

Solid–Liquid Phase Equilibria in the Ternary System  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 273, 298, and 323 K

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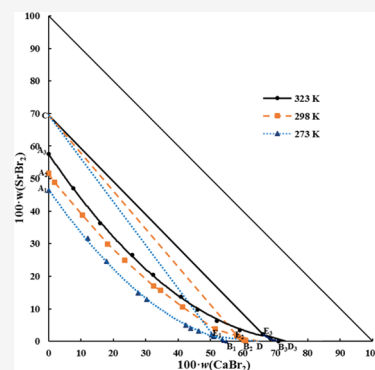


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**ABSTRACT:** In this paper, the stable phase equilibrium data of the ternary system  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at  $T = 273$ , 298, and 323 K and 101.3 kPa have been determined by isothermal the dissolution equilibrium method. The phase diagrams of them at the investigated temperatures have been drawn. It is found that the isothermal phase diagrams of the  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  system at  $T = 273$ , 298, and 323 K are classified as a simple co-saturation type consisting of an invariant point and two univariant curves. The equilibrium solid phases corresponding to an invariant point of the system were detected as  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  at 273 and 298 K and those identified as  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  at 323 K. In this system, calcium bromide exhibits a strong salting-out effect on strontium bromide. Furthermore, isothermal solubilities at three temperatures were compared and discussed.



## 1. INTRODUCTION

Bromine is widely used in the national economy and is one of the scarce materials in our country. Because bromine and its compounds can be used as flame retardants, dyes, water purifiers, insecticides, and general disinfectants, the current domestic consumption situation is suffering from short supply. Therefore, the effective development of bromine resources in brine is of great significance to China's economic development. The phase equilibrium and phase diagram study of the bromine-containing water–salt system is helpful to explore the evaporation law of bromine in brine, enrich the development of electrolyte solution theory, and provide important basic thermodynamic data for bromine resources in oil field brine.<sup>1</sup> As we all know, rich resources and wide distribution are the advantages of China's brine resources, and it contains a large amount of Na, Mg, Li, and other minerals as well as important components such as bromine. For example, the bromine content in the underground brine in Sichuan Basin oil and gas field is generally up to 300 mg/L, which has a higher bromine content than seawater.<sup>2,3</sup> The composition of these brines varies greatly, but most of them belong to the Li–Na–K–Mg–Ca–Sr–Cl–Br–NO<sub>3</sub>–SO<sub>4</sub>–borate–H<sub>2</sub>O system.

Acting as an important subsystem of such a multicomponent system, the phase equilibrium of the ternary system  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  has not been presented in the previous work. Some related research is available, which involves calcium bromide or strontium bromide alone participating in the dissolution of multiple components. Solubility measurements containing calcium bromide have been conducted in ternary systems  $\text{NaBr}$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$  ( $T = 348$  K),  $\text{KBr}$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$

( $T = 348$  K),<sup>4</sup>  $\text{NH}_4\text{Br}$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$  ( $T = 298.15$  and  $323.15$  K),<sup>5</sup> and quaternary systems  $\text{NaBr}$ – $\text{KBr}$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$  ( $T = 298$  K),<sup>6</sup>  $\text{NaBr}$ – $\text{MgBr}_2$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$  ( $T = 298$  K),<sup>7</sup> and  $\text{KBr}$ – $\text{MgBr}_2$ – $\text{CaBr}_2$ – $\text{H}_2\text{O}$  ( $T = 298$  and  $323$  K).<sup>8</sup> Solid–liquid equilibrium involving strontium bromide has been exhibited in ternary systems  $\text{NaBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  ( $T = 288$  and  $323$  K),  $\text{KBr}$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  ( $T = 288$  and  $323$  K),<sup>9,10</sup> and  $\text{MgBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  ( $T = 298$  and  $323$  K).<sup>11</sup>

This work aims at presenting the solid–liquid phase equilibrium for the ternary system  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at  $T = 273$ , 298, and 323 K. The determined solubility data enrich the thermodynamic database of bromine-containing brine and provide a theoretical basis for the comprehensive utilization of brine to obtain the corresponding inorganic chemical products.

## 2. EXPERIMENTS

**2.1. Reagents and Instruments.** The sample description is listed in Table 1, in which  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  (99.0% mass fraction purity) and  $\text{CaBr}_2 \cdot \text{H}_2\text{O}$  (99.0% mass fraction purity) were supplied by Aladdin Reagent (Shanghai) Co., Ltd. The UPT-11-40L type water purification treatment instrument manufactured by Chengdu Youpu Equipment Co., Ltd. was employed to produce ultrapure water with a resistivity of 18 MΩ·cm. A

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Table 1. Sample Description

chemical reagent	CAS Reg. no.	mass fraction purity (%)	supplier	analysis method
SrBr <sub>2</sub> ·6H <sub>2</sub> O	7789-53-9	≥99.0	Aladdin Reagent (Shanghai) Co., Ltd., China	silver nitrate volumetric method
CaBr <sub>2</sub> ·H <sub>2</sub> O	71626-99-8	≥99.0	Aladdin Reagent (Shanghai) Co., Ltd., China	EDTA volumetric method

DHJF-4002 type constant-temperature stirring reaction bath manufactured by Zhengzhou Greatwall Scientific Industrial and Tread Co., Ltd. was selected as the place where the isothermal dissolution equilibrium for the sample was reached. The 101-2AB type electric blast dryer manufactured by the Tianjin Taisite Instrument Co., Ltd. was used for drying the sample.

