl}_{2(aq)}$ solution as below $5.5 \text{ mol} \cdot \text{kg}^{-1}$. Above that concentration, the model values deviate remarkably from the experimental ones, as shown by the dashed line in figure 1. Their deviation is large, up to 0.023 at the saturation point ($\sim 7.3 \text{ mol} \cdot \text{kg}^{-1}$) of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$ at $T = 298.15$ K. This large deviation makes the model parameters unsuitable as a criterion for assessment of the experimental solubility isotherms. Thus, we evaluated the model parameters again by fitting them to the water activity data recommended by Rard [10], as presented in table 4. The model values (solid line in figure 1) with the new model parameters represent the water activity better than the old ones [4].

The model parameters for SrCl_2 are taken from our previous work [5].

Using the binary model parameters, we calculated the water activities in the ternary system at $T = 298.15$ K and compared them with the experimental values. As shown in table 5, the average

TABLE 4
The PSC model parameters at $T = 298.15$ K.

solute	PSC model parameters							$m_{\text{max}} / \text{mol} \cdot \text{kg}^{-1}$	σ^d
	α_{MX}	B_{MX}	α_{MX}^1	B_{MX}^1	$W_{1,MX}$	$U_{1,MX}$	$V_{1,MX}$		
SrCl_2^a	13	74.15689	2.0	104.2767	20.6085	64.6124	−64.6919	3.519 _(sat)	0.0003
CaCl_2^b	13	55.3960	2.0	114.4700	0	19.1480	−36.4970	11.0	0.0255
CaCl_2^c	13	349.2988	2.0	−100.0655	0	56.4866	−47.3256	11.0	0.0028

^a Parameters taken from the literature [5].

^b Parameters taken from the literature [4].

^c Parameters of this work obtained by fitting water activities of CaCl_2 solution in the literature [10].

^d Standard deviation, $\sigma = \left(\frac{\sum_{i=1}^n (a_w(\text{exp}) - a_w(\text{calc}))^2}{n-1} \right)^{1/2}$.

TABLE 5

Comparison of experimental and predicted water activities in the ternary system (CaCl₂ + SrCl₂ + H₂O) at T = 298.15 K

$m_{(\text{CaCl}_2)}/\text{mol} \cdot \text{kg}^{-1}$	$m_{(\text{SrCl}_2)}/\text{mol} \cdot \text{kg}^{-1}$	$a_w(\text{exp})^a$	$a_w(\text{cal})^b$	Deviation ^c
0.2229	0	0.9897	0.9888	0.0009
0.3709	0	0.9823	0.9814	0.0009
0.1598	0.3730	0.9742	0.9738	0.0004
0.2655	0.2654	0.9742	0.9738	0.0004
0.3704	0.1592	0.9742	0.9737	0.0005
0.4734	0.0529	0.9742	0.9737	0.0005
0.6548	0	0.9667	0.9669	−0.0002
0.8413	0	0.9555	0.9565	−0.0010
0.2782	0.6494	0.9511	0.9515	−0.0005
0.4616	0.4615	0.9511	0.9518	−0.0007
0.6433	0.2764	0.9511	0.9519	−0.0009
0.8200	0.0916	0.9511	0.9524	−0.0013
0.9307	0	0.9496	0.9512	−0.0016
1.2538	0	0.9250	0.9297	−0.0047
1.4089	0	0.9147	0.9179	−0.0031
0.4632	1.0811	0.9068	0.9078	−0.0010
0.7669	0.7666	0.9068	0.9084	−0.0016
1.0647	0.4575	0.9068	0.9090	−0.0022
1.3612	0.1521	0.9068	0.9095	−0.0027
1.5085	0	0.9068	0.9098	−0.0029
1.6217	0	0.8969	0.9001	−0.0031
1.6625	0	0.8930	0.8964	−0.0034
1.7772	0	0.8831	0.8859	−0.0028
0.6380	1.4893	0.8553	0.8555	−0.0001
1.0554	1.0550	0.8553	0.8558	−0.0004
1.4636	0.6289	0.8553	0.8563	−0.0009
1.8702	0.2090	0.8553	0.8563	−0.0010
2.0707	0	0.8553	0.8566	−0.0013
2.1865	0	0.8431	0.8442	−0.0011
2.2169	0	0.8395	0.8409	−0.0014
0.7213	1.6838	0.8277	0.8273	0.0004
1.1925	1.1921	0.8277	0.8273	0.0004
1.6532	0.7104	0.8277	0.8275	0.0002
2.1121	0.2360	0.8277	0.8272	0.0005
2.3381	0	0.8277	0.8273	0.0004
2.5405	0	0.8044	0.8038	0.0006
0.7948	1.8554	0.8018	0.8011	0.0008
1.3123	1.3119	0.8018	0.8010	0.0008
1.8190	0.7816	0.8018	0.8008	0.0010
2.3168	0.2589	0.8018	0.8010	0.0008
2.5172	0.0519	0.8018	0.8007	0.0011
2.7238	0	0.7831	0.7817	0.0014
0.9051	2.1128	0.7583	0.7599	−0.0017
1.4945	1.4940	0.7583	0.7591	−0.0008
2.9217	0	0.7583	0.7571	0.0012
2.0686	0.8889	0.7583	0.7587	−0.0004
2.6407	0.2951	0.7583	0.7573	0.0009
1.0391	2.4255	0.7100	0.7084	0.0016
1.7119	1.7113	0.7100	0.7073	0.0027
2.3690	1.0180	0.7100	0.7060	0.0040
3.0127	0.3366	0.7100	0.7051	0.0048
3.2714	0.0675	0.7100	0.7043	0.0057
2.9792	1.2802	0.6024	0.5989	0.0035
3.7825	0.4226	0.6024	0.5967	0.0057
4.0938	0.0844	0.6024	0.5966	0.0058
4.3131	0.4819	0.5293	0.5263	0.0030
4.6620	0.0961	0.5293	0.5263	0.0029
5.5049	0.1135	0.4311	0.4334	−0.0023
6.5495	0.1350	0.3377	0.3401	−0.0024
7.1235	0.1469	0.2985	0.2990	−0.0005
σ^c				0.0017

