

Solid–Liquid Equilibria in the Ternary System LiBr–SrBr<sub>2</sub>–H<sub>2</sub>O at 273.15, 308.15 and 323.15 K

Pei-Huan Jiang, Chun-Xia He, Shi-Hua Sang,\* Xing-Liu, and Lan-Rong Zhao

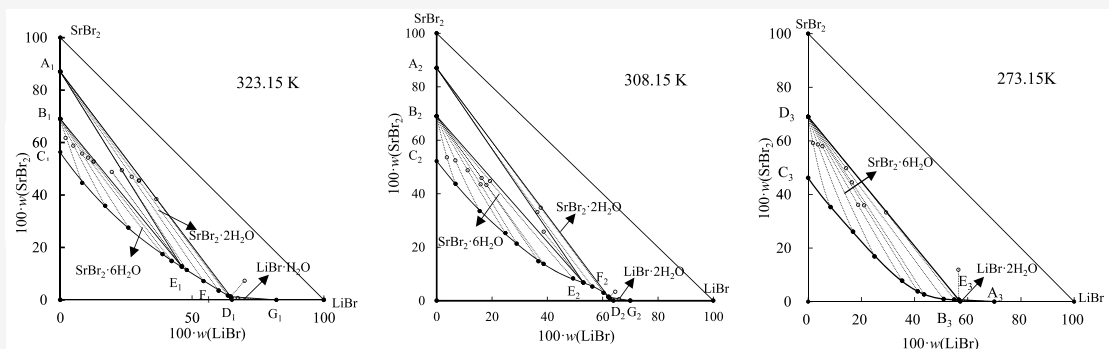
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**ABSTRACT:** The solid–liquid equilibria in the ternary system LiBr–SrBr<sub>2</sub>–H<sub>2</sub>O at 273.15, 308.15, and 323.15 K were studied by isothermal dissolution equilibrium method in this work. At three different temperatures, the ternary system LiBr–SrBr<sub>2</sub>–H<sub>2</sub>O belongs to hydrate type I saturation. The phase diagram at 273.15 K includes one cosaturation point, two univariant curves, and two crystallization zones corresponding to LiBr·2H<sub>2</sub>O and SrBr<sub>2</sub>·6H<sub>2</sub>O. The other two phase diagrams contain two cosaturation points, three univariant curves, and three crystallization fields corresponding to LiBr·2H<sub>2</sub>O, SrBr<sub>2</sub>·2H<sub>2</sub>O, and SrBr<sub>2</sub>·6H<sub>2</sub>O at 308.15 K and LiBr·H<sub>2</sub>O, SrBr<sub>2</sub>·2H<sub>2</sub>O, and SrBr<sub>2</sub>·6H<sub>2</sub>O at 323.15 K, respectively. Lithium bromide has an obvious salting-out effect on strontium bromide. The crystallization area of lithium bromide hydrate is the smallest, and lithium bromide is difficult to crystallize out of the solution at different temperatures.

## 1. INTRODUCTION

Natural brines are an important industrial resource for lithium. Currently, salt lake brines are used widely for industrial lithium production, such as Searles and Silver Peak in the United States, Atacama in Chile, and Qaidam Basin in China. Generally, the concentration of lithium in brine is low, so it is difficult to extract directly. In most cases, lithium is extracted after separating and extracting various other salts. However, the brines with industrial grade are mostly in the arid area, so it should be more reasonable to adopt natural evaporation and gradual separation in the treatment of brines. Therefore, the study of the phase equilibrium relations of water–salt systems containing lithium is essential for designing the extraction of lithium salts from natural brines.<sup>1</sup>

As strontium and its compounds are more and more widely used in electronics, building materials, metallurgy, chemical industry, and other aspects, the demand for strontium is increasing. Therefore, the effective development of strontium in these brines has become a hot spot.<sup>2</sup> China is rich in underground brine resources, which not only contain sodium and potassium but also contain strontium, etc.<sup>3</sup> The underground brine in Sichuan Basin not only has a high

concentration of NaCl, but also contains a variety of useful components, such as K, Br, Sr, Li, etc. Its maximum salinity can reach 382 g/L.<sup>4</sup> The temperature of underground brine is not constant, so the study on multi-temperature phase equilibria will provide important guidance for the comprehensive utilization, development of underground brine, and industrial applications in Sichuan Basin. Many researches on phase equilibrium systems containing bromine or strontium have been reported in recent years.<sup>5–8</sup> The phase equilibria of ternary system SrBr<sub>2</sub>–MgBr<sub>2</sub>–H<sub>2</sub>O at 298 and 323 K were also published.<sup>9</sup> The phase equilibria of quaternary system NaBr–KBr–SrBr<sub>2</sub>–H<sub>2</sub>O and its related subsystems at 323 K have been studied.<sup>10</sup> Sichuan underground brine mainly contains potassium, magnesium, strontium, lithium, sodium, chlorine and bromine. Until now, there have been few reports about