**2.2. Experimental Method.** The isothermal experiments for solubility determination at 273, 298, and 323 K in the ternary system CaBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O were carried out using the method of the isothermal dissolution equilibrium. In this experiment, the sample was subjected to a constant-temperature dissolution reaction after being sealed in a rigid plastic bottle. Initially, a binary solid–liquid mixed sample was prepared by adding excess salt with a certain amount of high-purity water. Then, the configured solid–liquid mixed sample was placed in a low-temperature constant-temperature stirring bath and fully stirred under the action of the magnetic force at the investigated temperature. After full agitation and standing clarification, 2 mL of binary saturated solution was accurately transferred into a volumetric flask using a fast pipette and weighed. The removed samples were diluted to a fixed volume and the solubility was measured. In the binary saturated sample, another component was added at a certain concentration interval until the two components reached a co-saturation. The above stirring and standing operations were repeated, and the solubility measurement of each sample was completed. At the same time, the wet solid phase of each sample was taken out to measure the content. The remaining solid phase at the bottom of the bottle was washed with absolute ethanol, dried at the experimental temperature in an electric blast dryer, and ground into a powder sample for X-ray

powder crystal diffraction identification. The Schreinemakers' method<sup>12</sup> along with X-ray diffraction (XRD) identification were used to confirm the precipitates at solubility isotherm.

**2.3. Analytical Methods.** The bromine ion concentration (Br<sup>−</sup>) was determined by selecting the volumetric method using silver nitrate standard solution as the titrant and potassium chromate solution as the indicator with an uncertainty of  $u_r(w(\text{Br}^-)) = 0.003$ . In an alkaline solution with pH greater than 12, EDTA was used as a titrant to determine the total amount of Ca<sup>2+</sup> and Sr<sup>2+</sup> with K–B as an indicator evaluated with an uncertainty of  $u_r(w(\text{Ca}^{2+} + \text{Sr}^{2+})) = 0.003$ . To determine the calcium content, we need to prepare a test solution and add a 1:1 sulfuric acid solution. Then, the sample was heated and evaporated until the white smoke of sulfur trioxide is exhausted so that calcium and strontium were precipitated as sulfates. Finally, we added the ammonium acetate solution to extract calcium to separate calcium and strontium. The calcium content (Ca<sup>2+</sup>) was determined by the same titration method as that used when calcium and strontium coexisted with an uncertainty of  $u_r(w(\text{Ca}^{2+})) = 0.005$ . The concentration of strontium ion (Sr<sup>2+</sup>) was obtained by the ICP-OES instrument analysis method and combined with the ion balance subtraction method to evaluate uncertainty of  $u_r(w(\text{Sr}^{2+})) = 0.008$ . The final result of the sample concentration used the average of three measurements.

### 3. RESULTS AND DISCUSSION

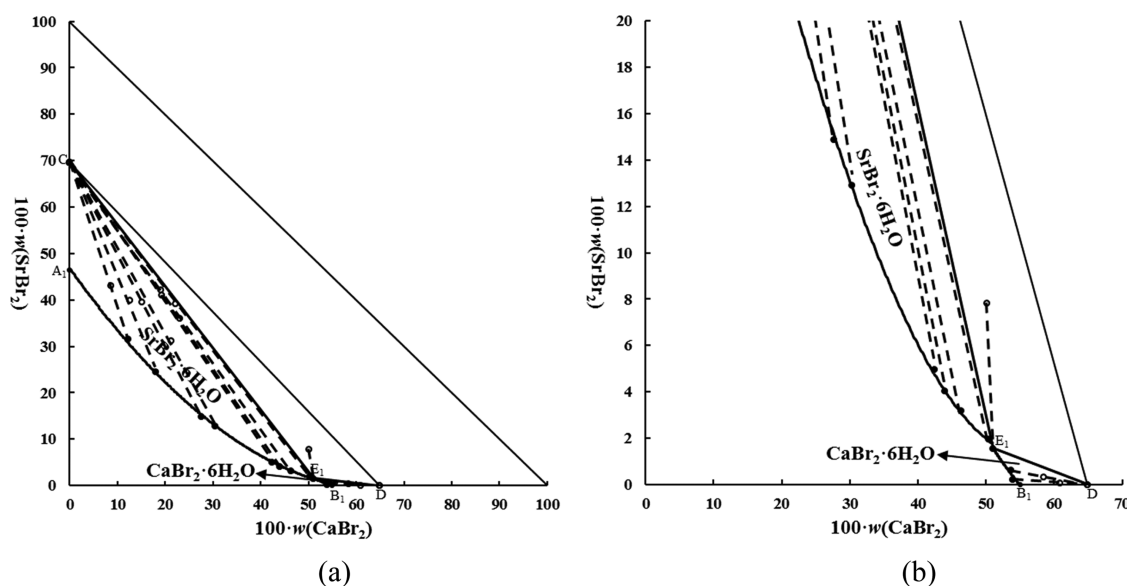
**3.1. CaBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O System at 273 K and 101.3 kPa.** The determined solubilities of the two components in the ternary system CaBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O at 273 K and 101.3 kPa are listed in Table 2. Using these measurement data, the isothermal ( $T = 273$  K) phase diagram of the ternary system CaBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O is plotted in Figure 1, in which the composition is expressed as the weight fraction. In the right triangle isothermal phase diagram, the abscissa direction is the mass fraction of calcium bromide, and the corresponding ordinate is expressed by the mass fraction of strontium bromide.

