

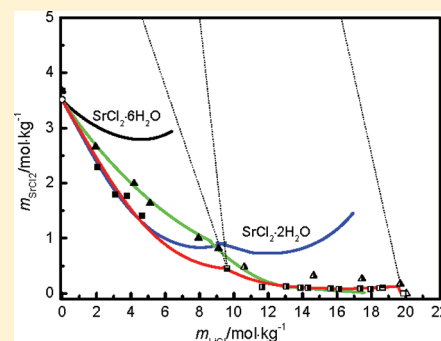
Isopiestic Measurement and Solubility Evaluation of the Ternary System $\text{LiCl-SrCl}_2\text{-H}_2\text{O}$ at 298.15 K

Lijiang Guo,[†] Bai Sun,[†] Dewen Zeng,^{*,†,‡} Yan Yao,[†] and Haijun Han[†]

[†]Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, P. R. China

[‡]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China

ABSTRACT: Water activity in the ternary system $\text{LiCl-SrCl}_2\text{-H}_2\text{O}$ and its sub-binary systems has been elaborately measured by the isopiestic method. The measured water activities were used to justify the reliability of solubility isotherms reported in literature by correlating them with two thermodynamic models, that is, the extended Pitzer model and the Pitzer–Simonson–Clegg model. It was found that the extended Pitzer model cannot correlate consistently the water activities measured and either set of the solubility isotherms reported in literature for this concerned system, no matter how its parameters were adjusted. However, the Pitzer–Simonson–Clegg model can correlate consistently our measured water activities and the solubility isotherms reported by the literature (Kydyrov et al. *Issled. Obl. Khim. Tekhnol. Miner. Solei Okislov* **1965**, 146–150), which should be more reliable than solubility data reported in other references.



1. INTRODUCTION

Oil field brines in Nanyishan¹ area of Qinghai-Tibet Plateau, China, are connate waters which are found during deep rock penetration by the drill and are rich in lithium, strontium, and calcium chloride. To extract the lithium resource from the brine, thermodynamic properties of the ternary system $\text{LiCl-SrCl}_2\text{-H}_2\text{O}$, including water activities and solubility isotherms, are of importance. Up to now, a large number of water activity data have been reported in the sub-binary systems.^{2–7} Meanwhile, two sets of completely different solubility data were reported^{8,9} at 298.15 K. To justify the reliability of solubility data, one approach is to correlate them with water activity in the ternary system by thermodynamic models, as we did previously.¹⁰ However, the water activities in the ternary system are lacking at the present time. In this case, we will elaborately measure water activity in the ternary system, as well as in the binary systems for comparison, and then two thermodynamic models, the extended Pitzer model⁷ and Pitzer–Simonson–Clegg model,^{11–13} will be selected to correlate water activity and solubility isotherms. The goal is to determine the reliability of the experimental solubility data.

2. EXPERIMENTAL SECTION

Isopiestic measurements of water activity for the system $\text{LiCl-SrCl}_2\text{-H}_2\text{O}$ were carried out in equipment described elsewhere,^{14,15} in which there are 14 cups in an isopiestic chamber and the temperature accuracy was controlled within ± 0.01 K. NaCl and H_2SO_4 were used as a reference system. The water purified by deionization followed by distillation twice (once with trace K_2MnO_4) with a conductance of smaller 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 (Sinopharm Chemical Reagent Co., Ltd. G. R.) was purified by recrystallization

three times, and the contents of each impurity element of K, Ca, Mg, and Fe were detected to be smaller than 0.01 %. The H_2SO_4 (Beijing Chemical Works, G. R.) was used as the stock solution without further purification, and its content was determined by precipitation with BaCl_2 solution. The largest relative deviation among three parallel samples was controlled below 0.05 %. SrCl_2 (Sinopharm Chemical Reagent Co., Ltd., G. R.) was purified by recrystallization three times, and the contents of each impurity element of Ca, Mg, K, Na, Fe, and Ba were smaller than 0.01 %. The analytical agent of LiCl (Shanghai China Lithium Industrial Co., Ltd.) was purified by recrystallization four times, and the contents of main impurity elements of K, Na, Mg, Ca, and Fe were less than 0.01 %. The impurities of salts were analyzed by ICP emission spectrometers (Thermo Electron Corporation, ICAP 6500 DUO). The contents of the SrCl_2 and LiCl stock solutions were determined by precipitation with AgNO_3 , also the largest relative deviation among three parallel samples was controlled below 0.05 %. In all, the purity of the salts NaCl , LiCl , and SrCl_2 used in this work should be conservatively evaluated to be not smaller than 99.9 % in mass and that for H_2SO_4 not smaller than 99.95 % in mass.

Before the isopiestic experiments, stock solutions with different Y_{LiCl} ($Y_{\text{LiCl}} = m_{\text{LiCl}} / (m_{\text{SrCl}_2} + m_{\text{LiCl}})$, exactly, 0, 0.299759, 0.500153, 0.700377, 0.800637, 0.900363, 0.950163, 0.989826, and 1) were prepared by mixing the two pure stock solutions of SrCl_2 and LiCl . Before the first isopiestic measurement, appropriate amounts of various stock solutions were added in each weighed cups and weighed; the difference is the solution

Received: September 26, 2011

Accepted: January 6, 2012

Published: February 2, 2012

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 at 333 K, to keep the water activity of each sample roughly at a same level. NaCl and H₂SO₄ solutions were used as references at higher and lower water activity, respectively. In each experimental run, duplicate samples for reference solution and some of the mixture solutions are used to check the reliability of the experimental results. After the test samples are located, the isopiestic chamber was closed and slowly evacuated, and the solutions were carefully degassed to being nearly free of air. The equilibrium time was set to be (4 to 9) days depending on salt concentration. When equilibrium was attained the sample cups were closed with the caps fixed previously on the capping device inside the isopiestic chamber, and then the chamber was removed from the thermostat bath. Clean dry air was admitted to the chamber, and all of the cups sealed with the caps were placed into a desiccator for 30 min and were then weighed. From the vacuum-corrected masses of solutions and the mole amount of salt or acid of the added stock solutions the isopiestic equilibrium molalities of the solutions were determined. In the subsequent experiments, samples were roughly evaporated or diluted to another water activity level, carrying the same isopiestic measurement as described above. The goal water activity level was budgeted to make the point well-distributed, and all levels were all under the reported solubility isotherm lines to ensure that there was no presentation of crystal in each isopiestic measurement.

3. RESULTS

The osmotic coefficients ϕ for the NaCl reference solutions were calculated according to the literature¹⁶ as recommended by Pitzer,¹⁷ and that for the H₂SO₄ solution was calculated according to the literature.¹⁸ We fitted the osmotic coefficients of the reference systems reported in the literature, obtaining their ϕ as a function of m , as shown by eq 1.

$$\begin{aligned} \phi = & a + b(m/\text{mol}\cdot\text{kg}^{-1})^{0.5} + c(m/\text{mol}\cdot\text{kg}^{-1}) \\ & + d(m/\text{mol}\cdot\text{kg}^{-1})^{1.5} + e(m/\text{mol}\cdot\text{kg}^{-1})^2 \\ & + f(m/\text{mol}\cdot\text{kg}^{-1})^{2.5} + g(m/\text{mol}\cdot\text{kg}^{-1})^3 \\ & + h(m/\text{mol}\cdot\text{kg}^{-1})^{3.5} \end{aligned} \quad (1)$$

where a , b , c , d , e , f , g , and h are parameters and are given in Table 1.

Table 1. Fitted Parameters of Equation 1 for NaCl and H₂SO₄ References

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

^aFitting the osmotic coefficients of NaCl in literature.¹⁶ ^bFitting the osmotic coefficients of H₂SO₄ in literature.¹⁸ ^cStandard deviation, $\sigma = ((\sum_i^n (\phi(\text{exp}) - \phi(\text{calc}))^2)/n)^{1/2}$.

The osmotic coefficients of the test solutions are calculated using the following equation,

$$\phi = \frac{\nu^* m^* \phi^*}{\sum_i \nu_i m_i} \quad (2)$$

where quantities with asterisks are denoted for isopiestic reference standard, $\nu^* = 2$ denotes the number of ions formed by the complete dissociation of one molecule of NaCl, and $\nu^* = 3$ for H₂SO₄, m^* is isopiestic equilibrium molality of reference, ϕ^* is the osmotic coefficient of reference standard, and $\sum_i \nu_i m_i = 2m_{\text{LiCl}} + 3m_{\text{SrCl}_2}$ for the LiCl–SrCl₂–H₂O ternary system. The water activities a_w of the reference were calculated using the following equation,

$$\ln a_w = \frac{-\nu \cdot M_w \cdot m \cdot \phi}{1000} \quad (3)$$

where ν is the number of ions formed by the complete dissociation of one molecule of reference standard, exactly, $\nu = 2$ for NaCl and $\nu = 3$ for H₂SO₄. M_w is molar mass of H₂O, and ϕ is osmotic coefficient of the reference standard.

The measured results are tabulated in Table 2. In each record of isopiestic experiment run, the concentration and water activities of the references were tabulated in the first line, and the following data were the isopiestic concentration of salts in mixture solutions or pure solutions, along with the uncertainty arisen from the impurity. The water activities of all solutions in each set of isopiestic measurement were equal to the water activity of reference at isopiestic equilibrium. The largest relative concentration deviation of the two duplicated samples was ± 0.3 %. Combining the uncertainty 0.1 % from impurity, the total uncertainty of the measured salt concentration should be smaller than 0.4 %, corresponding with the largest deviation of water activities ± 0.0026 .

Our measured water activities in the LiCl–H₂O binary system agree well with the literature^{19–22} and are slightly different from the Pitzer model values²³ and quite different from the experimental data reported by Guendouzi et al.,²⁴ as shown in Figure 1. Our measured water activities for the SrCl₂–H₂O system agree well with literature,^{2,4,5,7} as shown in Figure 2.