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systems containing lithium bromide, but there are many systems containing lithium chloride have been studied. The ternary system  $\text{LiCl}-\text{SrCl}_2-\text{H}_2\text{O}$  at 308 K<sup>11</sup> has been studied. In addition, multi-temperature phase equilibria of the system  $\text{LiCl}-\text{KCl}-\text{RbCl}-\text{H}_2\text{O}$  and its subsystems were also reported in recent years.<sup>12–14</sup> So far, the phase equilibrium system  $\text{LiBr}-\text{SrBr}_2-\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K are not reported. The solid–liquid equilibria in ternary system  $\text{LiBr}-\text{SrBr}_2-\text{H}_2\text{O}$  at three temperatures are studied in this work. The phase equilibrium data and phase diagram obtained at different temperatures from this study can provide a theoretical basis for the extraction of the underground brine in Sichuan Basin and the corresponding production technology.

## 2. EXPERIMENTAL SECTION

**2.1. Reagents and Instruments.** All of the chemical reagents used in the experiments were of analytically purity (Table 1). Deionized water was used to prepare and analyze samples.

Table 1. Chemical Reagents

chemical name	CAS	purity (mass fraction)	source	analysis method
strontium bromide hexahydrate ( $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ )	7789-53-9	≥99%	Aladdin Industrial Corporation	chemical titration
lithium bromide ( $\text{LiBr}$ )	7550-35-8	≥99%	Aladdin Industrial Corporation	chemical titration

The instrument details used in the experiment were listed in Table 2 below.

Table 2. Instruments

instrument name	type and accuracy	source	area
ultrapure water device	UPT-II-20T	Youpu Chaochun Technology Co., Ltd.	Sichuan
analytical balance	AL104, 0.0001 g	Mettler Toledo Instruments Co., Ltd.	Shanghai
water bath oscillator	HZS-HA, ±0.1 K	Donglian Electronic Technology Development Co., Ltd.	Harbin
incubator	SHH-250, ±0.1 K	Yingbo Experimental Instrument Co., Ltd.	Chongqing
oven	DHG-9076A	Jinghong Experimental Equipment Co., Ltd.	Shanghai

**2.2. Experimental Method.** In this work, the stable phase equilibria were studied by the isothermal dissolution equilibrium method. The samples of a ternary system were prepared by gradually adding the second salt to a binary solid–liquid equilibrium system at 273.15, 308.15, and 323.15 K, each group of mixtures to add a metered amount of distilled water. These samples were put into 50 mL glass bottles. These glass bottles were oscillated to equilibrium. The water bath oscillator is used to study the phase equilibria at 323.15 K (±0.1 K), and the incubator is used to study the phase equilibria at 273.15 and 308.15 K (±0.1 K). The supernatants are periodically taken out for liquid phase composition analysis. The system reaches a thermodynamic equilibrium if the composition of the solution no longer changes. Then the

solid phases and liquid phases are taken out for analysis, respectively.

**2.3. Analysis Methods.** In this work, the liquid phase and wet solid phase were measured by the chemical analysis.<sup>15</sup> The contents of strontium ion ( $\text{Sr}^{2+}$ ) was analyzed by EDTA complexation titration. During the analysis,  $\text{Li}^+$  has a strong interference with  $\text{Sr}^{2+}$  in EDTA complexation titration, since  $\text{Li}^+$  reacts with eriochrome black T at pH = 10 and thus leads to a higher content of  $\text{Sr}^{2+}$ . According to the content of lithium in the measured liquid, adding an appropriate amount of mixed alcohol to inhibit the interference of  $\text{Li}^+$ .<sup>16,17</sup> Then, quantitative Mg-EDTA solution and a buffer solution (ammonium hydroxide with pH = 10) were added to control the pH value of solution, and  $\text{Sr}^{2+}$  was analyzed by using EDTA complexometric titration, and eriochrome black T was used as an indicator. The maximum relative standard uncertainties are not greater than 0.5%.

The content of  $\text{Br}^-$  was analyzed by titration with a silver nitrate standard solution. The maximum relative standard uncertainties are not greater than 0.3%.

The content of lithium ion ( $\text{Li}^+$ ) was obtained by the ion balance subtraction method.

The compositions of the solid phases were analyzed by the Schreinemakers wet residue method. The solid phase on the extension of the line joining the liquid and wet residue compositions.