As can be seen from Table 2 and Figure 1, the investigated ternary system SrBr<sub>2</sub>–CaBr<sub>2</sub>–H<sub>2</sub>O belongs to a simple co-saturated system at 273 K owing to the absence of double salt and solid solution. The isothermal phase diagram at 273 K is

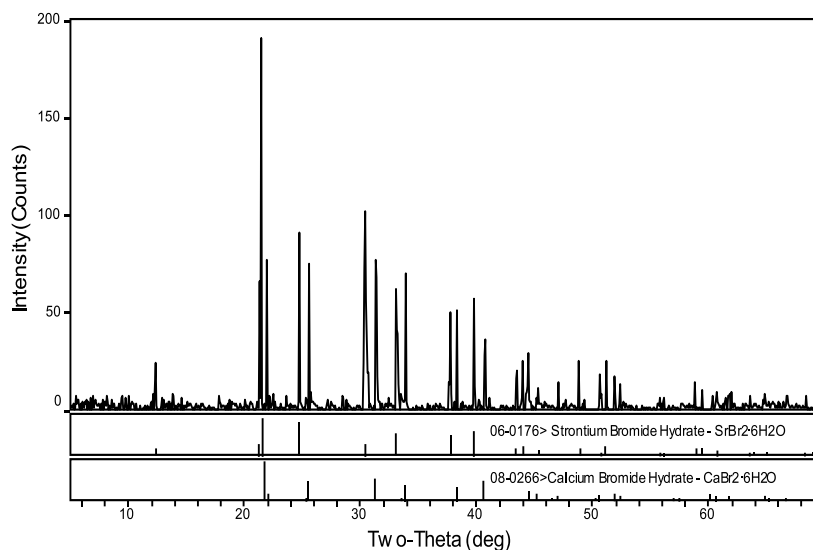
Table 2. Solubilities of Salts in the Ternary System CaBr<sub>2</sub>–SrBr<sub>2</sub>–H<sub>2</sub>O at 273 K and 101.3 kPa<sup>a</sup>

no.	composition of liquid phase (100·w(b))		composition of wet residue (100·w(b))		equilibrium solid phase
	100·w(CaBr <sub>2</sub> )	100·w(SrBr <sub>2</sub> )	100·w(CaBr <sub>2</sub> )	100·w(SrBr <sub>2</sub> )	
1, A <sub>1</sub>	0.00	46.39			SrBr <sub>2</sub> ·6H <sub>2</sub> O
2	12.09	31.66	8.55	43.10	SrBr <sub>2</sub> ·6H <sub>2</sub> O
3	17.93	24.62	12.63	39.89	SrBr <sub>2</sub> ·6H <sub>2</sub> O
4	27.59	14.87	15.08	39.50	SrBr <sub>2</sub> ·6H <sub>2</sub> O
5	30.33	12.91	21.11	31.24	SrBr <sub>2</sub> ·6H <sub>2</sub> O
6	42.35	4.96	18.95	42.26	SrBr <sub>2</sub> ·6H <sub>2</sub> O
7	43.88	4.06	23.09	36.04	SrBr <sub>2</sub> ·6H <sub>2</sub> O
8	46.31	3.19	19.19	41.05	SrBr <sub>2</sub> ·6H <sub>2</sub> O
9	50.33	1.98	22.09	39.20	SrBr <sub>2</sub> ·6H <sub>2</sub> O
10, E <sub>1</sub>	51.02	1.56	50.06	7.85	SrBr <sub>2</sub> ·6H <sub>2</sub> O + CaBr <sub>2</sub> ·6H <sub>2</sub> O
11	53.60	0.63	58.45	0.34	CaBr <sub>2</sub> ·6H <sub>2</sub> O
12	53.90	0.22	60.86	0.08	CaBr <sub>2</sub> ·6H <sub>2</sub> O
12, B <sub>1</sub>	55.00	0.00			CaBr <sub>2</sub> ·6H <sub>2</sub> O

<sup>a</sup>Notation: Standard uncertainties for temperature and pressure are  $u(T) = 0.1$  K and  $u(P) = 1$  kPa, respectively. Relative standard uncertainties for solubility are  $u_r(w(\text{CaBr}_2)) = 0.005$ ,  $u_r(w(\text{SrBr}_2)) = 0.008$ .