Using the isopiestic method,²⁵ we also measured the water activity of the saturated SrCl₂ solution and the solubility at 298.15 K and found their values were 0.7121 ± 0.0013 and $(3.5125 \pm 0.014) \text{ mol}\cdot\text{kg}^{-1}$, respectively. Rard⁴ gave a solubility value of $3.5195 \pm 0.0022 \text{ mol}\cdot\text{kg}^{-1}$ for SrCl₂·6H₂O in the same experimental method, and Pollio²⁶ predicted the water activity of saturated SrCl₂ solution at 298.15 K using the Pitzer model, the value of which is 0.712. We did not detect the crystal type in equilibrium with the saturated solution. Considering that both our solubility data and Rard's are identical in the evaluated error range, the solubility data point of $3.5125 \pm 0.014 \text{ mol}\cdot\text{kg}^{-1}$ in this work should be that for SrCl₂·6H₂O.

The experimentally measured equal-water activity lines of the LiCl–SrCl₂–H₂O ternary system are shown in Figure 3, where composition points with a same water activity at low and middle salt concentrations stand roughly in a straight line; that is, the mixing behavior obeys the Zdanovskii's rule, which means no strong ion association or the apparent constancy of interaction between the component electrolytes in the ternary aqueous solution.²⁷ At high salt concentrations, because of the strong nonsymmetry of solubility of the two salts, it is unknown if the mixing of the two binary solution obeys Zdanovskii's rule.

Table 2. Isopiestic Molalities and Water Activities of the Ternary System LiCl–SrCl₂–H₂O with NaCl (aq) and H₂SO₄ (aq) as a Reference at 298.15 K^a

| no. | m_{SrCl_2} | m_{LiCl} | no. | m_{SrCl_2} | m_{LiCl} | | |
|-----------------|---|---|-----------------|---|----------------------|-----------------|-----------------|
| | mol·kg ⁻¹ | mol·kg ⁻¹ | | mol·kg ⁻¹ | mol·kg ⁻¹ | | |
| 1 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 0.2689 \pm 0.0003, a_w = 0.9911$ | | 20 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 4.7735 \pm 0.0048, a_w = 0.8172$ | | | |
| | 0.2034 ± 0.0002 | 0 | | 2.5454 ± 0.0025 | 0 | | |
| | 0.1486 ± 0.0001 | 0.0636 ± 0.0001 | | 1.9832 ± 0.0020 | 0.8490 ± 0.0008 | | |
| | 0.1123 ± 0.0002 | 0.1124 ± 0.0001 | | 1.5348 ± 0.0015 | 1.5357 ± 0.0015 | | |
| | 0.0715 ± 0.0001 | 0.1671 ± 0.0002 | | 1.0026 ± 0.0010 | 2.3436 ± 0.0023 | | |
| | 0.0484 ± 0.0001 | 0.1945 ± 0.0002 | | 0.7014 ± 0.0007 | 2.8167 ± 0.0028 | | |
| | 0.0251 ± 0.0001 | 0.2263 ± 0.0002 | | 0.3688 ± 0.0004 | 3.3323 ± 0.0033 | | |
| 2 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 0.3125 \pm 0.0003, a_w = 0.9897$ | | 21 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 5.0528 \pm 0.0051, a_w = 0.8044$ | | | |
| | 0.2256 ± 0.0002 | 0 | | 2.6617 ± 0.0027 | 0 | | |
| 3 | | 0.3044 ± 0.0003 | 22 | | 4.1247 ± 0.0041 | | |
| | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 0.5363 \pm 0.0005, a_w = 0.9823$ | 0 | | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 5.0834 \pm 0.0051, a_w = 0.8030$ | 0 | | |
| 4 | 0.3770 ± 0.0003 | 0 | 23 | 2.6795 ± 0.0027 | 0 | | |
| | 0 | 0.5140 ± 0.0005 | | 2.091 ± 0.0021 | 0.8951 ± 0.0009 | | |
| | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 0.6282 \pm 0.0006, a_w = 0.9793$ | | | 1.6195 ± 0.0016 | 1.6205 ± 0.0016 | | |
| | 0.4407 ± 0.0004 | 0 | | 1.058 ± 0.0011 | 2.4731 ± 0.0025 | | |
| | 0.3328 ± 0.0003 | 0.1424 ± 0.0001 | | 0.7408 ± 0.0007 | 2.9751 ± 0.0030 | | |
| | 0.2512 ± 0.0003 | 0.2513 ± 0.0002 | | 0.3895 ± 0.0004 | 3.5201 ± 0.0035 | | |
| | 0.1610 ± 0.0002 | 0.3764 ± 0.0004 | | 0.2001 ± 0.0002 | 3.8152 ± 0.0038 | | |
| 5 | 0.1105 ± 0.0001 | 0.4439 ± 0.0004 | 24 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 5.4734 \pm 0.0055, a_w = 0.7848$ | | | |
| | 0.0573 ± 0.0001 | 0.5178 ± 0.0005 | | 2.8485 ± 0.0028 | 0 | | |
| | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 1.0054 \pm 0.0010, a_w = 0.9667$ | | | 2.2249 ± 0.0022 | 0.9525 ± 0.0010 | | |
| | 0.6740 ± 0.0007 | 0 | | 1.7262 ± 0.0017 | 1.7273 ± 0.0017 | | |
| | 0 | 0.9298 ± 0.0009 | | 1.1277 ± 0.0011 | 2.6361 ± 0.0026 | | |
| | 6 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 1.2068 \pm 0.0012, a_w = 0.9598$ | | | 25 | 0.7902 ± 0.0008 | 3.1735 ± 0.0032 |
| | | 0.7931 ± 0.0008 | | 0 | | 0.4159 ± 0.0004 | 3.758 ± 0.0038 |
| 0.6062 ± 0.0006 | | 0.2595 ± 0.0003 | 0.2137 ± 0.0002 | 4.0749 ± 0.0041 | | | |
| 0.4607 ± 0.0005 | | 0.4609 ± 0.0005 | 24 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 5.5098 \pm 0.0055, a_w = 0.7831$ | | | |
| 0.2953 ± 0.0003 | | 0.6903 ± 0.0007 | | 2.8582 ± 0.0029 | | 0 | |
| 0.2042 ± 0.0002 | | 0.8199 ± 0.0008 | 0 | 4.4572 ± 0.0045 | | | |
| 0.1058 ± 0.0001 | | 0.9564 ± 0.0010 | 25 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 5.5438 \pm 0.0055, a_w = 0.7815$ | | | |
| 0 | 1.0951 ± 0.0011 | 2.8776 ± 0.0029 | | 0 | | | |
| 7 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 1.3303 \pm 0.0013, a_w = 0.9555$ | | 26 | 2.2249 ± 0.0022 | 0.9525 ± 0.0009 | | |
| | 0.8644 ± 0.0009 | 0 | | 1.7262 ± 0.0017 | 1.7273 ± 0.0017 | | |
| | 0 | 1.2160 ± 0.0012 | | 1.1277 ± 0.0011 | 2.6361 ± 0.0026 | | |
| 8 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 1.4993 \pm 0.0015, a_w = 0.9496$ | | 27 | 0.7902 ± 0.0008 | 3.1735 ± 0.0032 | | |
| | 0.9593 ± 0.0009 | 0 | | 0.4159 ± 0.0004 | 3.7582 ± 0.0038 | | |
| | 0 | 1.3546 ± 0.0013 | | 0.2137 ± 0.0002 | 4.0749 ± 0.0041 | | |
| 9 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 1.7693 \pm 0.0018, a_w = 0.9400$ | | 28 | 0.0450 ± 0.0001 | 4.3811 ± 0.0044 | | |
| | 1.1095 ± 0.0011 | 0 | | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 6.0245 \pm 0.0060, a_w = 0.7588$ | | | |
| | 0.8511 ± 0.0009 | 0.3643 ± 0.0004 | | 3.0867 ± 0.0031 | 0 | | |
| | 0.6502 ± 0.0007 | 0.6506 ± 0.0007 | | 2.4109 ± 0.0024 | 1.0320 ± 0.0010 | | |
| | 0.4183 ± 0.0004 | 0.9778 ± 0.0009 | | 1.8714 ± 0.0019 | 1.8725 ± 0.0019 | | |
| | 0.2897 ± 0.0003 | 1.1634 ± 0.0012 | | 1.2258 ± 0.0012 | 2.8654 ± 0.0029 | | |
| | 0.1507 ± 0.0002 | 1.3617 ± 0.0014 | | 0.8596 ± 0.0009 | 3.4522 ± 0.0035 | | |
| 10 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 2.0934 \pm 0.0021, a_w = 0.9281$ | | 27 | 0.4530 ± 0.0005 | 4.0938 ± 0.0041 | | |
| | 1.2779 ± 0.0013 | 0 | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 4.8184 \pm 0.0048, a_w = 0.7178$ | | | |
| | 0.9840 ± 0.0010 | 0.4212 ± 0.0004 | | 3.4660 ± 0.0035 | 0 | | |
| | 0.7519 ± 0.0008 | 0.7524 ± 0.0008 | | 2.7121 ± 0.0027 | 1.161 ± 0.0011 | | |
| | 0.4856 ± 0.0005 | 1.1352 ± 0.0011 | | 2.1094 ± 0.0021 | 2.1107 ± 0.0021 | | |
| | 0.3369 ± 0.0003 | 1.3530 ± 0.0013 | | 1.3807 ± 0.0014 | 3.2274 ± 0.0032 | | |
| | 0.1753 ± 0.0002 | 1.5845 ± 0.0016 | | 0.9695 ± 0.0010 | 3.8933 ± 0.0039 | | |
| 11 | 0 | 1.8063 ± 0.0018 | 0.5113 ± 0.0005 | 4.6201 ± 0.0046 | | | |
| | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 2.1769 \pm 0.0022, a_w = 0.9250$ | | 0.2631 ± 0.0003 | 5.0153 ± 0.0050 | | | |
| | 1.3210 ± 0.0013 | 0 | 0.0549 ± 0.0001 | 5.3378 ± 0.0053 | | | |
| 12 | 0 | 1.9158 ± 0.0019 | 28 | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 6.5698 \pm 0.0066, a_w = 0.5828$ | | | |
| | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 2.4491 \pm 0.0024, a_w = 0.9147$ | | | 1.3117 ± 0.0013 | 5.2679 ± 0.0053 | | |
| | 1.4599 ± 0.0015 | 0 | | 0.6914 ± 0.0007 | 6.2477 ± 0.0062 | | |
| | 0 | 2.1340 ± 0.0021 | | 0.3560 ± 0.0004 | 6.7864 ± 0.0068 | | |