## 3. RESULTS AND DISCUSSION

**3.1. Binary System  $\text{LiBr}-\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K.** The solubility relationships of the binary system  $\text{LiBr}-\text{H}_2\text{O}$  at different temperatures<sup>18–20</sup> have been compared, as shown in Figure 1. Our research group has made a detailed

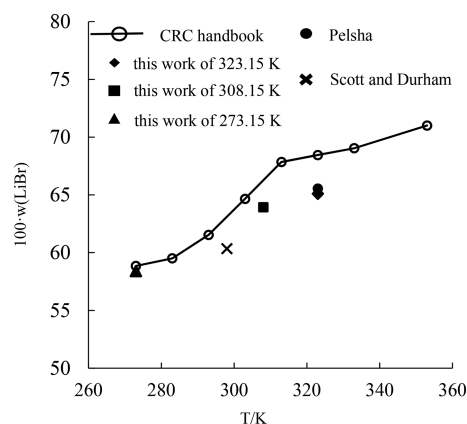
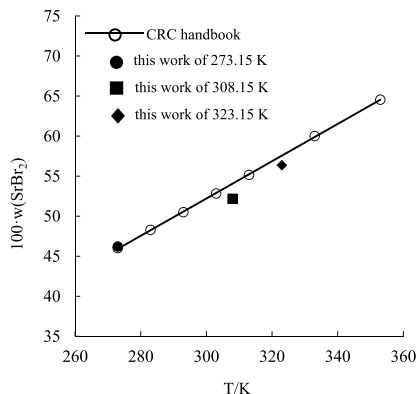


Figure 1. Comparison of the experimental solubility data of  $\text{LiBr}$  at different temperatures: (●) ref 18; (×) ref 19; (○) ref 20; (■), (◆), and (▲), this work.

study on the comparison between the CRC's data and the experimental data of lithium bromide at 273.15 and 308.15 K, which can prove the reliability of the data.<sup>21</sup> There are no solubility data for the binary system  $\text{LiBr}-\text{H}_2\text{O}$  at 323.15 K in the CRC Handbook. As shown in Figure 1, the experimental solubilities of salts at different temperatures are lower than the reference value. Therefore, the solubility data of the binary system  $\text{LiBr}-\text{H}_2\text{O}$  at 323.15 K in the chemical handbook need to be verified further.

**3.2. Binary System  $\text{SrBr}_2-\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K.** The solubility data of strontium bromide are very

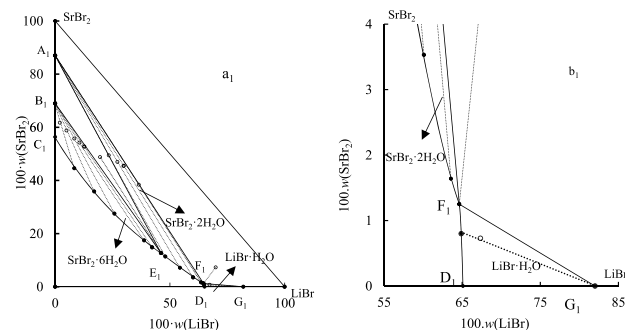
scarce. The cosaturation point fractions of binary system  $\text{SrBr}_2\text{--H}_2\text{O}$  at 273.15, 308.15, and 323.15 K are 46.20%, 52.17%, and 56.36% in this work, respectively. These results are compared with our past experimental results and those reported in CRC handbook (Figure 2). Our group has done several experiments and analyses, and the maximum relative standard uncertainties of our solubility data are less than 0.5%.



**Figure 2.** Comparison of the experimental solubility data of  $\text{SrBr}_2$  at different temperatures: (○) ref 20; (■), (◆), and (●), this work.

**3.3. Ternary System  $\text{LiBr--SrBr}_2\text{--H}_2\text{O}$  at 323.15 K and 0.1 MPa.** The mass fraction of the liquid phase and solid phase in the  $\text{LiBr--SrBr}_2\text{--H}_2\text{O}$  system at 323.15 K obtained in this work are listed in Table 3. According to the liquid phase composition obtained from the experiment, the equilibrium phase diagram of the system is shown in Figure 3.