**Figure 1.** (a) Isothermal phase diagram of the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273 K. (b) Partially enlarged isothermal phase diagram of the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273 K.



**Figure 2.** X-ray diffraction pattern of the invariant point  $E_1$  (saturated with  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$ ) in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273 K.

composed of an invariant point, two solubility curves, and two single solid-phase crystallization regions. The hollow points and solid points in the figure indicate the wet slag points and saturated liquid phase points, respectively. The connection lines between the saturated liquid phase points and the wet slag points were represented by dotted lines.

Points  $A_1$  and  $B_1$  located on the vertical and horizontal axis represent the invariant points of the  $\text{SrBr}_2\text{--H}_2\text{O}$  and  $\text{CaBr}_2\text{--H}_2\text{O}$  binary systems, respectively. The two points C and D existing on the coordinate axis represent the pure solid phases of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$ , respectively. The invariant point noted as  $E_1$  of the system at 273 K is the intersection of the two solubility curves  $A_1E_1$  and  $B_1E_1$ , where is precipitated with equilibrium solids of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$ . One of the solubility curves remarked by  $A_1E_1$  is saturated with  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$ . As the mass fraction of  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$  becomes larger, the trend of the  $A_1E_1$  line gradually changed from an abrupt decline to a gentle one, indicating that the dissolving

ability of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  gradually decreases. In addition, another solubility curve  $B_1E_1$  deposited with  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$  is significantly shorter than  $A_1E_1$ . There are several phase regions in Figure 1. The area below the  $A_1E_1B_1$  line is an unsaturated liquid phase area without crystal precipitation. The  $A_1CE_1$  area is the crystalline region of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$ . Analogously, the  $B_1DE_1$  area is the crystalline area of  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$ , and the  $CDE_1$  area is the common crystallization area of  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$ . From the solid–liquid equilibrium phase diagram, it can be seen that the crystalline region of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  is larger than that of  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$  because the solubility of  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  is smaller than that of  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$ . Although these two components are soluble in aqueous solutions,  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$  exhibits a strong salting-out effect on  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$ . The invariant point  $E_1$  is at  $w(\text{CaBr}_2) = 51.02\%$ ,  $w(\text{SrBr}_2) = 1.56\%$ , where two solid phases  $\text{CaBr}_2\cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2\cdot 6\text{H}_2\text{O}$  coexists simultaneously. The X-ray diffraction pattern of the invariant point  $E_1$  in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at

Table 3. Solubilities of Salts in the Ternary System  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 298 K and 101.3 kPa<sup>a</sup>

no.	composition of liquid phase (100·w(b))		composition of wet residue (100·w(b))		equilibrium solid phase
	100·w( $\text{CaBr}_2$ )	100·w( $\text{SrBr}_2$ )	100·w( $\text{CaBr}_2$ )	100·w( $\text{SrBr}_2$ )	
1, $A_2$	0.00	51.60			$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
2	1.84	48.87	0.42	63.09	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
3	10.55	38.75	2.48	60.82	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
4	18.28	29.93	7.93	52.94	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
5	23.46	25.02	9.39	52.12	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
6	32.50	17.00	11.19	51.96	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
7	34.62	15.65	12.35	50.63	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
8	41.39	10.58	18.61	44.1	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
9	51.39	3.80	14.87	50.23	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
10, $E_2$	58.14	1.73	56.34	6.37	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
11	58.49	1.60	60.16	1.03	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
12	58.73	1.36	61.01	0.83	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
13	59.46	0.77	61.82	0.41	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
14	60.17	0.21	62.04	0.10	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
15, $B_2$	61.00	0.00			$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$

<sup>a</sup>Notation: Standard uncertainties for temperature and pressure are  $u(T) = 0.1$  K and  $u(P) = 1$  kPa, respectively. Relative standard uncertainties for solubility are  $u_r(w(\text{CaBr}_2)) = 0.005$  and  $u_r(w(\text{SrBr}_2)) = 0.008$ .