^a $a_w(\text{exp})$, water activities measured in this work;

^b $a_w(\text{cal})$, model values;

^c deviation = $a_w(\text{exp}) - a_w(\text{model})$; $\sigma = \sum_{i=1}^n |a_w(\text{exp}) - a_w(\text{cal})|/n$.

deviation between model and experimental values is 0.0017, which falls within the range of experimental error. That result means that the interaction between the CaCl₂ and SrCl₂ salts is quite weak in the framework of the PSC model. On one hand, the binary model parameters can represent the properties (component activities) of the ternary system, and on the other hand, they can be used to evaluate the solubility isotherms.

By calculating the component activities at the experimental saturation points of SrCl₂ · 6H₂O_(s) and CaCl₂ · 6H₂O_(s) at T = 298.15 K in their respective binary systems [1], we obtained their solubility products, $\ln K = -7.6690$ and -2.4363 for SrCl₂ · 6H₂O_(s) and CaCl₂ · 6H₂O_(s), respectively. Under the assumption that the solid phase is the pure solid phase SrCl₂ · 6H₂O_(s), we predicted the solubility isotherm for SrCl₂ · 6H₂O_(s) in the (CaCl₂ + SrCl₂ + H₂O) ternary system at T = 298.15 K using the binary model parameters and found that the predicted isotherm (dash dotted line in figure 3) agrees with the experimental isotherm on the SrCl₂ rich side and deviates from the experimental isotherm on the CaCl₂ rich side the experimental data [1]. Moreover, the predicted solubility isotherm for CaCl₂ · 6H₂O_(s) (dash line in figure 3) differs remarkably from the experimental point (left-full squares in figure 3). The reliability of the latter is strongly doubtful.

Bi *et al.* [1] reported that a solubility isotherm exists for the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) between the two isotherms for the solid phases CaCl₂ · 6H₂O_(s) and SrCl₂ · 6H₂O_(s). They also reported the composition pairs of the solid solution and aqueous solution in each equilibrium run, as shown in figure 4. Because the mixing behavior of CaCl₂ · 6H₂O and SrCl₂ · 6H₂O in the solid solution is unknown, we assumed that the solid solution is an ideal solution and predicted its solubility isotherm, as presented in the solid line in figure 4. The calculation strategy had been formulated in our previous work [18] and is briefly introduced in Appendix of this paper. It is surprising that the predicted solubility isotherm of the assumed ideal solid solution agrees with the experimental points very well over the entire concentration range. This result indicates that the assumption of the ideal solid solution may be true. We notice that both types of crystals belong to the hexagonal system with similar crystal cell parameters: $a = b = 7.8759$, $c = 3.9545$ for CaCl₂ · 6H₂O_(s) and $a = b = 7.9596$, $c = 4.1234$ for SrCl₂ · 6H₂O_(s) [20], making it easy for them to form a solid solution.