Table 2. continued

| no. | m_{SrCl_2} | | m_{LiCl} | | no. | m_{SrCl_2} | | m_{LiCl} | |
|-----|---|--|----------------------|--|-----|--|--|----------------------|--|
| | mol·kg ⁻¹ | | mol·kg ⁻¹ | | | mol·kg ⁻¹ | | mol·kg ⁻¹ | |
| 13 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 2.9055 \pm 0.0029, a_w = 0.8969$ | | | | 29 | 0.0743 ± 0.0001 | | 7.2277 ± 0.0072 | |
| | 1.6840 ± 0.0017 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 8.3763 \pm 0.0084, a_w = 0.4562$ | | 0.8694 ± 0.0009 | |
| | 0 | | 2.4962 ± 0.0025 | | | 0.4468 ± 0.0004 | | 7.8565 ± 0.0079 | |
| 14 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 3.0046 \pm 0.0030, a_w = 0.8930$ | | | | 30 | 0.0931 ± 0.0001 | | 9.0596 ± 0.0091 | |
| | 1.7291 ± 0.0017 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 9.6008 \pm 0.0096, a_w = 0.3824$ | | 0.5076 ± 0.0005 | |
| | 0 | | 2.5707 ± 0.0026 | | | 0.5070 ± 0.0005 | | 9.6670 ± 0.0097 | |
| 15 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 3.1264 \pm 0.0031, a_w = 0.8881$ | | | | 31 | 0.1059 ± 0.0001 | | 10.2982 ± 0.0103 | |
| | 1.7938 ± 0.0018 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 11.9188 \pm 0.0119, a_w = 0.2707$ | | 0 | |
| | 1.3888 ± 0.0014 | | 0.5945 ± 0.0006 | | | 0.1301 ± 0.0001 | | 12.6527 ± 0.0127 | |
| | 1.0689 ± 0.0011 | | 1.0695 ± 0.0011 | | | 0 | | 12.8068 ± 0.0128 | |
| | 0.6937 ± 0.0007 | | 1.6214 ± 0.0016 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 13.1932 \pm 0.0132, a_w = 0.2232$ | | 0.1443 ± 0.0001 | |
| | 0.4827 ± 0.0005 | | 1.9386 ± 0.0019 | | | 0 | | 14.0363 ± 0.0140 | |
| 16 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 3.2494 \pm 0.0032, a_w = 0.8831$ | | | | 32 | 0 | | 14.1556 ± 0.0141 | |
| | 1.8459 ± 0.0018 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 14.2454 \pm 0.0142, a_w = 0.1902$ | | 0.1568 ± 0.0002 | |
| | 0 | | 2.7610 ± 0.0028 | | | 0 | | 15.2515 ± 0.0153 | |
| 17 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 3.5608 \pm 0.0036, a_w = 0.8702$ | | | | 33 | 0.1691 ± 0.0002 | | 16.4488 ± 0.0164 | |
| | 1.9919 ± 0.0020 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 15.3000 \pm 0.0153, a_w = 0.1621$ | | 0 | |
| | 1.5474 ± 0.0015 | | 0.6624 ± 0.0007 | | | 0.1848 ± 0.0002 | | 17.9792 ± 0.0178 | |
| | 1.1909 ± 0.0012 | | 1.1916 ± 0.0012 | | | 0 | | 18.0973 ± 0.0181 | |
| | 0.7765 ± 0.0008 | | 1.8151 ± 0.0018 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 16.5179 \pm 0.0165, a_w = 0.1348$ | | 0.1878 ± 0.0002 | |
| | 0.5412 ± 0.0005 | | 2.1734 ± 0.0021 | | | 0 | | 18.2719 ± 0.0183 | |
| 18 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 4.1915 \pm 0.0042, a_w = 0.8431$ | | | | 34 | 0.1938 ± 0.0002 | | 18.851 ± 0.0189 | |
| | 2.2853 ± 0.0023 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 16.7540 \pm 0.0168, a_w = 0.1302$ | | 0 | |
| | 0 | | 3.4851 ± 0.0035 | | | 0 | | 18.992 ± 0.0190 | |
| 19 | $m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1}) = 4.2794 \pm 0.0043, a_w = 0.8395$ | | | | 35 | 0 | | | |
| | 2.3172 ± 0.0023 | | 0 | | | $m_{\text{H}_2\text{SO}_4}/(\text{mol}\cdot\text{kg}^{-1}) = 17.1374 \pm 0.0171, a_w = 0.1230$ | | | |
| | 0 | | 3.5465 ± 0.0035 | | | 0 | | | |

^aWater activity a_w is calculated according to ref 16 for NaCl and ref 18 for H₂SO₄.

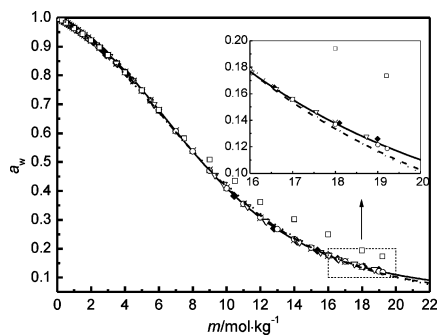


Figure 1. Measured water activities of the system LiCl–H₂O at 298.15 K and their comparison with literature. O, ref 19; X, ref 20; ☆, ref 21; ▽, ref 22; □, ref 24; ◆, this work; ···, Pitzer model with parameters of ref 23; ---, extended Pitzer model values; —, Pitzer–Simonson–Clegg model values.

4. MODELING

By correlating the water activities determined in this work and contradictory solubility data with thermodynamic models, one can expect to give a reasonable judgment on the reliability of the solubility data. The evaluation strategy is briefly described as follows. At first, two thermodynamic models which are known suitable for highly soluble

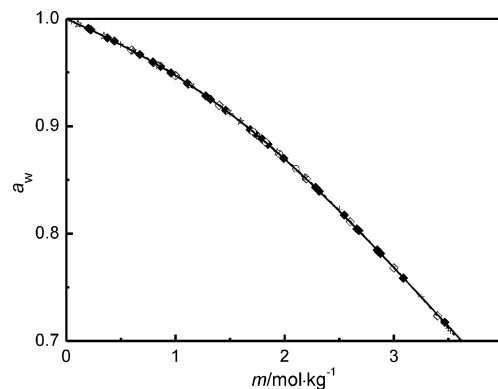


Figure 2. Measured water activities of the system SrCl₂–H₂O at 298.15 K and their comparison with literature. ☆, ref 2; ◇, ref 4; +, ref 5; ○, ref 7; ◆, this work; ···, extended Pitzer model with the parameters reported by Rard;⁷ —, Pitzer–Simonson–Clegg model values.

electrolyte systems, that is, the extended Pitzer model and Pitzer–Simonson–Clegg model, are selected for the correlation task; by fitting to water activity in each binary system, model parameters are determined. At the saturation point of SrCl₂·6H₂O in the binary system SrCl₂–H₂O, the solubility product $\ln K$ of SrCl₂·6H₂O corresponding with the

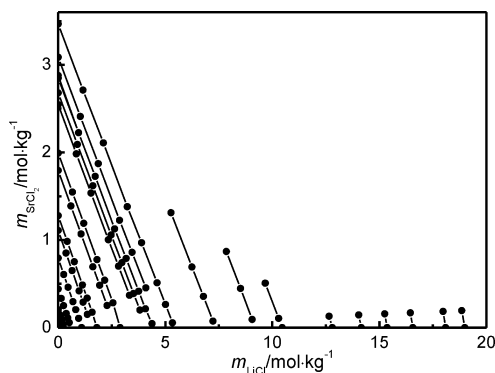
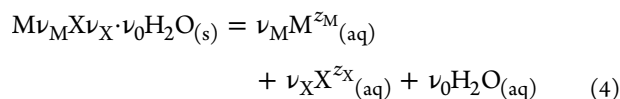


Figure 3. Experimental isopiestic lines in the system LiCl–SrCl₂–H₂O at 298.15 K.

solubility equilibrium



$$\ln K = \nu_M \ln(m_M \gamma_M) + \nu_X \ln(m_X \gamma_X) + \nu_0 \ln a_W \quad (5)$$

is determined by calculating the activities of each component. Using the determined $\ln K$ as a criterion, the solubility isotherm for the solid phase SrCl₂·6H₂O is predicted in the ternary system; in the case that the predicted solubility isotherms do not agree with the experimental data, we will fit the ternary model parameters to water activities determined in this work and predict with both binary and ternary model parameters the solubility isotherm for SrCl₂·6H₂O again. In case the predicted solubility isotherm for SrCl₂·6H₂O do not agree with experimental data yet, we will fit the ternary model parameter with both the water activity determined in this work and different sets of solubility data of SrCl₂·6H₂O, respectively, and calculate the solubility isotherm for SrCl₂·6H₂O again. In case the calculated solubility isotherm of SrCl₂·6H₂O agrees with one set of experimental data, we will regularly change the parameter $\ln K$ for the second solid phase SrCl₂·2H₂O, until the calculated solubility isotherm of SrCl₂·2H₂O fit the corresponding experimental data. In case a selected thermodynamic model can correlate consistently experimental water activity in both binary and ternary systems and experimental solubility isotherms for both SrCl₂·6H₂O and SrCl₂·2H₂O, one can reasonably consider that this set of experimental solubility data is relatively reliable.