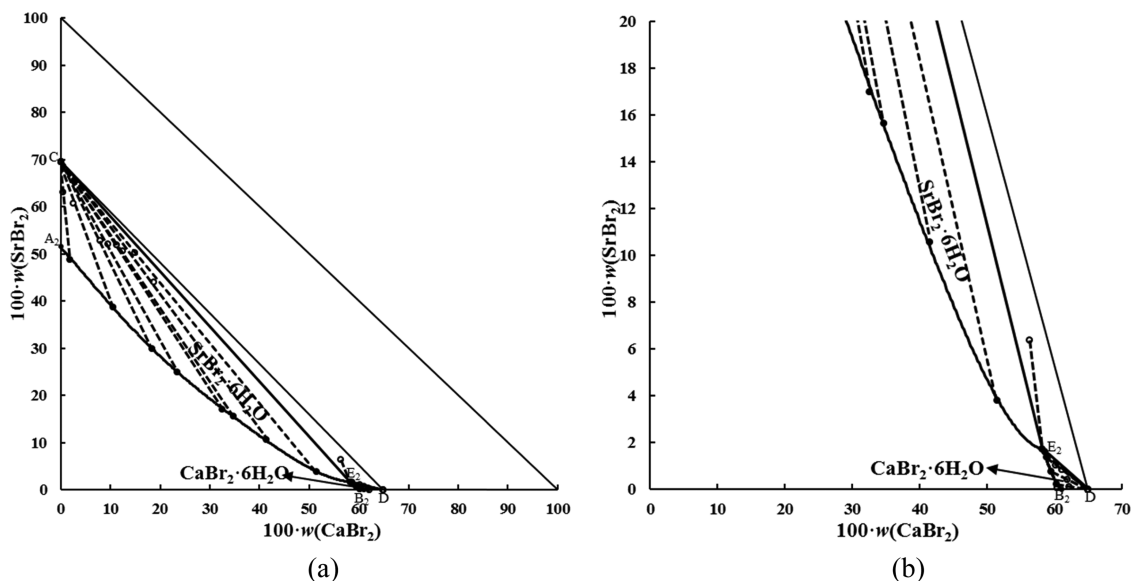


Figure 3. (a) Isothermal phase diagram of the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 298 K. (b) Partial enlarged isothermal phase diagram of the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 298 K.

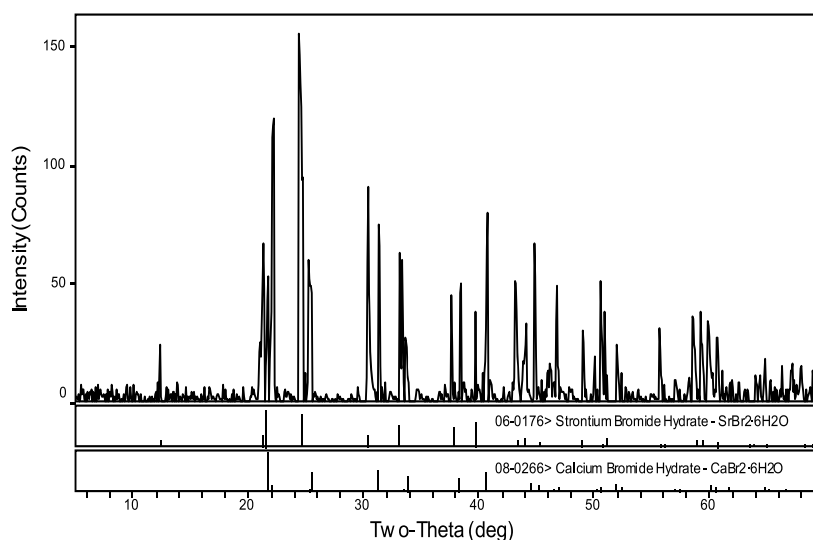
273 K is shown in Figure 2, which identified the crystalline solid phase at the invariant point  $E_1$  as  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ . The XRD identification result was consistent with the determination of wet residue.

**3.2.  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  System at 298 K and 101.3 kPa.** Solubility data of the salts in the liquid phase and wet residue for the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 298 K and 101.3 kPa are presented in Table 3. Also, the corresponding isothermal phase diagram at 298 K is plotted in Figure 3.

As described in Table 3 and Figure 3, two solubility curves, an invariant point, and two single solid-phase crystallization regions comprised the isothermal phase diagram for the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 298 K. Two binary invariant points noted as  $A_2$  and  $B_2$  correspond to the binary systems  $\text{SrBr}_2\text{--H}_2\text{O}$  and  $\text{CaBr}_2\text{--H}_2\text{O}$ , respectively. Solubility curves  $A_2E_2$  (saturated with  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ) and  $B_2E_2$  (saturated with  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ ) intersect at an invariant point  $E_2$  (saturated with

$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ ). Regions  $A_2CE_2$  and  $B_2DE_2$  denote the crystallization regions of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ , respectively.

On the saturation line  $AE_2$ , as the solubility of calcium bromide increases, the solubility of strontium bromide decreases from the boundary point of 51.60% to the invariant point of 1.73%. However, on the saturation line  $BE_2$ , the solubility of calcium bromide is little affected by strontium bromide, which decreases from the boundary point of 61.00% to the invariant point of 58.14%. It means that calcium bromide exhibits a strong salting-out effect on strontium bromide. The crystallization area of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  occupies most of the crystallization space, and it is easy to separate from the saturated solution as the first precipitation sequence. The X-ray diffraction pattern of the invariant point  $E_2$  (saturated with  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ ) in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 298 K is shown in Figure 4.