Furthermore, Bi *et al.* [1] reported that two co-saturation points exist between every two of the three solid phases of SrCl₂ · 6H₂O_(s), CaCl₂ · 6H₂O_(s) and (SrCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s). This means that the chemical potential of SrCl₂ · 6H₂O_(s) in the solid solution in equilibrium with the co-saturation aqueous solution (CaCl₂: 21.51 wt.%, SrCl₂: 12.34 wt.%) [1] is equivalent to that of the pure

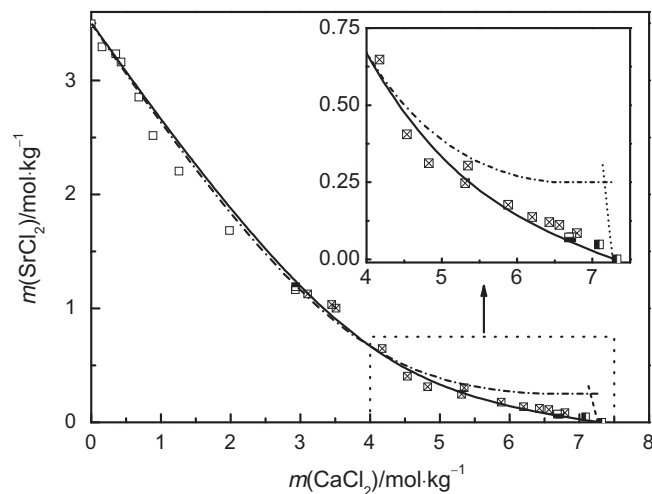


FIGURE 3. Solubility isotherms of the system (CaCl₂ + SrCl₂ + H₂O) at T = 298.15 K. All symbols are experimental values [1]: □, SrCl₂ · 6H₂O; ■, solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s); ▨, SrCl₂ · 6H₂O_(s) + the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s); ▩, CaCl₂ · 6H₂O_(s) + the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s); ---, CaCl₂ · 6H₂O_(s); all lines are model values: ---, predicted solubility isotherm for SrCl₂ · 6H₂O_(s); —, predicted solubility isotherms for CaCl₂ · 6H₂O_(s); —, predicted isotherm for the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) when it is treated as an ideal mixture.

TABLE 6

Calculated equilibrium composition pairs between the aqueous and solid solutions

Aqueous solution				Solid solution		
100w				100w		
CaCl ₂	SrCl ₂	H ₂ O	$\frac{100w_{\text{CaCl}_2}}{w_{\text{CaCl}_2} + w_{\text{SrCl}_2}}$	CaCl ₂ · 6H ₂ O	SrCl ₂ · 6H ₂ O	$\frac{100w_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}}{w_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}} + w_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}}}$
5.00	29.90	65.10	14.32	0.27	99.73	0.27
10.00	24.26	65.74	29.19	0.86	99.14	0.86
15.00	18.87	66.13	44.29	1.57	98.43	1.57
20.00	13.84	66.16	59.10	3.03	96.97	3.03
25.00	9.33	65.67	72.82	5.78	94.22	5.78