4.1. Extended Pitzer Model. Since thermodynamic properties of the mixture electrolyte solution containing SrCl₂ have been successfully described by the extended Pitzer model,⁷ this model was selected to represent the thermodynamic

properties of the titled ternary system at first. This model is briefly repeated in Appendix A of this paper.

By fitting to the water activity data in literature²⁰ and this work in Table 2, we obtained the binary model parameters for LiCl as shown in Table 3. For the binary parameters of SrCl₂, we took the ones reported by Rard et al.⁷ On the parameter evaluation process, we applied the least-squares method to find the “best” set of parameters by regular changing the model parameters.

The extended Pitzer model can represent sufficiently the water activities of SrCl₂ aqueous solution, as shown in Figure 2, but is somewhat insufficient for LiCl aqueous solution, though better than the Pitzer model²³ (see Figure 1). The standard deviation of water activity between model and experimental data were 0.0004 and 0.0032 for SrCl₂ and LiCl, respectively, as shown in Table 3.

Applying the binary extended Pitzer model parameters, we predicted the water activities of the LiCl–SrCl₂–H₂O ternary system and its solubility isotherm at 298.15 K. Before the calculation of the solubility isotherm, the solubility product parameter $\ln K$ for SrCl₂·6H₂O was determined by calculating the component activities or activity coefficients at saturation point in the binary system SrCl₂–H₂O. The determined $\ln K$ was used as a criterion on the calculation of the solubility isotherm in the ternary system. The predicted solubility isotherms (dotted lines in Figure 4) deviate remarkably from

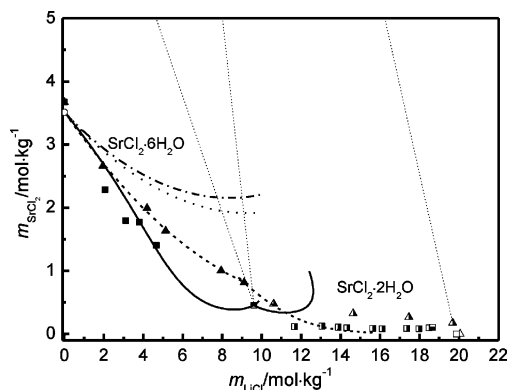


Figure 4. Solubility isotherm comparison of experimental and calculated by the extended Pitzer model of the system LiCl–SrCl₂–H₂O at 298.15 K. All symbols are experimental data: ▲, SrCl₂·6H₂O;⁸ △, SrCl₂·2H₂O;⁸ □, LiCl·H₂O;⁸ ■, SrCl₂·6H₂O;⁹ □, SrCl₂·2H₂O;⁹ □, LiCl·H₂O;⁹ ■, co-saturated point of SrCl₂·6H₂O and SrCl₂·2H₂O;⁹ □, co-saturated point of SrCl₂·2H₂O and LiCl·H₂O;⁹ ○, SrCl₂·6H₂O determined by isopiestic method from Rard⁴ and in this work. All lines are extended Pitzer model values: —, with binary parameters only; ···, with binary parameters and ternary parameters fitted to experimental water activities in the ternary system; ---, with binary parameter and ternary parameters obtained by fitting to experimental water activities in this work and solubility data in ref 8; —, with binary parameters and ternary parameters obtained by fitting to experimental water activities in this work and solubility isotherms in ref 9.

Table 3. Extended Pitzer Model Parameters for the Binary Systems LiCl–H₂O and SrCl₂–H₂O at 298.15 K

| solute | β_{MX}^0 | α_1 | β_{MX}^1 | C_{MX}^0 | ω | C_{MX}^1 | σ^* |
|--------------------------------|----------------|------------|----------------|------------|----------|------------|------------|
| LiCl ^a | 0.2281 | 2.0 | 0.7539 | −0.002651 | 2.5 | −0.8745 | 0.0032 |
| SrCl ₂ ^b | 0.2827 | 2.0 | 1.5625 | −0.000225 | 2.5 | −0.0921 | 0.0004 |

^aParameters determined by fitting to experimental water activities of this work and ref 20. ^bParameters from ref 7. ^{*}Standard deviation, $\sigma = ((\sum_i^n (a_w(\text{exp}) - a_w(\text{calc}))^2)/n)^{1/2}$.

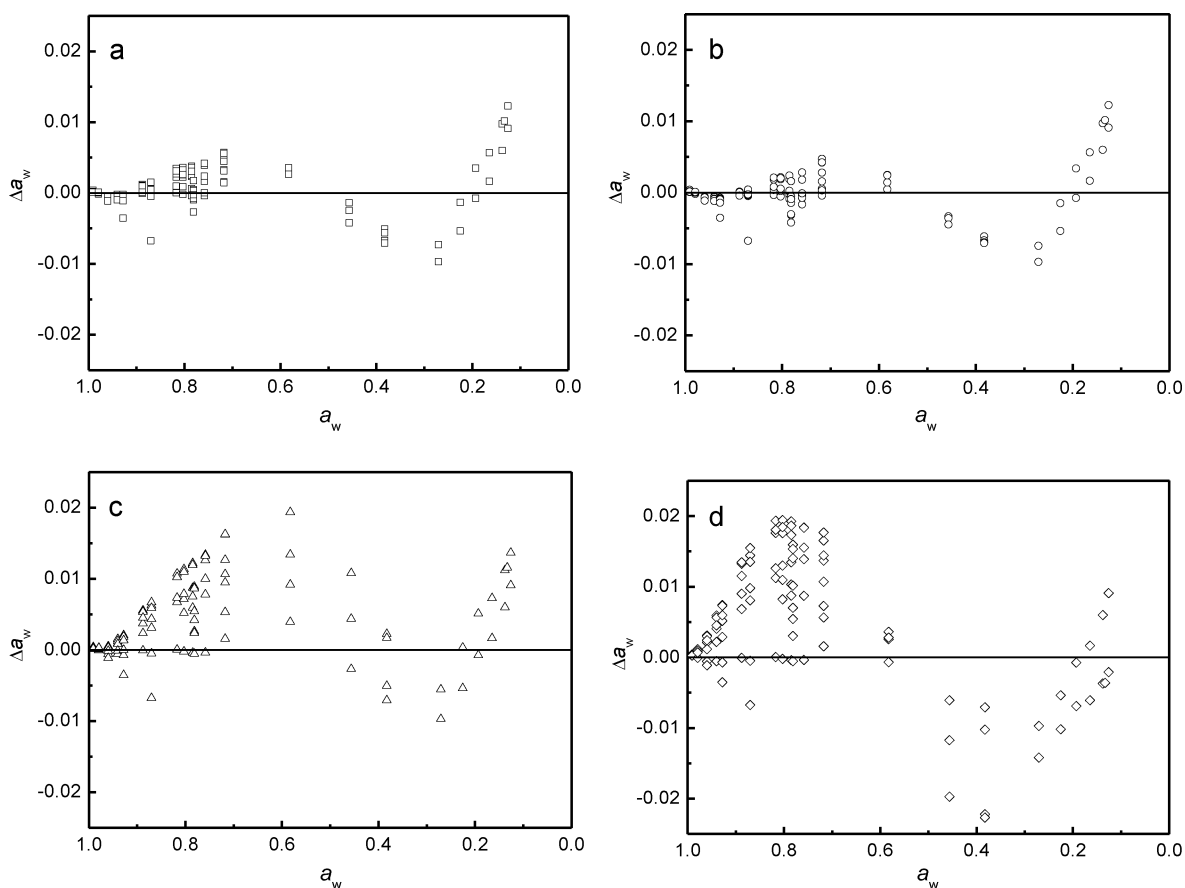


Figure 5. Deviation of water activity in the ternary system calculated by the extended Pitzer model from experimental values at 298.15 K. a: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc1})$; b: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc2})$; c: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc3})$; d: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc4})$; $a_w(\text{calc1})$, water activities calculated by the pure solution parameters only; $a_w(\text{calc2})$, water activities calculated by the ternary mixture parameters fitted to the experimental water activities; $a_w(\text{calc3})$, water activities calculated by the ternary mixture parameters fitted to the experimental water activities and the solubility isotherms of ref 8; $a_w(\text{calc4})$, water activities calculated by the ternary mixture parameters fitted to the experimental water activities and the solubility isotherms of ref 9.

the experimental data.^{8,9} Meanwhile, the predicted water activities of the ternary system deviate from our experimental values (in Table 2) quite largely, as shown in Figure 5a. It seems that the extended Pitzer model with binary parameters only is insufficient in representing the properties of the ternary system, and mixture model parameters are needed to finish the task.