The stable phase diagram consists of two invariant points, three univariant solubility curves, and three crystallization regions corresponding to  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  ( $\text{B}_1\text{C}_1\text{E}_1$ ),  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$  ( $\text{A}_1\text{E}_1\text{F}_1$ ), and  $\text{LiBr}\cdot \text{H}_2\text{O}$  ( $\text{F}_1\text{D}_1\text{G}_1$ ); no double salt or solid solution formed. The equilibrium solid phases at  $\text{F}_1$  are  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$  and  $\text{LiBr}\cdot \text{H}_2\text{O}$  ( $w(\text{LiBr}) = 64.63\%$ ,  $w(\text{SrBr}_2) = 1.25\%$ ). The equilibrium solid phases at  $\text{E}_1$  are  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$  ( $w(\text{LiBr}) = 46.11\%$ ,  $w(\text{SrBr}_2) = 12.70\%$ ). In Figure 3, point  $\text{C}_1$  is the solubility of  $\text{SrBr}_2$  and point  $\text{D}_1$  is the solubility of  $\text{LiBr}$ . The isothermal solubility curves of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$ , and  $\text{LiBr}\cdot \text{H}_2\text{O}$  are  $\text{C}_1\text{E}_1$ ,  $\text{E}_1\text{F}_1$ , and  $\text{F}_1\text{D}_1$ , respectively.



**Figure 3.** Phase diagram ( $a_1$ ) and partially enlarged diagram ( $b_1$ ) of the ternary system  $\text{LiBr--SrBr}_2\text{--H}_2\text{O}$  at 323.15 K: (○) wet residue points; (●) composition of saturated solution.

According to the univariant curves  $\text{C}_1\text{E}_1$  and  $\text{E}_1\text{F}_1$ , with the gradual increase of lithium bromide, the content of strontium bromide decreases rapidly, and  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  transforms into  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$ .  $\text{LiBr}\cdot 2\text{H}_2\text{O}$  dehydrates and transforms into  $\text{LiBr}\cdot \text{H}_2\text{O}$  at 323.15 K, resulting in a decrease in the mass fraction of strontium bromide; that is, lithium bromide has an obvious salting-out effect on  $\text{SrBr}_2$ . The crystallization area of  $\text{LiBr}\cdot \text{H}_2\text{O}$  is the smallest, which indicates that  $\text{LiBr}$  has the largest solubility.

**3.4. Ternary System  $\text{LiBr--SrBr}_2\text{--H}_2\text{O}$  at 308.15 K and 0.1 MPa.** The mass fraction of the liquid phase and solid phase in the  $\text{LiBr--SrBr}_2\text{--H}_2\text{O}$  system at 308.15 K obtained are listed in Table 4. The stable equilibrium phase diagram of the system is drawn in Figure 4.

In Table 4 and Figure 4, the points  $\text{E}_2$  and  $\text{F}_2$  are two co-saturation points of the system.  $\text{B}_2\text{C}_2\text{E}_2$ ,  $\text{A}_2\text{E}_2\text{F}_2$ , and  $\text{F}_2\text{D}_2\text{G}_2$  are the crystallization regions of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$ , and  $\text{LiBr}\cdot 2\text{H}_2\text{O}$ , respectively. There are solids  $\text{LiBr}\cdot 2\text{H}_2\text{O}$  and  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$  at point  $\text{F}_2$  ( $w(\text{LiBr}) = 62.16\%$ ,  $w(\text{SrBr}_2) = 1.36\%$ ). The solids at point  $\text{E}_2$  are  $\text{SrBr}_2\cdot 2\text{H}_2\text{O}$  and  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  ( $w(\text{LiBr}) = 53.03\%$ ,  $w(\text{SrBr}_2) = 6.76\%$ ). There are no solid solutions or double salts. The crystallization region of  $\text{LiBr}\cdot 2\text{H}_2\text{O}$  is still the smallest, indicating that its solubility is the largest.

**Table 3.** Solubility Data of the System  $\text{LiBr--SrBr}_2\text{--H}_2\text{O}$  at 323.15 K and 0.1 MPa<sup>a</sup>

no.	composition of liquid phase 100-w(B)		composition of wet residue 100-w(B)		equilibrium solid(s)
	w(LiBr)	w(SrBr <sub>2</sub> )	w(LiBr)	w(SrBr <sub>2</sub> )	
1, $\text{D}_1$	65.10	0			$\text{LiBr}\cdot \text{H}_2\text{O}$
2	64.88	0.80	67.34	0.73	$\text{LiBr}\cdot \text{H}_2\text{O}$
3, $\text{F}_1$	64.63	1.25	69.94	7.30	$\text{SrBr}_2\cdot 2\text{H}_2\text{O} + \text{LiBr}\cdot \text{H}_2\text{O}$
4	63.56	1.44	36.46	38.42	$\text{SrBr}_2\cdot 2\text{H}_2\text{O}$
5	60.11	3.53	29.9	45.48	$\text{SrBr}_2\cdot 2\text{H}_2\text{O}$
6	54.36	7.15	27.11	46.98	$\text{SrBr}_2\cdot 2\text{H}_2\text{O}$
7	48.00	11.38	23.36	49.46	$\text{SrBr}_2\cdot 2\text{H}_2\text{O}$
8, $\text{E}_1$	46.11	12.70	19.57	48.79	$\text{SrBr}_2\cdot 6\text{H}_2\text{O} + \text{SrBr}_2\cdot 2\text{H}_2\text{O}$
9	42.27	14.82	12.67	52.74	$\text{SrBr}_2\cdot 6\text{H}_2\text{O}$
10	38.77	17.44	10.56	54.23	$\text{SrBr}_2\cdot 6\text{H}_2\text{O}$
11	25.84	27.52	8.33	55.78	$\text{SrBr}_2\cdot 6\text{H}_2\text{O}$
12	17.03	35.87	5.06	58.80	$\text{SrBr}_2\cdot 6\text{H}_2\text{O}$
13	8.33	44.60	2.22	61.75	$\text{SrBr}_2\cdot 6\text{H}_2\text{O}$
14, $\text{C}_1$	0	56.36			$\text{SrBr}_2\cdot 6\text{H}_2\text{O}$