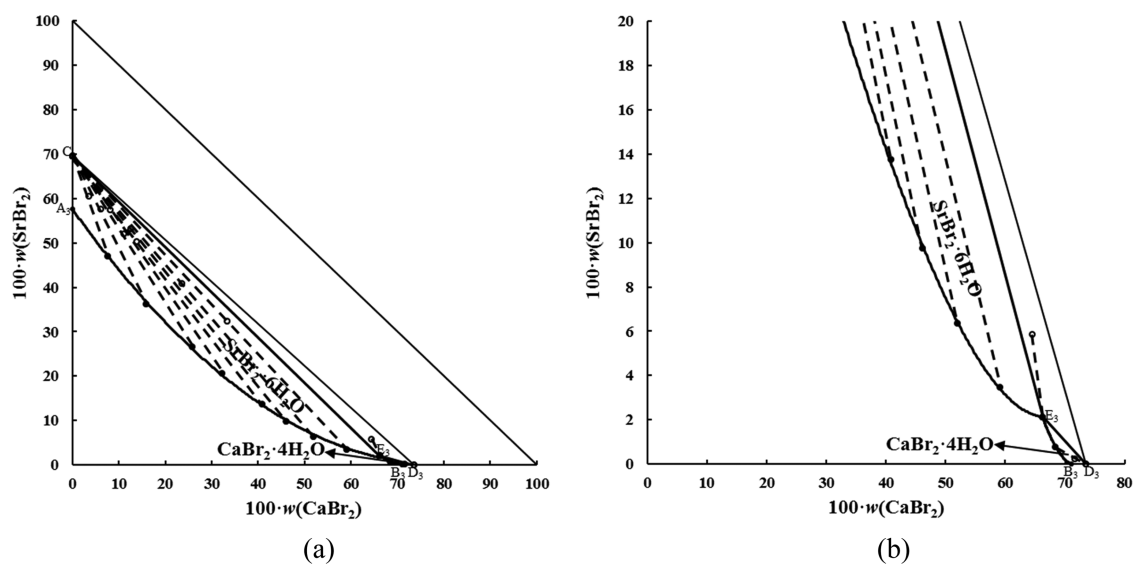


**Figure 4.** X-ray diffraction pattern of the invariant point  $E_2$  (saturated with  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ ) in the ternary system  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 298 K.

**Table 4.** Solubilities of Salts in the Ternary System  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 323 K and 101.3 kPa<sup>a</sup>

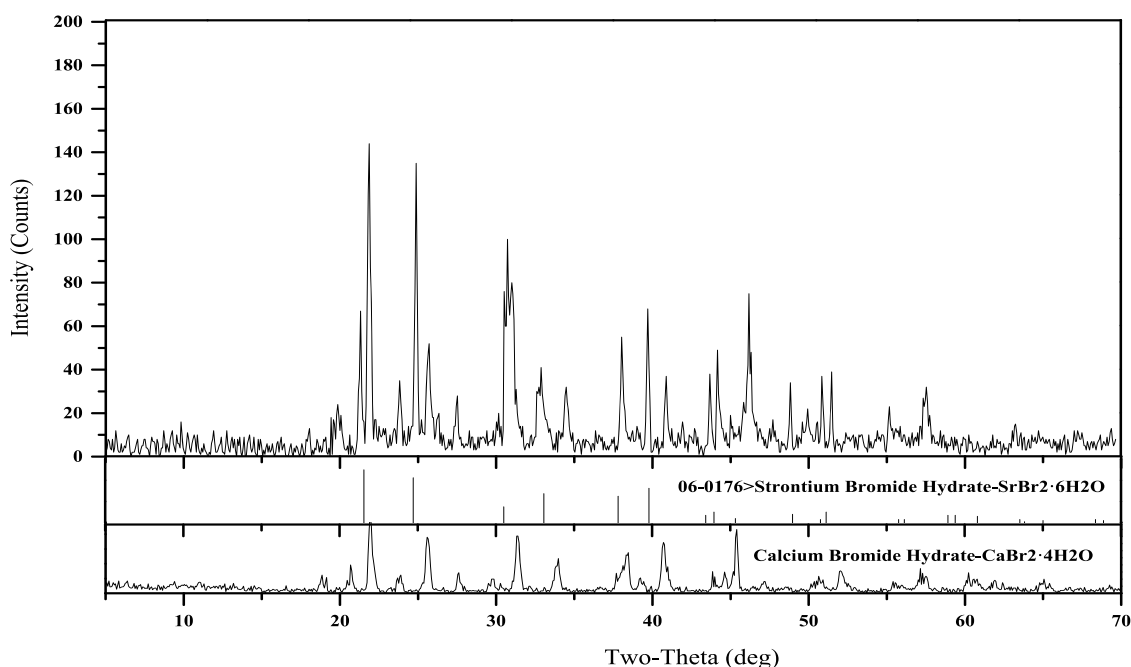
no.	composition of liquid phase (100·w(b))		composition of wet residue (100·w(b))		equilibrium solid phase
	100·w( $\text{CaBr}_2$ )	100·w( $\text{SrBr}_2$ )	100·w( $\text{CaBr}_2$ )	100·w( $\text{SrBr}_2$ )	
1, $A_3$	0.00	57.60			$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
2	7.65	47.09	3.46	60.52	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
3	15.95	36.26	6.18	57.65	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
4	25.86	26.61	11.14	52.04	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
5	32.26	20.55	13.87	50.33	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
6	40.84	13.78	8.23	57.37	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
7	46.09	9.75	12.49	51.16	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
8	51.98	6.36	23.60	40.72	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
9	59.09	3.47	33.41	32.45	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
10, $E_3$	66.23	2.13	64.48	5.85	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 4\text{H}_2\text{O}$
11	68.41	0.79	71.58	0.25	$\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$
12, $B_3$	71.00	0.00			$\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$

<sup>a</sup>Notation: Standard uncertainties for temperature and pressure are  $u(T) = 0.1$  K and  $u(P) = 1$  kPa, respectively. Relative standard uncertainties for solubility are  $u_r(w(\text{CaBr}_2)) = 0.005$  and  $u_r(w(\text{SrBr}_2)) = 0.008$ .