We fit the ternary mixture parameters $\theta_{\text{Li,Sr}}$ and $\psi_{\text{Li,SrCl}}$ to our measured water activities in Table 2 and obtained their values shown in Table 4. Applying both the binary

Table 4. Mixture Extended Pitzer Model Parameters for the System $\text{LiCl-SrCl}_2\text{-H}_2\text{O}$ at 298.15 K

| $\theta_{\text{Li,Sr}}$ | $\psi_{\text{Li,SrCl}}$ | data for parametrization | σ^a |
|-------------------------|-------------------------|---|------------|
| -0.0359 | 0.001921 | a_w in Table 2 | 0.0034 |
| 0.1239 | -0.00151 | a_w in Table 2 and solubility data in ref 8 | 0.0072 |
| 0.5791 | -0.07701 | a_w in Table 2 and solubility data in ref 9 | 0.0102 |

^aStandard deviation, $\sigma = ((\sum_i^n (a_w(\text{exp}) - a_w(\text{calc}))^2)/n)^{1/2}$.

and the ternary parameters, we predicted the solubility isotherms at 298.15 K again, as shown by dotted-dashed

line in Figure 4. No remarkable improvement has been achieved for the solubility isotherms, for either water activity (Figure 5b).

To get more reliable mixture parameters, we fit the ternary parameters to the water activities that we measured in the ternary system (Table 2) and the two sets of solubility isotherms for $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ reported by different authors,^{8,9} respectively, and obtained other two sets of mixture parameters listed in Table 4. Using these two sets of mixture parameters and with the binary parameters, we calculated the solubility isotherms for $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and the water activities of the ternary system, finding that the extended Pitzer model can roughly represent both sets of solubility isotherms for $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, as shown in Figure 4. After that, we regularly changed and found a “best” parameter value of $\ln K$ for $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, calculating its solubility isotherm. It was shown that neither of the two sets of calculated solubility isotherms for $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ (the dashed and solid lines in Figure 4) is consistent with the experimental values. The calculated water activities in the ternary system have no improvement either, as shown in Figure 5c,d.

4.2. Pitzer–Simonson–Clegg Model. The Pitzer–Simonson–Clegg model^{11–13} may also be a good selection

Table 5. Binary Pitzer–Simonson–Clegg Model Parameters at 298.15 K

| solute | α_{MX} | B_{MX} | α_{MX}^1 | B_{MX}^1 | $W_{1,MX}$ | $U_{1,MX}$ | $V_{1,MX}$ | σ^c |
|--------------------------------|---------------|----------|-----------------|------------|------------|------------|------------|------------|
| LiCl ^a | 13 | 230.0103 | 0 | 0 | 0.0305 | 29.0985 | -33.7297 | 0.0028 |
| SrCl ₂ ^b | 13 | 74.1569 | 2.0 | 104.2767 | 20.6085 | 64.6124 | -64.6919 | 0.0003 |

^aTaken from our previous work in ref 28. ^bParameters obtained by fitting to water activities in this work. ^cStandard deviation, $\sigma = ((\sum_i^n (a_w(\text{exp}) - a_w(\text{calc}))^2)/n)^{1/2}$.

to describe the titled highly soluble salt aqueous solutions, as it has been successfully applied to describe the property of highly soluble ternary systems containing LiCl²⁸ or CaCl₂.²⁹

In our previous work,³⁰ we corrected some print failures in the formulation of the water activity and salt activity coefficients in the framework of the Pitzer–Simonson–Clegg model and present them in Appendix B of this work.

The binary model parameters in eq 1B for LiCl solution at 298.15 K are taken from our previous work,²⁸ and those for SrCl₂ solution were fitted to our experimental values, as shown in Table 5. The standard deviations of fitting are 0.0028 and 0.0003 for LiCl and SrCl₂, respectively, slightly better than those by the extended Pitzer model. The calculated water activities of LiCl and SrCl₂ solutions are presented by solid lines in Figures 1 and 2, respectively.

Applying the binary model parameters, we predicted the solubility isotherm for SrCl₂·6H₂O and the water activities in the ternary system LiCl–SrCl₂–H₂O at 298.15 K and found that both the predicted solubility isotherm (dotted–dashed lines in Figure 6) and water activities (Figure 7a) deviate from

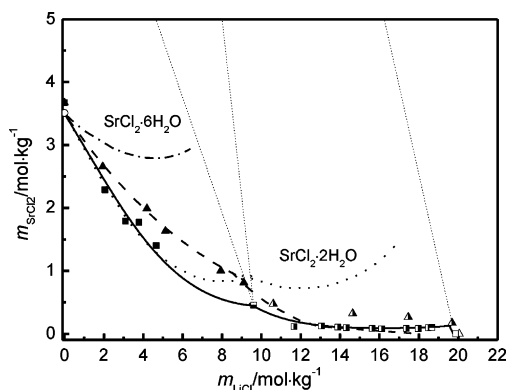


Figure 6. Comparison of experimental and calculated solubility isotherms in the system LiCl–SrCl₂–H₂O at 298.15 K. All symbols are experimental values: \blacktriangle , SrCl₂·6H₂O;⁸ \blacktriangle , SrCl₂·2H₂O;⁸ \triangle , LiCl·H₂O;⁸ \blacksquare , SrCl₂·6H₂O;⁹ \square , SrCl₂·2H₂O;⁹ \square , LiCl·H₂O;⁹ \blacksquare , co-saturated point of SrCl₂·6H₂O and SrCl₂·2H₂O;⁹ \square , co-saturated point of SrCl₂·2H₂O and LiCl·H₂O;⁹ \circ , SrCl₂·6H₂O determined by isopiestic method from Rard⁴ and in this work; all lines are calculated by the Pitzer–Simonson–Clegg model: $-\cdot-$, with binary parameters only; \cdots , with binary parameters and ternary parameters obtained by fitting to experimental water activities in the ternary system; $-\cdot-\cdot-$, with binary parameters and ternary parameters obtained by fitting to experimental water activities and solubility data in ref 8; $-\cdot-\cdot-$, with binary parameters and ternary parameters obtained by fitting to experimental water activities and solubility isotherms in ref 9.

the experiment data remarkably. As the extended Pitzer model, the Pitzer–Simonson–Clegg model cannot predict the

solubility isotherm for SrCl₂·6H₂O of the ternary system with only binary parameters, either.

We fitted the ternary mixture Pitzer–Simonson–Clegg model parameters to our experimental water activities in Table 2 and obtained their values in Table 6. Applying both the binary and the ternary parameters, we obtained the predicted solubility isotherm for SrCl₂·6H₂O (dotted lines in Figure 6), which are near to the experimental data;^{8,9} however, no matter how we changed the parameter $\ln K$ for SrCl₂·2H₂O, the calculated solubility isotherm for SrCl₂·2H₂O does not agree with any one of the two sets of experimental data. Possibly, fitting to water activities in the ternary system measured in this work is insufficient for evaluating a “reasonable” set of model parameters to calculate the solubility isotherms.

To gain a more “reasonable” set of parameters, we fitted the ternary model parameters to water activity in the ternary system measured in this work and the two sets of solubility isotherm for SrCl₂·6H₂O,^{8,9} respectively, and got their values listed in Table 6. Applying the two sets of mixture parameters, respectively, and the binary parameters in Table 5, we calculated the solubility isotherm for SrCl₂·6H₂O, as shown by the dashed lines and solid lines in Figure 6. Both of them agree with each corresponding experimental data point. The deviations of calculated water activities from the experimental values are shown in Figure 7c,d. Both are similar in magnitude.

When we regularly changed the parameter $\ln K$ for SrCl₂·2H₂O and calculated its solubility isotherm, we found that the isotherm for SrCl₂·2H₂O (dashed lines in Figure 6) calculated by the mixture parameters fitted to experimental water activities and the solubility data of Blidin⁸ deviates largely from the experimental data;⁸ however, the solubility isotherm for SrCl₂·2H₂O (solid lines in Figure 6) calculated by the mixture parameters fitted to experimental water activities and the solubility data of Kydynov et al.⁹ agrees with the corresponding experimental data⁹ very well.

Based on the above results, one can conclude that the Pitzer–Simonson–Clegg model can consistently correlate binary and ternary water activities and the solubility isotherms of Kydynov et al.⁹ of the LiCl–SrCl₂–H₂O system at 298.15 K. From this point of view, the solubility isotherms determined by Kydynov et al.⁹ should be relatively more reliable than those reported by Blidin.⁸ We observed also that the solubility of SrCl₂·6H₂O in the binary system SrCl₂–H₂O reported by Kydynov et al.⁹ slightly differs from that reported by Rard⁴ and in this work (the circle symbol in Figure 6). Our calculated cosaturated point for the two phases SrCl₂·6H₂O and LiCl·H₂O also differs from that reported by Kydynov et al.⁹ Strictly speaking, their data are waiting for further determination.