<sup>a</sup> $w(\text{B})$ , mass fraction of component B in saturated solution. Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(P) = 0.9$  kPa. Maximum relative standard uncertainties  $u_r$  are  $u_r[w(\text{SrBr}_2)] = 0.005$  and  $u_r[w(\text{LiBr})] = 0.003$ .

Table 4. Solubility Data of the System  $\text{LiBr}\text{--}\text{SrBr}_2\text{--}\text{H}_2\text{O}$  at 308.15 K and 0.1 MPa<sup>a</sup>

no.	composition of solution 100-w(B)		composition of wet residue 100-w(B)		equilibrium solid(s)
	w(LiBr)	w(SrBr <sub>2</sub> )	w(LiBr)	w(SrBr <sub>2</sub> )	
1, D <sub>2</sub>	63.93	0			LiBr·2H <sub>2</sub> O
2	62.56	0.89	65.88	0.55	LiBr·2H <sub>2</sub> O
3, F <sub>2</sub>	62.16	1.36	64.56	3.33	SrBr <sub>2</sub> ·2H <sub>2</sub> O + LiBr·2H <sub>2</sub> O
4	60.33	2.95	37.64	34.77	SrBr <sub>2</sub> ·2H <sub>2</sub> O
5	56.27	5.26	36.41	33.13	SrBr <sub>2</sub> ·2H <sub>2</sub> O
6, E <sub>2</sub>	53.03	6.76	38.68	25.77	SrBr <sub>2</sub> ·6H <sub>2</sub> O + SrBr <sub>2</sub> ·2H <sub>2</sub> O
7	49.33	8.29	19.27	44.27	SrBr <sub>2</sub> ·6H <sub>2</sub> O
8	38.67	13.76	17.98	43.28	SrBr <sub>2</sub> ·6H <sub>2</sub> O
9	36.78	14.72	16.24	45.85	SrBr <sub>2</sub> ·6H <sub>2</sub> O
10	28.92	21.33	15.89	43.50	SrBr <sub>2</sub> ·6H <sub>2</sub> O
11	24.86	25.29	11.23	48.77	SrBr <sub>2</sub> ·6H <sub>2</sub> O
12	15.55	33.48	6.77	52.44	SrBr <sub>2</sub> ·6H <sub>2</sub> O
13	6.85	43.69	3.71	53.59	SrBr <sub>2</sub> ·6H <sub>2</sub> O
14, C <sub>2</sub>	0	52.17			SrBr <sub>2</sub> ·6H <sub>2</sub> O

<sup>a</sup>w(B), mass fraction of component B in saturated solution. Standard uncertainties *u* are *u*(*T*) = 0.1 K and *u*(*P*) = 0.9 kPa. Maximum relative standard uncertainties *u<sub>r</sub>* are *u<sub>r</sub>*[w(SrBr<sub>2</sub>)] = 0.005 and *u<sub>r</sub>*[w(LiBr)] = 0.003.

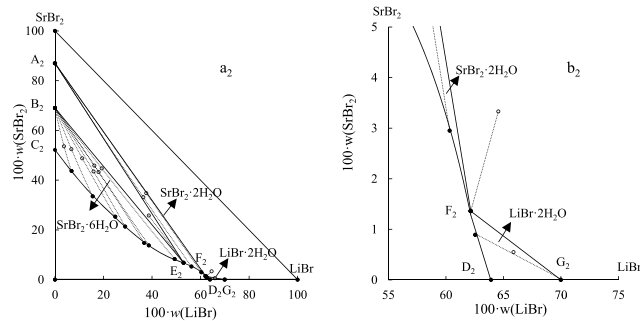


Figure 4. Phase diagram (a<sub>2</sub>) and partially enlarged diagram (b<sub>2</sub>) of the ternary system  $\text{LiBr}\text{--}\text{SrBr}_2\text{--}\text{H}_2\text{O}$  at 308.15 K: (○) wet residue points; (●) composition of saturated solution.