**Figure 5.** (a) Isothermal phase diagram of the ternary system  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 323 K. (b) Partial enlarged isothermal phase diagram of the ternary system  $\text{CaBr}_2$ – $\text{SrBr}_2$ – $\text{H}_2\text{O}$  at 323 K.





**Figure 6.** X-ray diffraction pattern of the invariant point  $E_3$  (saturated with  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ ) in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 323 K.

**3.3.  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  System at 323 K and 101.3 kPa.** The solubility data of salts in the liquid phase and wet residue for the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 323 K and 101.3 kPa are presented in Table 4. Also, the corresponding isothermal phase diagram at 323 K is plotted in Figure 5.

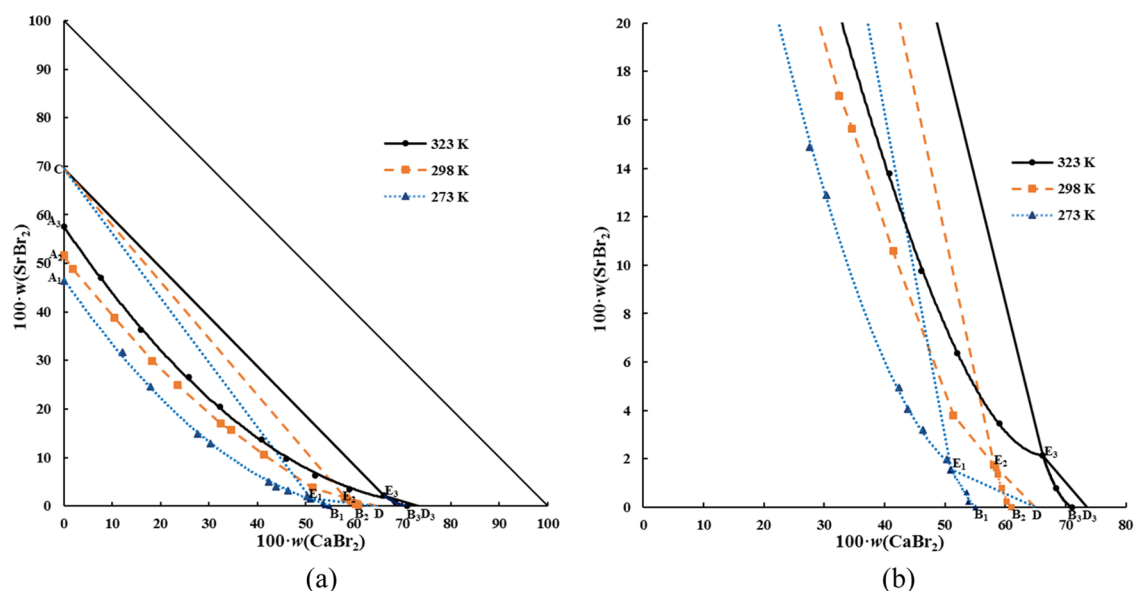
As described in Table 4 and Figure 5, two solubility curves, an invariant point and two single solid-phase crystallization regions, were involved in forming the isothermal phase diagram for the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 323 K. Two binary invariant points noted as  $A_3$  and  $B_3$  correspond to the binary systems  $\text{SrBr}_2\text{--H}_2\text{O}$  and  $\text{CaBr}_2\text{--H}_2\text{O}$ , respectively. Solubility curves  $A_3E_3$  (saturated with  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ) and  $B_3E_3$  (saturated with  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ ) intersect at an invariant point  $E_3$  (saturated with  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ ). Regions  $A_3CE_3$  and  $B_3DE_3$  denote the crystallization regions of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ , respectively.

On the saturation line  $AE_3$ , as the solubility of calcium bromide increases, the solubility of strontium bromide decreases from the boundary point of 57.60% to the invariant point of 2.13%. However, on the saturation line  $BE_3$ , the solubility of calcium bromide is little affected by strontium bromide, which decreases from the boundary point of 71.00% to the invariant point of 66.23%. The result shows that calcium bromide has a strong salting-out effect on strontium bromide. The crystallization area of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  occupies most of the crystallization space, which prompts it to precipitate out and separate further during the isothermal evaporation process. The X-ray diffraction pattern of the invariant point  $E_3$  in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 323 K is shown in Figure 6. The equilibrium solid phase was determined as  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ . Due to the absence of a standard card for  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ , the sample pattern of the boundary point  $B_3$  served as a basic reference. Christov has proved that  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$  crystal has been stably formed in the ternary system of  $\text{NaBr--CaBr}_2\text{--H}_2\text{O}$  at 323 K.<sup>13</sup> The wet residue measurement also indicated that  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$  is a stable crystal at 323 K.