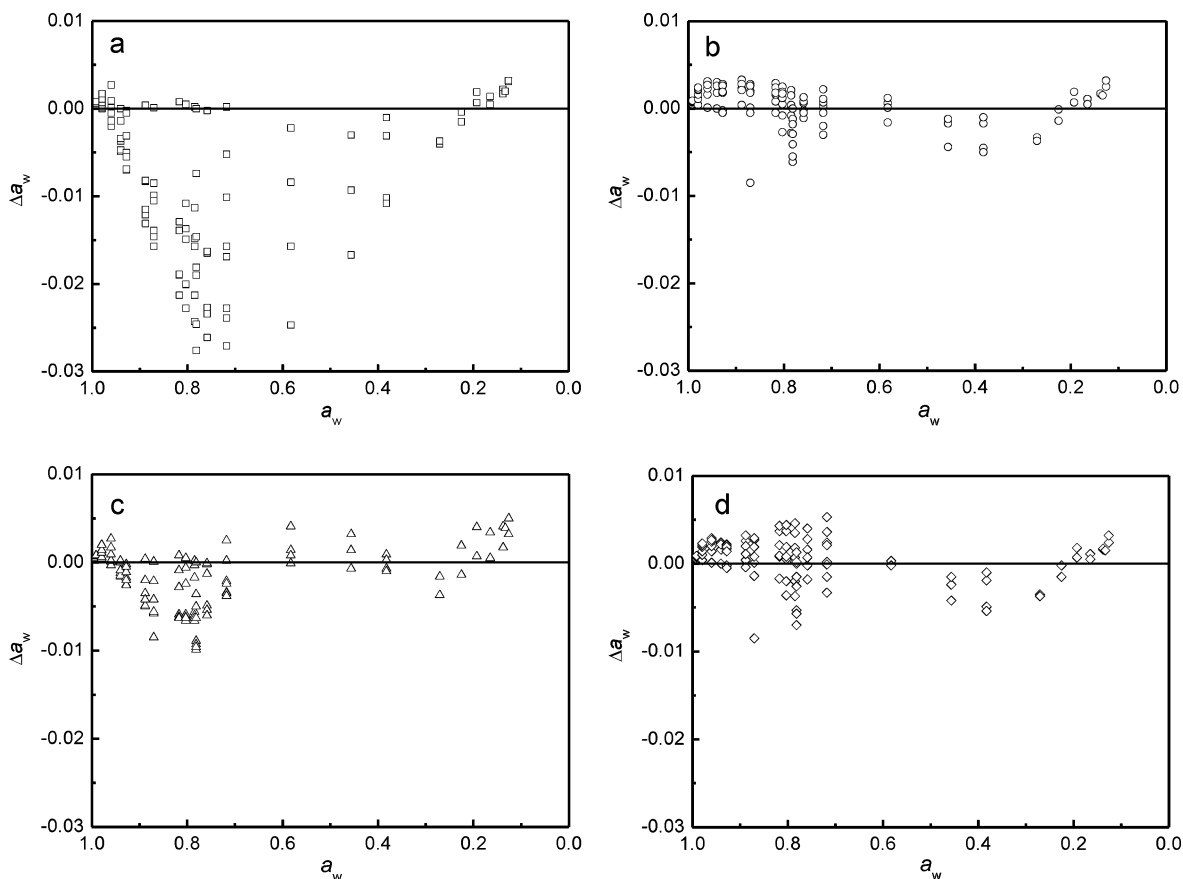


Figure 7. Deviation of water activity in the ternary system that calculated by Pitzer–Simonson–Clegg model from experimental values at 298.15 K. a: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc1})$; b: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc2})$; c: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc3})$; d: $\Delta a_w = a_w(\text{exp}) - a_w(\text{calc4})$; $a_w(\text{calc1})$, water activities calculated by the pure solution parameters only; $a_w(\text{calc2})$, water activities calculated by the ternary mixture parameters fitted to the experimental water activities; $a_w(\text{calc3})$, water activities calculated by the ternary mixture parameters fitted to the experimental water activities and the solubility isotherms of ref 8; $a_w(\text{calc4})$, water activities calculated by the ternary mixture parameters fitted to the experimental water activities and the solubility isotherms of ref 9.

Table 6. Mixture Pitzer–Simonson–Clegg Model Parameters at 298.15 K

| W_{LiSrCl} | Q_{LiSrCl} | U_{LiSrCl} | data for parametrization | σ^a |
|---------------------|---------------------|---------------------|---|------------|
| −38.4089 | 40.9937 | 19.4013 | a_w in Table 2 | 0.0023 |
| 26.0790 | −7.9378 | −6.4891 | a_w in Table 2 and solubility data in ref 8 | 0.0037 |
| −20.5063 | 29.6212 | 1.6683 | a_w in Table 2 and solubility data in ref 9 | 0.0025 |

^aStandard deviation, $\sigma = ((\sum_i^n (a_w(\text{exp}) - a_w(\text{calc}))^2)/n)^{1/2}$.

5. CONCLUSIONS

We elaborately measured the water activities of the ternary system LiCl–SrCl₂–H₂O and its sub-binary systems at 298.15 K by the isopiestic method. The measured results for the binary systems are in good agreement with literature data.

The extended Pitzer model and Pitzer–Simonson–Clegg model were used to predict and correlate the thermodynamic properties of the ternary system LiCl–SrCl₂–H₂O, including binary and ternary water activities, and solubility isotherms from different authors.^{8,9}

When the extended Pitzer model was used, the water activities for the ternary system can be represented using binary and mixture parameters, but for the solubility isotherms, no consistent results could be obtained, no matter how the model parameters were adjusted. However, the Pitzer–Simonson–

Clegg model can consistently correlate the binary and ternary water activity and the solubility isotherms reported by Kydymov et al.,⁹ but not the solubility isotherms reported by Blidin.⁸ From this point of view, the solubility isotherms reported by Kydymov et al.⁹ should be relatively more reliable.

■ APPENDIX A: EXTENDED PITZER MODEL⁷

For a binary system MX–H₂O,

$$\phi = 1 - \frac{|z_M z_X| A_\phi I^{1/2}}{(1 + bI^{1/2})} + \left(\frac{2\nu_M \nu_X}{\nu} \right) m B_{\text{MX}}^\phi + \left(\frac{4\nu_M^2 \nu_X z_M}{\nu} \right) m^2 C_{\text{MX}}^{T\phi} \quad (1A)$$

$$B_{\text{MX}}^\phi = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)} \exp(-\alpha I^{1/2}) \quad (2A)$$

$$C_{\text{MX}}^{T\phi} = C_{\text{MX}}^{(0)} + C_{\text{MX}}^{(1)} \exp(-\omega_{\text{MX}} I^{1/2}) \quad (3A)$$

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (4A)$$

For a multicomponent system,

$$\begin{aligned} & \frac{(\sum_i m_i)}{2}(\phi - 1) \\ &= -\frac{A^\phi I^{3/2}}{1 + bI^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}^{T\phi}) \\ &+ \sum_{c < c'} \sum_{c'} m_c m_{c'} (\Phi_{cc'}^\phi + \sum_a m_a \Psi_{cc'a}) \\ &+ \sum_{a < a'} \sum_{a'} m_a m_{a'} (\Phi_{aa'}^\phi + \sum_c m_c \Psi_{aa'c}) \end{aligned} \quad (5A)$$

$$\begin{aligned} \ln \gamma_M &= z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}^T) \\ &+ \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \Psi_{Mca}) \\ &+ \sum_{a < a'} \sum_{a'} m_a m_{a'} \Psi_{aa'M} \\ &+ |z_M| \sum_c \sum_a m_c m_a C_{ca}^T \end{aligned} \quad (6A)$$

$$\begin{aligned} \ln \gamma_X &= z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}^T) \\ &+ \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \Psi_{Xac}) \\ &+ \sum_{c < c'} \sum_{c'} m_c m_{c'} \Psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}^T \end{aligned} \quad (7A)$$

$$\begin{aligned} F &= -A^\phi \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right] \\ &+ \sum_c \sum_a m_c m_a \left(B'_{ca} + \frac{ZC_{ca}^{T'}}{2} \right) \\ &+ \sum_{c < c'} \sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a < a'} \sum_{a'} m_a m_{a'} \Phi'_{aa'} \end{aligned} \quad (8A)$$

where

$$A^\phi = \frac{1}{3} (2\pi N_0 d_w / 1000)^{1/2} (e^2 / DkT)^{3/2} \quad (9A)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 \sqrt{I}} + \beta_{MX}^{(2)} e^{-\alpha_2 \sqrt{I}} \quad (10A)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 \sqrt{I}) + \beta_{MX}^{(2)} g(\alpha_2 \sqrt{I}) \quad (11A)$$

$$B'_{MX} = \beta_{MX}^{(1)} g'(\alpha_1 \sqrt{I}) + \beta_{MX}^{(2)} g'(\alpha_2 \sqrt{I}) \quad (12A)$$

$$C_{MX}^{T\phi} = C_{MX}^{(0)} + C_{MX}^{(1)} \exp(-\omega_{MX} \sqrt{I}) \quad (13A)$$

$$C_{MX}^T = C_{MX}^{(0)} + 4C_{MX}^{(1)} h(\omega_{MX} \sqrt{I}) \quad (14A)$$

$$C_{MX}^{T'} = 4C_{MX}^{(1)} h'(\omega_{MX} \sqrt{I}) / I \quad (15A)$$

$$g(x) = 2[1 - (1 + x)\exp(-x)] / x^2 \quad (16A)$$

$$g'(x) = -2[1 - (1 + x + x^2/2)\exp(-x)] / x^2 \quad (17A)$$

$$h(x) = \{6 - [6 + x(6 + 3x + x^2)]\exp(-x)\} / x^4 \quad (18A)$$

$$h'(x) = \exp(-x) / 2 - 2h(x) \quad (19A)$$

$$Z = \sum_i m_i |z_i| \quad (20A)$$

$$\Phi_{ij} = \theta_{ij} + \theta_{ij}^E(I) \quad (21A)$$

$$\Phi'_{ij} = \theta_{ij}^{E'}(I) \quad (22A)$$

$$\Phi_{ij}^\phi = \theta_{ij} + \theta_{ij}^E(I) + I\theta_{ij}^{E'}(I) \quad (23A)$$

$$x_{ij} = 6z_i z_j A_\phi I^{1/2} \quad (24A)$$

$$\theta_{ij}^E = (z_i z_j / 4I) [J(x_{ij}) - 1/2J(x_{ii}) - 1/2J(x_{jj})] \quad (25A)$$

$$\begin{aligned} \theta_{ij}^{E'} &= \partial \theta_{ij}^E / \partial I \\ &= -\theta_{ij}^E / I + (z_i z_j / 8I^2) [x_{ij}'(x_{ij}) \\ &\quad - (1/2)x_{ii}'(x_{ii}) - (1/2)x_{jj}'(x_{jj})] \end{aligned} \quad (26A)$$

$$J(x_{ij}) = x_{ij}' / [4 + C_1 x_{ij}^{C_2} \exp(C_3 x_{ij}^{C_4})] \quad (27A)$$

$$J'(x_{ij}) = \partial J(x_{ij}) / \partial x_{ij} \quad (28A)$$

with $C_1 = 4.581$, $C_2 = 0.7237$, $C_3 = 0.0120$, and $C_4 = 0.528$.