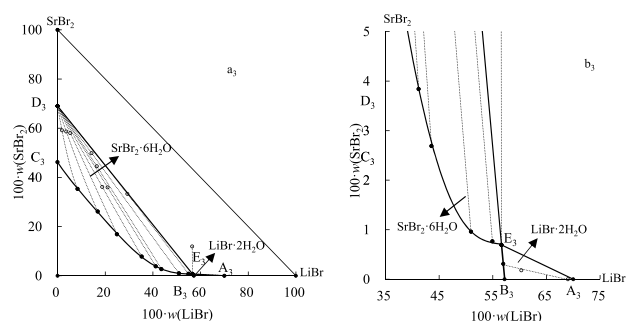


Figure 5. Phase diagram (a<sub>3</sub>) and partially enlarged diagram (b<sub>3</sub>) of the ternary system  $\text{LiBr}\text{--}\text{SrBr}_2\text{--}\text{H}_2\text{O}$  at 273.15 K (○), wet residue points; (●), composition of saturated solution.

**3.5. Ternary System  $\text{LiBr}\text{--}\text{SrBr}_2\text{--}\text{H}_2\text{O}$  at 273.15 K and 0.1 MPa.** The equilibrium composition of the liquid phase and solid phase in the  $\text{LiBr}\text{--}\text{SrBr}_2\text{--}\text{H}_2\text{O}$  system at 273.15 K obtained in this work are listed in Table 5. The equilibrium phase diagram of the system is drawn in Figure 5.

The phase diagram contains one invariant point (E<sub>3</sub>), two univariant curves (B<sub>3</sub>E<sub>3</sub> and E<sub>3</sub>C<sub>3</sub>), and two crystallization regions. The solids in A<sub>3</sub>B<sub>3</sub>E<sub>3</sub> and E<sub>3</sub>C<sub>3</sub>D<sub>3</sub> are LiBr·2H<sub>2</sub>O and SrBr<sub>2</sub>·6H<sub>2</sub>O, respectively. The solid phases at point E<sub>3</sub> (w(LiBr) = 56.63%, w(SrBr<sub>2</sub>) = 0.69%) are LiBr·2H<sub>2</sub>O and

Table 5. Solubility Data of the System  $\text{LiBr}\text{--}\text{SrBr}_2\text{--}\text{H}_2\text{O}$  at 273.15 K and 0.1 MPa<sup>a</sup>

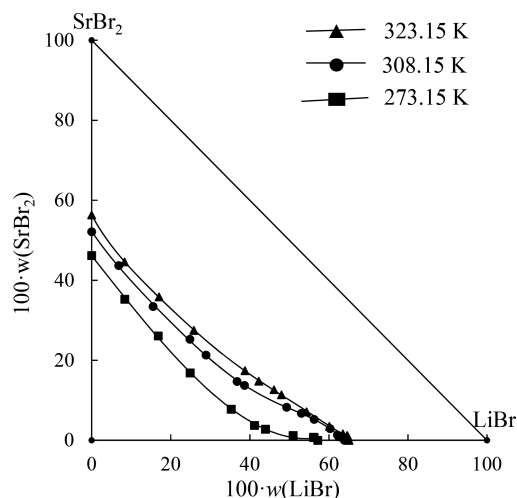
no.	composition of solution 100-w(B)		composition of wet residue 100-w(B)		equilibrium solid(s)
	w(LiBr)	w(SrBr <sub>2</sub> )	w(LiBr)	w(SrBr <sub>2</sub> )	
1, B <sub>3</sub>	58.41	0			LiBr·2H <sub>2</sub> O
2	56.97	0.31	60.33	0.18	LiBr·2H <sub>2</sub> O
3, E <sub>3</sub>	56.63	0.69	56.49	11.91	LiBr·2H <sub>2</sub> O + SrBr <sub>2</sub> ·6H <sub>2</sub> O
4	54.94	0.77	29.31	33.30	SrBr <sub>2</sub> ·6H <sub>2</sub> O
5	50.96	0.96	14.26	49.83	SrBr <sub>2</sub> ·6H <sub>2</sub> O
6	43.98	2.69	16.45	44.52	SrBr <sub>2</sub> ·6H <sub>2</sub> O
7	41.19	3.84	20.98	35.94	SrBr <sub>2</sub> ·6H <sub>2</sub> O
8	35.33	7.80	18.77	36.14	SrBr <sub>2</sub> ·6H <sub>2</sub> O
9	24.94	16.86	5.34	58.00	SrBr <sub>2</sub> ·6H <sub>2</sub> O
10	16.87	26.11	3.65	58.66	SrBr <sub>2</sub> ·6H <sub>2</sub> O
11	8.41	35.30	1.84	59.15	SrBr <sub>2</sub> ·6H <sub>2</sub> O
12, C <sub>3</sub>	0.00	46.20			SrBr <sub>2</sub> ·6H <sub>2</sub> O