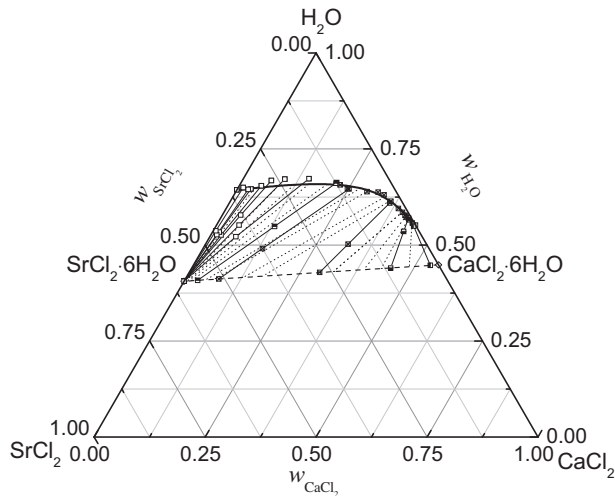


FIGURE 4. Solid solution + aqueous solution equilibria of the system (CaCl₂ + SrCl₂ + H₂O) at T = 298.15 K. All symbols are experimental values [1]: ○, between SrCl₂ · 6H₂O_(s) and aqueous solution; □, between the SrCl₂ · 6H₂O_(s) solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) and the aqueous solution; ■, between the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) and the aqueous solution; ▤, between CaCl₂ · 6H₂O_(s), the solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) and the aqueous solution; ▥, between CaCl₂ · 6H₂O_(s) and the aqueous solution; ---, calculated solubility isotherm for the assumed ideal solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s); ···, calculated equilibrium lines between aqueous solution and the assumed ideal solid solution.

solid phase SrCl₂ · 6H₂O_(s), which is thermodynamically incompressible. Applying the thermodynamic model, we calculated equilibrium composition pairs between the aqueous solution and the solid solution, and we present them in figure 5 (dotted lines) and table 6. The calculated equilibrium lines (dotted lines in figure 5) between the aqueous solution and the solid solution are roughly in agreement with the experimental results (dashed lines in figure 5). As shown in table 6, when the CaCl₂ content in the saturated aqueous solution is below 20 wt.%, the content of CaCl₂ · 6H₂O in the corresponding solid solution is below 3 wt.%. Such a low level of CaCl₂ · 6H₂O content in the solid solution is not easily detected by x-ray diffraction, which was used by the authors [1]. Thus, the solid solution may be arbitrarily assessed as the pure solid phase SrCl₂ · 6H₂O by the experimental researchers [1]. The same case may exist for the co-saturation point between CaCl₂ · 6H₂O and the solid solution.

According to Königsberger and Gamsjäger [21], this kind of solid solution–aqueous solution (SS–AS) system also can be described by Lippmann [22] $\sum K - x^s - x^{\text{act}}$ and $\phi \sum m - x^s - x^{\text{aq}}$ equilibrium diagrams. For this ternary system, where $\sum K = (a_{\text{w}(\text{Sr}^{2+})} + a_{\text{w}(\text{Ca}^{2+})}) \times a_{\text{w}(\text{Cl}^-)}$, x^s the mole fraction of SrCl₂ · 6H₂O in solid solution, $x^{\text{act}}_{\text{Sr}^{2+}} = a_{\text{w}(\text{Sr}^{2+})} / (a_{\text{w}(\text{Sr}^{2+})} + a_{\text{w}(\text{Ca}^{2+})})$, $x^{\text{aq}}_{\text{Sr}^{2+}} = m_{\text{Sr}^{2+}} / (m_{\text{Sr}^{2+}} + m_{\text{Ca}^{2+}})$, ϕ the osmotic coefficient and $\sum m = m_{\text{Sr}^{2+}} + m_{\text{Ca}^{2+}} + m_{\text{Cl}^-}$. We drew these kinds of equilibrium diagrams for the (CaCl₂ + SrCl₂ + H₂O) ternary

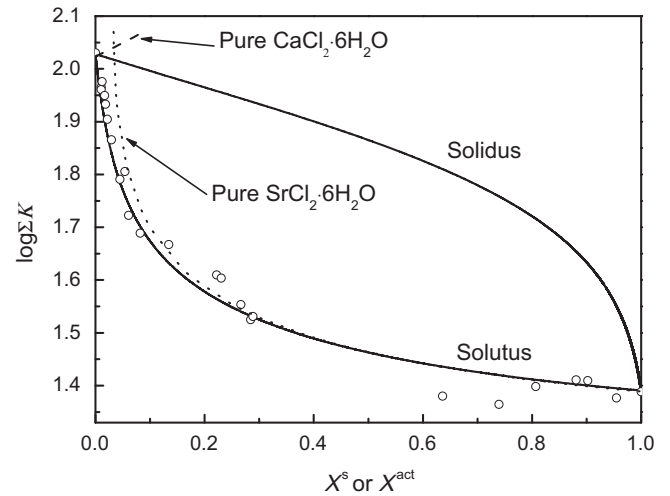


FIGURE 5. Lippmann $\sum K - x^s - x^{\text{act}}$ diagram of the system (CaCl₂ + SrCl₂ + H₂O) at T = 298.15 K. ○, experimental solutus points [1]; ---, calculated solidus and solutus for ideal solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s); ---, calculated solutus for the pure CaCl₂ · 6H₂O_(s); ···, calculated solutus for the pure SrCl₂ · 6H₂O_(s).