■ APPENDIX B: PITZER–SIMONSON–CLEGG MODEL^{11–13,28}

For a single-electrolyte solution, the Pitzer–Simonson–Clegg model describes the solvent activity coefficient f_1 as below:

$$\begin{aligned} \ln f_1 &= 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \\ &\quad - x_M x_X B_{MX} \exp(-\alpha_{MX} I_x^{1/2}) \\ &\quad - x_M x_X B_{MX}^1 \exp(-\alpha_{MX}^1 I_x^{1/2}) \\ &\quad + x_I^2 (W_{1,MX} + (x_I - x_1) U_{1,MX}) \\ &\quad + 4x_1 x_M x_X (2 - 3x_1) V_{1,MX} \end{aligned} \quad (1B)$$

Cation M:

$$\begin{aligned} \ln f_M &= -z_M^2 A_x [(2/\rho) \ln(1 + \rho I_x^{1/2}) \\ &\quad + I_x^{1/2} (1 - 2I_x / z_M^2) / (1 + \rho I_x^{1/2})] \\ &\quad + x_X B_{MX} g(\alpha_{MX} I_x^{1/2}) - x_M x_X B_{MX} \\ &\quad \times [z_M^2 g(\alpha_{MX} I_x^{1/2}) / (2I_x) + (1 - z_M^2 / (2I_x)) \\ &\quad \times \exp(-\alpha_{MX} I_x^{1/2})] + x_X B_{MX}^1 g(\alpha_{MX}^1 I_x^{1/2}) \\ &\quad - x_M x_X B_{MX}^1 [z_M^2 g(\alpha_{MX}^1 I_x^{1/2}) / (2I_x) \\ &\quad + (1 - z_M^2 / (2I_x)) \exp(-\alpha_{MX}^1 I_x^{1/2})] \\ &\quad + x_I ((z_M + z_X) / (2z_X) - x_I) W_{1,MX} \\ &\quad + x_I x_I ((z_M + z_X) / z_X - 2x_I) U_{1,MX} + 4x_I^2 \\ &\quad \times x_X (1 - 3x_M) V_{1,MX} - \frac{1}{2} [(z_M + z_X) / z_X] W_{1,MX} \end{aligned} \quad (2B)$$

and anion X:

$$\begin{aligned} \ln f_X = & -z_X^2 A_x [(2/\rho) \ln(1 + \rho I_x^{1/2}) \\ & + I_x^{1/2} (1 - 2I_x/z_X^2) / (1 + \rho I_x^{1/2})] \\ & + x_M B_{MX} g(\alpha_{MX} I_x^{1/2}) \\ & - x_M x_X B_{MX} [z_X^2 g(\alpha_{MX} I_x^{1/2}) / (2I_x) \\ & + (1 - z_X^2 / (2I_x)) \exp(-\alpha_{MX} I_x^{1/2})] \\ & + x_M B_{MX}^1 g(\alpha_{MX}^1 I_x^{1/2}) \\ & - x_M x_X B_{MX}^1 [z_X^2 g(\alpha_{MX}^1 I_x^{1/2}) / (2I_x) \\ & + (1 - z_X^2 / (2I_x)) \exp(-\alpha_{MX}^1 I_x^{1/2})] \\ & + x_1 ((z_M + z_X) / (2z_M) - x_1) W_{1,MX} \\ & + x_1 x_I ((z_M + z_X) / z_M - 2x_1) U_{1,MX} \\ & + 4x_1^2 x_M (1 - 3x_X) V_{1,MX} \\ & - \frac{1}{2} [(z_M + z_X) / z_M] W_{1,MX} \end{aligned} \quad (3B)$$

where $\rho = 2150(d_1/DT)^{1/2}$; $x_1 = x_M + x_X = 1 - x_j$; A_x and I_x are Debye–Hückel parameter and ionic strength based on mole fraction; x_X , x_M , d_1 , D , and T are mole fractions of anion and cation, density of the solvent water, dielectric constant of the solvent, and thermodynamic temperature, respectively; B_{MX} , B_{MX}^1 , $W_{1,MX}$, $U_{1,MX}$, $V_{1,MX}$, α_{MX} , and α_{MX}^1 are model parameters.

For a symmetrical or unsymmetrical ternary system MX–NX–H₂O, the activity coefficient of water f_1 , cation M f_M , and anion f_X are expressed as the following:

$$\begin{aligned} \ln f_1 = & 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \\ & - x_M x_X B_{MX} \exp(-\alpha_{MX} I_x^{1/2}) \\ & - x_M x_X B_{MX}^1 \exp(-\alpha_{MX}^1 I_x^{1/2}) \\ & - x_N x_X B_{NX} \exp(-\alpha_{NX} I_x^{1/2}) \\ & - x_N x_X B_{NX}^1 \exp(-\alpha_{NX}^1 I_x^{1/2}) \\ & - 2x_M x_N (v_{MN} + I_x v'_{MN}) + (1 - x_1) \\ & \times (1/F) \{ E_M (z_M + z_X) / (z_M z_X) W_{1,MX} \\ & + E_N (z_N + z_X) / (z_N z_X) W_{1,NX} \} \\ & + (1 - 2x_1) x_x \{ x_M (z_M + z_X)^2 \\ & / (z_M z_X) U_{1,MX} + x_N (z_N + z_X)^2 \\ & / (z_N z_X) U_{1,NX} \} + 4x_1 (2 - 3x_1) x_X \\ & \times (x_M V_{1,MX} + x_N V_{1,NX}) \\ & - 2x_M x_N W_{MNX} - 4x_M x_N (x_M / v_{M(X)}) U_{MNX} \\ & - x_N / v_{N(X)} U_{MNX} \\ & + 4(1 - 2x_1) x_M x_N Q_{1,MNX} \end{aligned} \quad (4B)$$

$$\begin{aligned} \ln f_M = & -z_M^2 A_x [(2/\rho) \ln(1 + \rho I_x^{1/2}) + I_x^{1/2} (1 - 2I_x/z_M^2) \\ & / (1 + \rho I_x^{1/2})] + x_X B_{MX} g(\alpha_{MX} I_x^{1/2}) \\ & + x_X B_{MX}^1 g(\alpha_{MX}^1 I_x^{1/2}) - x_M x_X B_{MX} \\ & \times [z_M^2 g(\alpha_{MX} I_x^{1/2}) / (2I_x) + (1 - z_M^2 / (2I_x)) \\ & \times \exp(-\alpha_{MX} I_x^{1/2})] - x_M x_X B_{MX}^1 [z_M^2 g(\alpha_{MX}^1 I_x^{1/2}) \\ & / (2I_x) + (1 - z_M^2 / (2I_x)) \exp(-\alpha_{MX}^1 I_x^{1/2})] \\ & - x_N x_X B_{NX} [z_M^2 g(\alpha_{NX} I_x^{1/2}) / (2I_x) \\ & + (1 - z_M^2 / (2I_x)) \exp(-\alpha_{NX} I_x^{1/2})] \\ & - x_N x_X B_{NX}^1 [z_M^2 g(\alpha_{NX}^1 I_x^{1/2}) / (2I_x) \\ & + (1 - z_M^2 / (2I_x)) \exp(-\alpha_{NX}^1 I_x^{1/2})] \\ & + 2x_N (v_{MN} - x_M (v_{MN} + v'_{MN} (I_x - z_M^2/2))) \\ & + x_1 [(z_M + z_X) / z_X W_{1,MX} - (z_M/2 + 1/F) \\ & \times (E_M (z_M + z_X) / (z_M z_X) W_{1,MX}) + E_N (z_N + z_X) \\ & / (z_N z_X) W_{1,NX}] + x_1 x_X [(z_M + z_X)^2 / (z_M z_X) U_{1,MX} \\ & - 2(x_M (z_M + z_X)^2 / (z_M z_X) U_{1,MX} + x_N (z_N + z_X)^2 \\ & / (z_N z_X) U_{1,NX})] + 4x_1^2 x_X (V_{1,MX} - 3x_M V_{1,MX} \\ & - 3x_N V_{1,NX}) + 2(x_N W_{MNX} - x_M x_N W_{MNX}) \\ & + 2[x_N (2x_M / v_{M(X)} - x_N / v_{N(X)}) U_{MNX} \\ & - 2x_M x_N (x_M / v_{M(X)} - x_N / v_{N(X)}) U_{MNX}] \\ & + 4x_1 (x_N Q_{1,MNX} - 2x_M x_N Q_{1,MNX}) \\ & - \left[(1 - E_M/2) (z_M + z_X) / z_X W_{1,MX} \right. \\ & \left. - \frac{1}{2} z_M E_N (z_N + z_X) / (z_N z_X) W_{1,NX} \right] \end{aligned} \quad (5B)$$