<sup>a</sup>w(B), mass fraction of component B in saturated solution. Standard uncertainties *u* are *u*(*T*) = 0.1 K and *u*(*P*) = 0.9 kPa. Maximum relative standard uncertainties *u<sub>r</sub>* are *u<sub>r</sub>*[w(SrBr<sub>2</sub>)] = 0.005 and *u<sub>r</sub>*[w(LiBr)] = 0.003.



$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ .  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  has the largest solubility, indicating that lithium bromide is difficult to crystallize from the solution.

**3.6. Comparison of the Ternary System  $\text{LiBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K.** The phase diagrams at 273.15, 308.15, and 323.15 K are all plotted in Figure 6.



**Figure 6.** Equilibrium phase diagrams of ternary system  $\text{LiBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K.

Solubility diagrams of the ternary system  $\text{LiBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K are compared in Figure 6. Obviously, the solubility curves are basically similar. As the temperature increases, the crystallization zones of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  decrease. Strontium bromide hexahydrate transforms into strontium bromide dihydrate in system at 308.15 K, there are both strontium bromide hexahydrate and strontium bromide dihydrate at the invariant point. At temperatures between 308.15 and 323.15 K, the crystallization zone of  $\text{SrBr}_2 \cdot 2\text{H}_2\text{O}$  increases with increasing temperature. The crystallization region of lithium bromide dihydrate remains small as the temperature increases.  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  dehydrates and transforms into  $\text{LiBr} \cdot \text{H}_2\text{O}$  at 323.15 K, resulting in a decrease in the mass fraction of strontium bromide, that is, lithium bromide has an obvious salting-out effect on  $\text{SrBr}_2$ .

#### 4. CONCLUSIONS

The solid–liquid phase equilibria of ternary system  $\text{LiBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 273.15, 308.15, and 323.15 K were studied with the method of isothermal dissolution equilibrium in this work. The ternary system  $\text{LiBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  has no solid solutions or double salts formed. The three equilibrium solid phases at 308.15 and 323.15 K are  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrBr}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrBr}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{LiBr} \cdot \text{H}_2\text{O}$ , respectively. The phase diagram at 273.15 K contains two crystallization regions, which correspond to  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{LiBr} \cdot 2\text{H}_2\text{O}$ . At temperatures between 308.15 and 323.15 K,  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  dehydrates and transforms into  $\text{LiBr} \cdot \text{H}_2\text{O}$ , resulting in a decrease in the concentration of strontium bromide in solution; that is, lithium bromide has a strong salting-out effect on strontium bromide. Lithium bromide has the biggest solubility, so it is difficult to crystallize out from the solution at different temperatures. Strontium bromide dihydrate disappears at 273.15 K. Strontium bromide hexahydrate will transform into strontium bromide dihydrate in the system

at 308.15 K. There are both strontium bromide hexahydrate and strontium bromide dihydrate at the invariant point.

#### AUTHOR INFORMATION

##### Corresponding Author

**Shi-Hua Sang** – College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, China; Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, Sichuan, China; [orcid.org/0000-0002-5948-3882](https://orcid.org/0000-0002-5948-3882); Phone: 13032845233; Email: [sangshihua@sina.com.cn](mailto:sangshihua@sina.com.cn), [sangsh@cduet.edu.cn](mailto:sangsh@cduet.edu.cn)