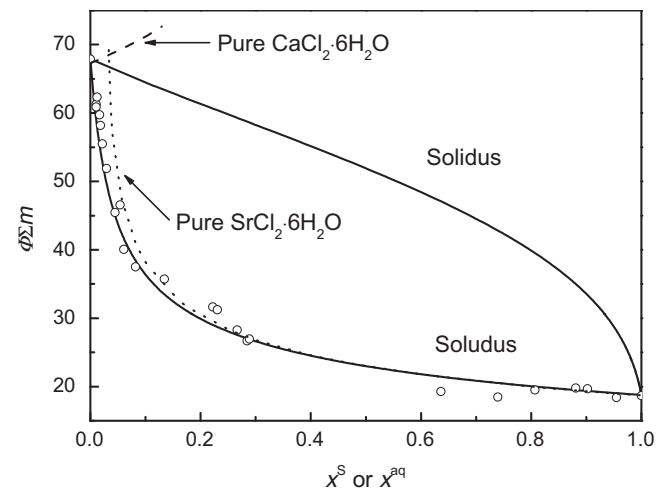


FIGURE 6. $\phi \sum m - x^s - x^{\text{aq}}$ diagram of the system (CaCl₂ + SrCl₂ + H₂O) at T = 298.15 K. ○, experimental solutus points [1]; ---, calculated solidus and solutus for ideal solid solution (CaCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s); ---, calculated solutus for the pure CaCl₂ · 6H₂O_(s); ···, calculated solutus for the pure SrCl₂ · 6H₂O_(s).

system at T = 298.15 K, as shown in figures 5 and 6. The calculated solutus lines (solid lines) for the ideal solid solution (SrCl₂ · 6H₂O + SrCl₂ · 6H₂O)_(s) agreed well with the experiment point [1], while the calculated solutus for the pure SrCl₂ · 6H₂O_(s) (dot lines) and CaCl₂ · 6H₂O_(s) (dash lines) deviated with the experiment point [1], which indicated again that the equilibrated solid phase in the

ternary system ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) at $T = 298.15$ K is the ideal solid solution ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 6\text{H}_2\text{O}$)_(s).

4. Conclusions

We elaborately measured the water activities of the ternary system ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) and its sub-binary ($\text{CaCl}_2 + \text{H}_2\text{O}$) system at $T = 298.15$ K by the isopiestic method. The measured results for the ($\text{CaCl}_2 + \text{H}_2\text{O}$) binary systems are in agreement with the literature data.

The PSC model was used to predict and correlate the water activities and solubility isotherms of the ternary system ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) at $T = 298.15$ K.

The water activities predicted by binary model parameters agree well with the experimental values for the ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) ternary system at $T = 298.15$ K. This indicates that the interaction between the CaCl_2 and SrCl_2 salts is quite weak in the framework of the PSC model, and the thermodynamic properties can be presented by the PSC model with binary parameters only.

Under the assumption that the equilibrated solid phase is an ideal solid solution consisting of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, the predicted solubility isotherm in the ternary system ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) was consistent with experiment values [1] at $T = 298.15$ K; however, the predicted solubility isotherms for pure salts ($(\text{CaCl}_2 \cdot 6\text{H}_2\text{O})_{(s)}$ and $(\text{SrCl}_2 \cdot 6\text{H}_2\text{O})_{(s)}$) largely deviate from the experimental values. This indicates that the equilibrated solid phase is likely the ideal solid solution ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 6\text{H}_2\text{O}$)_(s) in the entire concentration range of the ternary system ($\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$) at $T = 298.15$ K, rather than the single pure solid phase $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$ or $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}_{(s)}$, and this conclusion also can be verified by the Lippmann $\sum K - x^s - x^{\text{act}}$ and $\phi \sum m - x^s - x^{\text{aq}}$ equilibrium diagrams of this ternary system.

Acknowledgments

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Appendix Appendix

Strategy of the equilibrium calculation between the solid solution ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 6\text{H}_2\text{O}$)_(s) and the aqueous solution.