$$\begin{aligned} \ln f_X = & -z_X^2 A_x [(2/\rho) \ln(1 + \rho I_x^{1/2}) + I_x^{1/2} (1 - 2I_x/z_X^2) \\ & / (1 + \rho I_x^{1/2})] + x_M B_{MX} g(\alpha_{MX} I_x^{1/2}) \\ & + x_M B_{MX}^1 g(\alpha_{MX}^1 I_x^{1/2}) + x_N B_{NX} g(\alpha_{NX} I_x^{1/2}) \\ & + x_N B_{NX}^1 g(\alpha_{NX}^1 I_x^{1/2}) - x_M x_X B_{MX} [z_X^2 g(\alpha_{MX} I_x^{1/2}) \\ & / (2I_x) + (1 - z_X^2 / (2I_x)) \exp(-\alpha_{MX} I_x^{1/2})] \\ & - x_M x_X B_{MX}^1 [z_X^2 g(\alpha_{MX}^1 I_x^{1/2}) / (2I_x) \\ & + (1 - z_X^2 / (2I_x)) \exp(-\alpha_{MX}^1 I_x^{1/2})] - x_N x_X B_{NX} \\ & \times [z_X^2 g(\alpha_{NX} I_x^{1/2}) / (2I_x) + (1 - z_X^2 / (2I_x)) \\ & \times \exp(-\alpha_{NX} I_x^{1/2})] - x_N x_X B_{NX}^1 [z_X^2 g(\alpha_{NX}^1 I_x^{1/2}) \\ & / (2I_x) + (1 - z_X^2 / (2I_x)) \exp(-\alpha_{NX}^1 I_x^{1/2})] \\ & - 2x_M x_N (v_{MN} + v'_{MN} (I_x - z_X^2/2)) \\ & + x_1 E_M [(z_M + z_X) / z_M W_{1,MX} - (z_X/2 + 1/F) \\ & \times (z_M + z_X) / (z_M z_X) W_{1,MX}] + x_1 E_N [(z_N + z_X) \\ & / z_N W_{1,NX} - (z_X/2 + 1/F) (z_N + z_X) / (z_N z_X) W_{1,NX}] \\ & + x_1 x_M [(z_M + z_X)^2 / (z_M z_X) U_{1,MX} - 2(x_X (z_M + z_X)^2 \\ & / (z_M z_X) U_{1,MX})] + x_1 x_N [(z_N + z_X)^2 / (z_N z_X) U_{1,NX} \\ & - 2(x_X (z_N + z_X)^2 / (z_N z_X) U_{1,NX})] \\ & + 4x_1^2 x_M (V_{1,MX} - 3x_X V_{1,MX}) \\ & + 4x_1^2 x_N (V_{1,NX} - 3x_X V_{1,NX}) - 2x_M x_N W_{MNX} \\ & - 4x_M x_N (x_M / v_{M(X)} - x_N / v_{N(X)}) U_{MNX} \\ & - 8x_1 x_M x_N Q_{1,MNX} - \frac{1}{2} [E_M (z_M + z_X) / z_M W_{1,MX}] \end{aligned} \quad (6B)$$

where W_{MNX} , $Q_{1,MNX}$, and U_{MNX} are ternary model parameters.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dewen_zeng@hotmail.com.

Funding

This work was financially supported by the 100 Top Talents Project and Innovative Project (KJ CX2-YW-H2O) of the Chinese Academy of Sciences and the National Nature Science Foundation of China under contract numbers 20773152 and 51134007.

■ REFERENCES

- (1) Li, Q. H.; Gu, T. X.; Yu, S. S.; Yao, Y.; Li, B.; Li, W. Study on the Precipitation Pathway of Nanyishan Oilfield Brine at Subzero Temperatures. *Acta Phys. Chim. Sin.* **2011**, *27*, 1803–1808.
- (2) Downes, C. J. Osmotic and Activity Coefficients for Mixtures of Potassium Chloride and Strontium Chloride in Water at 298.15 K. *J. Chem. Thermodyn.* **1974**, *6*, 317–323.
- (3) Macaskill, J. B.; White, D. R. Jr.; Robinson, R. A.; Bates, R. G. Isopiestic Measurements on Aqueous Mixtures of Sodium Chloride and Strontium Chloride. *J. Solution Chem.* **1978**, *7*, 339–347.
- (4) Rard, J. A.; Miller, D. G. Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous CsCl, SrCl₂, and Mixtures of NaCl and CsCl at 25 °C. *J. Chem. Eng. Data* **1982**, *27*, 169–173.
- (5) Goldberg, R. N.; Nuttall, R. L. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: the Alkaline Earth Metal Halides. *J. Phys. Chem. Ref. Data* **1978**, *7*, 263–310.
- (6) Rard, J. A.; Miller, D. G. Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of NaCl and SrCl₂ at 25 °C. *J. Chem. Eng. Data* **1982**, *27*, 342–346.
- (7) Clegg, S. L.; Rard, J. A.; Miller, D. G. Isopiestic Determination of the Osmotic and Activity Coefficients of NaCl + SrCl₂ + H₂O at 298.15 K and Representation with an Extended Ion-Interaction Model. *J. Chem. Eng. Data* **2005**, *50*, 1162–1170.
- (8) Blidin, V. P. Heterogeneous Equilibrium in Aqueous Ternary Systems of Lithium Chloride and the Chlorides of Barium, Strontium, and Calcium. *Dokl. Akad. Nauk SSSR* **1952**, *84*, 947–950.
- (9) Kydynov, M. K.; Lomteva, S. A.; Druzhinin, I. G. Solubility of Ternary Systems of Lithium, Sodium, and Strontium Chlorides at 25 °C. *Issled. Obl. Khim. Tekhnol. Miner. Solei Okislov* **1965**, 146–150.
- (10) Zeng, D.; Xu, W. F.; Voigt, W.; Yin, X. Thermodynamic Study of the System LiCl-CaCl₂-H₂O. *J. Chem. Thermodyn.* **2008**, *40*, 1157–1165.
- (11) Pitzer, K. S.; Simonson, J. M. Thermodynamics of Multicomponent, Miscible, Ionic Systems: Theory and Equations. *J. Phys. Chem.* **1986**, *90*, 3005–3009.
- (12) Clegg, S. L.; Pitzer, K. S. Thermodynamics of Multicomponent, Miscible, Ionic Solutions. Generalized Equations for Symmetrical Electrolytes. *J. Phys. Chem.* **1992**, *96*, 3513–3520.
- (13) Clegg, S. L.; Pitzer, K. S.; Brimblecombe, P. Thermodynamics of Multicomponent, Miscible, Ionic Solutions. 2. Mixture Including Unsymmetrical Electrolytes. *J. Phys. Chem.* **1992**, *96*, 9470–9479.
- (14) Zhang, Y.; Yao, Y.; Li, L. J.; Song, P. S. Isopiestic Determination of the Osmotic Coefficients and Pitzer Model Representation for Li₂B₄O₇(aq) at 298.15 K. *J. Chem. Thermodyn.* **2005**, *37*, 101–109.
- (15) Yin, S. T.; Yao, Y.; Li, B.; Tian, H. B. Isopiestic Studies of Aqueous MgB₄O₇ and MgSO₄ + MgB₄O₇ at 298.15 K and Representation with Pitzer's Ion-Interaction Model. *J. Solution Chem.* **2007**, *36*, 1745–1761.
- (16) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.
- (17) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*; CRC: Boca Raton, FL, 1991.
- (18) Rard, J. A. Isopiestic Determination of the Osmotic Coefficients of Aqueous H₂SO₄ at 25 °C. *J. Chem. Eng. Data* **1983**, *28*, 384–387.
- (19) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1985**, *1*, 1047–1100.
- (20) Gibbard, H. F. Jr.; Scatchard, J. G. Liquid-Vapor Equilibrium of Aqueous Lithium Chloride, from 25 to 100 °C and from 1.0 to 18.5 Molal, and Related Properties. *J. Chem. Eng. Data* **1973**, *18*, 293–298.
- (21) Robinson, R. A.; Stokes, R. H. *Electrolyte solutions*, 2nd ed. (revised); Butterworths: London, 1965.
- (22) Yao, Y.; Sun, B.; Song, P. S.; Zhang, Z.; Wang, R. L.; Chen, J. Q. Thermodynamics of Aqueous Electrolyte Solution-Isopiestic Determination of Osmotic and Activity Coefficients in LiCl-MgCl₂-H₂O at 25 °C. *Acta Chim. Sin.* **1992**, *50*, 839–848.
- (23) Christov, C. Thermodynamics of Formation of Double Salts and Mixed Crystals from Aqueous Solutions. *J. Chem. Thermodyn.* **2005**, *37*, 1036–1060.
- (24) Guendouzi, M. E. Solubility in the Ternary Aqueous Systems Containing M, Cl⁻, NO₃⁻, and SO₄²⁻ with M = NH₄⁺, Li⁺, or Mg²⁺ at T = 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 376–381.
- (25) Rard, J. A. Solubility Determinations by the Isopiestic Method and Application to Aqueous Lanthanide Nitrates at 25 °C. *J. Solution Chem.* **1985**, *14*, 457–471.
- (26) Pollio, M. L.; Kitic, D.; Resnik, S. L. Research Note: A_w Values of Six Saturated Salt Solutions at 25 °C. Re-examination for the Purpose of Maintaining a Constant Relative Humidity in Water Sorption Measurements. *Lebensm. Wiss. Technol.* **1996**, *29*, 376–378.
- (27) May, P. M. Improved Thermodynamic Calculations for Concentrated Mixed Electrolyte Systems Including Ion Pairing (or the Absence of it). *Mar. Chem.* **2006**, *99*, 62–69.
- (28) Ouyang, H. T.; Zeng, D.; Zhou, H. Y.; Han, H. J.; Yao, Y. Solubility of the Ternary System LiCl + NH₄Cl + H₂O. *J. Chem. Eng. Data* **2011**, *56*, 1096–1104.
- (29) Dong, O. Y.; Zeng, D.; Zhou, H. Y.; Han, H. J.; Yin, X.; Du, Y. Phase Change Materials in the Ternary System NH₄Cl + CaCl₂ + H₂O. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2011**, *35*, 269–275.
- (30) Zeng, D.; Wu, Z. D.; Yao, Y.; Han, H. J. Isopiestic Determination of Water Activity on the System LiNO₃ + KNO₃ + H₂O at 273.1 and 298.1 K. *J. Solution Chem.* **2010**, *39*, 1360–1376.