**3.4. Comparison of the System  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273, 298, and 323 K.** In the binary system  $\text{CaBr}_2\text{--H}_2\text{O}$ , the solubility data of  $\text{CaBr}_2$  are 55.00% ( $T = 273$  K), 61.00% ( $T = 298$  K), and 71.00% ( $T = 323$  K), which are the same as the values in the CRC Handbook.<sup>14</sup> In another binary system  $\text{SrBr}_2\text{--H}_2\text{O}$ , the solubility of  $\text{SrBr}_2$  have the values 46.39% ( $T = 273$  K), 51.70% ( $T = 298$  K), and 57.60% ( $T = 323$  K), respectively, which are in good agreement with the reported values of 46.00, 51.70, and 57.60% in the CRC Handbook.<sup>14</sup> Composition and equilibrium solid phase of the invariant point in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273, 298, and 323 K are listed in Table 5, and the corresponding solubility comparison diagram is plotted in Figure 7. It can be seen from the comparison of the data in Table 5 and Figure 7 that the solubility and temperature are positively correlated, and the solubility of  $\text{SrBr}_2$  in the binary system of water is increasing, which is marked as  $A_1$ ,  $A_2$ , and  $A_3$ . Comparing the data of  $\text{CaBr}_2$  binary saturation points  $B_1$ ,  $B_2$ , and  $B_3$ , the saturation

**Table 5.** Composition and Equilibrium Solid Phase of Invariant Point in the Ternary System  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273, 298, and 323 K

$T$ (K)	invariant point	composition of the invariant point (100·w(b))		solid phase
		$b = \text{CaBr}_2$	$\text{SrBr}_2$	
273	$A_1$	0	46.39	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
298	$A_2$	0	51.60	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
323	$A_3$	0	57.60	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
273	$E_1$	51.02	1.56	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
298	$E_2$	58.14	1.73	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
323	$E_3$	66.23	2.13	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{CaBr}_2 \cdot 4\text{H}_2\text{O}$
273	$B_1$	55.00	0	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
298	$B_2$	61.00	0	$\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$
323	$B_3$	71.00	0	$\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$



**Figure 7.** (a) Solubility comparison diagram of the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273, 298, and 323 K. (b) Partial enlarged solubility comparison diagram of the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273, 298, and 323 K.

concentration is also increasing. Compared with the location of the invariant points  $E_1$ ,  $E_2$ , and  $E_3$  of the ternary system, it continuously shifts with temperature. The solubility of  $\text{SrBr}_2$  and  $\text{CaBr}_2$  increases, reaching the maximum at 323 K and the minimum at 273 K. It can be seen that even at different temperatures, the trend changes of each solubility are approximately the same. The solubility of  $\text{SrBr}_2$  decreases with the increase of  $\text{CaBr}_2$ , and calcium bromide has a strong salting-out effect on strontium bromide. Due to the influence of temperature, there are certain differences in the crystallization regions at different temperatures, and the equilibrium crystalline forms will change. At 273 and 298 K, there are two crystalline forms, namely,  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ , while at 323 K, the crystalline forms are  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ . With the increase of temperature, the equilibrium solid-phase  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$  is dehydrated at 323 K and transformed into  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ . In general, solid solutions are easily formed between elements of the same main group and the same crystal system with similar ionic radius. For example, it is formed in the precipitation of calcium chloride and strontium chloride at 298 K.<sup>15</sup> When the temperature rises to 323 K, the solid solution disappears,<sup>16</sup> indicating that the existence of the solid solution is not only affected by the coexisting substances but also by the temperature. The calcium bromide–strontium bromide–water system studied in this work has no solid solution formed between the components in a wide temperature range of 273–323 K, indicating that the crystallization characteristics of calcium strontium in the bromide system and the chloride system have a big difference.

#### 4. CONCLUSIONS

The isothermal dissolution equilibrium method was applied to measure the isothermal solubility in the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  at 273, 298, and 323 K. According to obtained solubility data, the isothermal phase diagrams at  $T = 273$ , 298, and 323 K for the ternary system  $\text{CaBr}_2\text{--SrBr}_2\text{--H}_2\text{O}$  were depicted. It is concluded that three isothermal phase diagrams are classified as a simple co-saturated type with the absence of a solid solution or a double salt. An invariant point, two

solubility curves and two crystallization regions participated in constructing the solid–liquid equilibrium phase diagrams. Equilibrium solid phases corresponding to invariant points at 273, 298, and 323 K were identified as  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CaBr}_2 \cdot 4\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ , respectively. Due to the strong salting-out effect of calcium bromide on strontium bromide, strontium bromide crystallizes out as a hexahydrate in a large concentration range, which makes it easier to crystallize and separate than calcium bromide.

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##### Notes

The authors declare no competing financial interest.

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