For the equilibrium between the aqueous solution (aq) and the solid solution (ss), we have

$$\begin{aligned} (\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 6\text{H}_2\text{O})_{(\text{ss})} &= \text{Ca}_{(\text{aq})}^{2+} + \text{Sr}_{(\text{aq})}^{2+} + \nu_{\text{Cl}^-} \text{Cl}_{(\text{aq})}^- \\ &\quad + n\text{H}_2\text{O}_{(\text{aq})}, \\ \mu_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} &= \mu_{\text{Ca}^{2+}(\text{aq})} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})} + n\mu_{\text{H}_2\text{O}(\text{aq})} \\ &= \mu_{\text{Ca}^{2+}(\text{aq})}^{\ominus} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})}^{\ominus} + n\mu_{\text{H}_2\text{O}(\text{aq})}^{\ominus} + RT \\ &\quad \times \ln(a_{\text{Ca}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6), \end{aligned} \quad (\text{A1})$$

$$\begin{aligned} \mu_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} &= \mu_{\text{Sr}^{2+}(\text{aq})} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})} + n\mu_{\text{H}_2\text{O}(\text{aq})} \\ &= \mu_{\text{Sr}^{2+}(\text{aq})}^{\ominus} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})}^{\ominus} + n\mu_{\text{H}_2\text{O}(\text{aq})}^{\ominus} + RT \\ &\quad \times \ln(a_{\text{Sr}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6). \end{aligned} \quad (\text{A2})$$

In solid solution, one has

$$\mu_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = \mu_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})}^{\ominus} + RT \ln a_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})}, \quad (\text{A3})$$

$$\mu_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = \mu_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})}^{\ominus} + RT \ln a_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})}. \quad (\text{A4})$$

For the solid-liquid equilibrium in the binary system, we have

$$\begin{aligned} \mu_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})}^{\ominus} &= \mu_{\text{Ca}^{2+}(\text{aq})}^{\ominus} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})}^{\ominus} + n\mu_{\text{H}_2\text{O}(\text{aq})}^{\ominus} + RT \\ &\quad \times \ln(a_{\text{Ca}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6) \\ &= \mu_{\text{Ca}^{2+}(\text{aq})}^{\ominus} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})}^{\ominus} + n\mu_{\text{H}_2\text{O}(\text{aq})}^{\ominus} + RT \\ &\quad \times \ln k_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}, \end{aligned} \quad (\text{A5})$$

$$\begin{aligned} \mu_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})}^{\ominus} &= \mu_{\text{Sr}^{2+}(\text{aq})}^{\ominus} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})}^{\ominus} + n\mu_{\text{H}_2\text{O}(\text{aq})}^{\ominus} + RT \\ &\quad \times \ln(a_{\text{Sr}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6) \\ &= \mu_{\text{Sr}^{2+}(\text{aq})}^{\ominus} + \nu_{\text{Cl}^-} \mu_{\text{Cl}^-(\text{aq})}^{\ominus} + n\mu_{\text{H}_2\text{O}(\text{aq})}^{\ominus} + RT \\ &\quad \times \ln k_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}}. \end{aligned} \quad (\text{A6})$$

Substituting equations (A1) and (A5) in equation (A3) and equations (A2) and (A6) in equation (A4), respectively, we obtain the activity relation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in the solid solution with that in the aqueous solution, respectively:

$$a_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = a_{\text{Ca}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6 / k_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}, \quad (\text{A7})$$

$$a_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = a_{\text{Sr}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6 / k_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}}. \quad (\text{A8})$$

If we assume the solid solution is an ideal mixture, i.e., $a_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = x_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})}$ and $a_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = x_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})}$, then we have

$$a_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} + a_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = x_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} + x_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{ss})} = 1. \quad (\text{A9})$$

Substituting equations (A7) and (A8) in equation (A9), we get

$$\begin{aligned} a_{\text{Ca}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6 / k_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}} + a_{\text{Sr}^{2+}(\text{aq})} a_{\text{Cl}^-(\text{aq})}^2 a_{\text{H}_2\text{O}(\text{aq})}^6 / k_{\text{SrCl}_2 \cdot 6\text{H}_2\text{O}} \\ = 1. \end{aligned} \quad (\text{A10})$$

Using equation (A10) as criterion, we can calculate the solubility isotherm for the ideal solid solution.

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