##### Authors

**Pei-Huan Jiang** – College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, China

**Chun-Xia He** – College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, China

**Xing-Liu** – College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, China

**Lan-Rong Zhao** – College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jced.9b01144>

#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

- (1) Song, P. S.; Li, B. Phase equilibrium study of water salt system containing lithium. *J. Salt Lake Res.* **1990**, 1 (1), 46–54 (in Chinese).
- (2) Zhou, X. Hydrogeochemical characteristics and formation of subsurface brines of deep aquifers in longnu temple brine-bearing structure, Sichuan Basin. *Geoscience* **1993**, 7 (1), 83–92 (in Chinese).
- (3) Lin, Y. T.; Pan, Z. R. Study on density and forming classification of gas field brine. *J. Salt Lake Res.* **2001**, 9 (3), 1–7 (in Chinese).
- (4) Yang, L. Z. The Status and Countermeasures of the Development and Utilization of Underground Brine Water Resources in the Sichuan Basin. *Acta Geologica Sichuan* **1992**, No. 03, 53–57 (in Chinese).
- (5) Assarsson, G. O. Equilibria in aqueous systems containing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Cl}^-$ . *J. Phys. Chem.* **1953**, 57 (2), 207–210.
- (6) Assarsson, G. O.; Balder, A. Equilibria in aqueous systems containing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  between 18 and 114°C. *J. Phys. Chem.* **1954**, 58 (3), 253–255.
- (7) Assarsson, G. O.; Balder, A. The poly-component aqueous systems containing the chlorides of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  between 18 and 93°C. *J. Phys. Chem.* **1955**, 59 (7), 631–633.
- (8) Meng, L. Z.; Li, D.; Deng, T. L.; et al. Measurement and Thermodynamic Modeling Study on the Solid and Liquid Equilibrium of Ternary System  $\text{NaBr}$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$  at 288.15 K. *J. Chem. Eng. Data* **2014**, 59 (12), 4193–4199.
- (9) Liu, Q.; Gao, Y. Y.; Sang, S. H.; et al. Solid-Liquid Equilibria in Ternary System  $\text{SrBr}_2$ – $\text{MgBr}_2$ – $\text{H}_2\text{O}$  at (298 and 323) K. *J. Chem. Eng. Jpn.* **2018**, 51 (1), 1–5.

- (10) Cui, R. Z.; Nie, G. L.; Sang, S. H.; Yang, L.; Wang, Z. C. Measurements of (Solid + Liquid) Phase Equilibria in the Quaternary System NaBr + KBr + SrBr<sub>2</sub> + H<sub>2</sub>O and Two Subsystems NaBr + SrBr<sub>2</sub> + H<sub>2</sub>O and KBr + SrBr<sub>2</sub> + H<sub>2</sub>O at T = 323 K. *J. Chem. Eng. Data* **2017**, 62 (10), 3187–3192.
- (11) Li, X. P.; Gao, Y. Y.; Sang, S. H. Studies on Phase Equilibria in the Ternary System LiCl–SrCl<sub>2</sub>–H<sub>2</sub>O and the Quaternary System KCl–LiCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 308 K. *J. Chem. Eng. Data* **2019**, 64 (9), 4077–4083.
- (12) Li, Z. Q.; Yu, X. D.; Yin, Q. H. Thermodynamics metastable phase equilibria of aqueous quaternary system LiCl + KCl + RbCl + H<sub>2</sub>O at 323.15 K. *Fluid Phase Equilib.* **2013**, 358 (11), 131–136.
- (13) Yanko, A. P. Study on Solubility of Ternary System LiCl–KCl–H<sub>2</sub>O (0°C–100°C). *J. Peking Univ. Nat. Sci. Ed.* **1961**, No. 1, 51–56.
- (14) Yin, Q. H.; Zeng, Y.; Yu, X. D.; et al. Metastable phase equilibrium in the quaternary system LiCl + KCl + RbCl + H<sub>2</sub>O at 348.15 K. *J. Chem. Eng. Data* **2013**, 58 (10), 2875–2880.
- (15) Institute of Qinghai Salt-lake, Chinese Academy of Sciences. *Analytical Methods of Brines and Salts*; Science Press: Beijing, 1988 (in Chinese).
- (16) Bi, Y. J. Phase equilibrium study of the quaternary system LiCl–CaCl<sub>2</sub>–SrCl<sub>2</sub>–H<sub>2</sub>O and its ternary subsystems at 298 K. *Chin. J. Inorg. Chem.* **2011**. (In Chinese).
- (17) Sun, B.; Li, H. J.; Zhao, J. EDTA mass titration of strontium content in the presence of lithium in chloride. *J. Salt. Sci. Chem. Ind.* **2014**, No. 3, 29–37 (In Chinese).
- (18) Pelsha, A. D. *Experimental Data on Solubility of Multi-component Water-Salt Systems*; Chemistry Press: Leningrad, 1973; p 65.
- (19) Scott, A. F.; Durham, E. J. The solubility of soluble electrolytes. II. The solubility of the alkali and alkaline earth bromides in hydrobromic acid. *J. Phys. Chem.* **1930**, 34, 531–537.
- (20) Haynes, W. M. *CRC Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, FL, 2001.
- (21) Ye, C.; Wu, Z. Z.; Sang, S. H.; Qi, X. Y.; Liu, X. Solid–Liquid Phase Equilibria of Ternary System KBr–LiBr–H<sub>2</sub>O at 273 and 308 K. *J. Chem. Eng. Data* **2019**, 64 (12), 5288–5294.