Measurements and theoretical simulations of phase equilibria in the quaternary systems NaBr + KBr + SrBr$_2$ + H$_2$O, NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O and their subsystems at 273.15 K

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ABSTRACT

Since various mineral elements (such as sodium, potassium, strontium, bromine) are rich in underground brine in Sichuan Basin of China, to utilize the bromine resources rationally, the phase equilibria of the quaternary systems NaBr + KBr + SrBr$_2$ + H$_2$O, NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O and their subsystems at 273.15 K were studied with the means of isothermal dissolution equilibrium method. The research systems are three ternary systems (NaBr + SrBr$_2$ + H$_2$O, KBr + SrBr$_2$ + H$_2$O and MgBr$_2$ + SrBr$_2$ + H$_2$O) and two quaternary systems (NaBr + KBr + SrBr$_2$ + H$_2$O and NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O). The corresponding solubility phase diagrams of the research systems listed above were plotted based on the measured experimental data.

The experimental results indicate that there is no formation of solid solution or double salts in five systems. Five phase diagrams all belong to hydrate type I and contain one invariant point. In three ternary systems, there are two isothermal solubility curves and two crystallization fields, and the equilibrium solid phases are NaBr•2H$_2$O and SrBr$_2$•6H$_2$O in the ternary system NaBr + SrBr$_2$ + H$_2$O, KBr and SrBr$_2$•6H$_2$O in the ternary system KBr + SrBr$_2$ + H$_2$O, and MgBr$_2$•6H$_2$O and SrBr$_2$•6H$_2$O in the ternary system MgBr$_2$ + SrBr$_2$ + H$_2$O, respectively. There are three isothermal solubility curves and three crystallization fields in two quaternary systems. The equilibrium solid phases are NaBr•2H$_2$O, KBr, and SrBr$_2$•6H$_2$O in the quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O. In the quaternary system NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O, the salts NaBr•2H$_2$O, MgBr$_2$•6H$_2$O and SrBr$_2$•6H$_2$O coexist at the invariant point.

The unreported mixing ion-interaction parameters of Pitzer equations $\theta_{Mg, Sr}$, $\Psi_{Mg, Sr, Br}$, $\Psi_{Na, Sr, Br}$, and $\Psi_{K, Sr, Br}$ are fitted with the solubility data at 273.15 K. The Pitzer ionic interaction model and the required parameters were employed to predict the solubilities of salts in five systems. The calculated results show that the predicted values are in accordance with the measured data, which verify the reliability of the selected parameters.

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1. Introduction

As a particular geological fluid solution, underground brine is gradually evolved and formed under the effects of high temperature, high pressure, and the interaction of water and rock in a deep and closed state [1]. Due to many complicated changes, the chemical compositions of the original sediment brines have changed, and the mineralization of the mineral elements in the underground brine is extremely high. For example, as one of the earliest dis-covered brines, the underground brine in Xuanda basin in northeast Sichuan of China contains potassium, bromine, iodine, boron, lithium, strontium, rubidium and many other mineral elements, the content of these elements even exceeds the requirements of comprehensive utilization and separate mining industry, forming high-quality chemical raw material water [2]. Therefore, it is essential to study the physical and chemical properties of brine for comprehensive development and mineralization rules of underground brine.

Bromine, which does not appear as a single substance in nature, is mainly dispersed in the earth's hydrosphere in the form of alkali metal and alkaline earth metal bromide, and it has special appli-

cation value in the development of national economy and science and technology [3]. The bromine resources of the underground brine in Sichuan Basin of China are widely distributed. Therefore, it is essential to rationally develop and utilize the bromine brine resources and to bring out their due economic and social benefits. The phase diagrams of water-salt systems have been widely used in describing the phase changes of water-salt systems because of their apparent geometric intuitions [4]. The research results of water-salt systems containing bromine will help to clarify the rules of bromine evaporation and enrichment in brines and to provide relevant thermodynamic basic data for the extraction of bromine resources, so the studies of phase equilibria of systems containing bromine at multi-temperature are essential.

In view of the occurrence of various mineral elements in underground brine in Sichuan Basin of China, the multi-component system can be simply summarized as $Li + Na + K + Ca + Mg + Sr + Cl + Br + SO_4 + B_4O_7 + H_2O$. In recent years, some experiments and theoretical simulations have been conducted about the subsystems of the above multi-component system at multiple temperatures. Based on the isopiestic experimental data, solubility data, and activity coefficient, Christov et al. [5-9] have conducted a series of research works about the subsystems of $Na + K + Mg + Ca + Br + SO_4 + H_2O$, and have given a series of single salt parameters and mixing parameters, which made a great contribution to the construction of the thermodynamic theoretical model. At the same time, the hydrate forms of sodium bromide at different temperatures were given. The ternary systems $NaBr + SrBr_2 + H_2O$ and $KBr + SrBr_2 + H_2O$ at 288.15 K have been researched by Meng et al., the solubilities were predicted based on the Pitzer Model, and the predicted values show good agreement with the experimental values [10]. Our research group has also carried out some researches on the phase equilibria in some subsystems of the quinary system $NaBr + KBr + MgBr_2 + SrBr_2 + H_2O$ at 298-348 K [11–15], and we found that strontium bromide exists in the form of $SrBr_2 \cdot 6H_2O$ within the temperature range of our studies.

It can be found from relevant literatures that water-salt systems containing strontium and bromide are mostly concentrated at 298–348 K. For industrial production and development, theoretical researches from low to high temperature are also essential. Due to the lack of Pitzer mixing ion parameters under multiple temperatures, especially for the systems containing strontium bromide, Pitzer mixing ion parameters are few, so the thermodynamic theoretical model of complex brine systems containing strontium bromide has not been reported. To make up the deficiency of equilibrium solubility data under multi-temperature condition, the phase equilibria of the systems containing strontium bromide at 273.15 K will be studied in this work. The main targets of this paper are as follows: (1) Measure the solubility of each salt in five systems (three ternary systems $NaBr + SrBr_2 + H_2O$, $KBr + SrBr_2 + H_2O$ and $MgBr_2 + SrBr_2 + H_2O$, two quaternary systems $NaBr + KBr + SrBr_2 + H_2O$ and $NaBr + MgBr_2 + SrBr_2 + H_2O$) with the isothermal dissolution equilibrium method; (2) Construct the phase diagrams of five systems based on the experimental values at 273.15 K; (3) Fit the unreported mixing ion-interaction parameters $\theta_{Mg, Sr}$, $\Psi_{Mg, Sr, Br}$, $\Psi_{Na, Sr, Br}$, and $\Psi_{K, Sr, Br}$ with the

solubility data; (4) Predict the solubilities of salts in five systems above with the Pitzer ionic interaction model and make comparisons between calculated values and experimental values.

2. Experimental section

2.1. Reagents and instruments

In the experiments, the detailed information of chemical reagents and instruments are shown in Tables 1 and 2, respectively. The deionized water produced by ultrapure water machine was acted as the solvent and was used for chemical analysis with a resistivity of 18.25 MΩ cm.

2.2. Experimental method

The isothermal dissolution equilibrium method [16] was selected to carry out the studies of the phase equilibria in this paper. From each subsystem, another new salt was added in a certain proportion, and the mixed salts were evenly blended with a certain amount of deionized water in the rigid grinding glass bottles. Then the glass bottles would be inserted into the oscillator that was placed in the incubator whose temperature was set to be 273.15 ($\pm$ 0.1) K, and the oscillator was shaking to establish the equilibria of the samples. After stirring for about a month, the oscillator was turned off, and then the samples were entirely stationary. When the liquid phase had been clarified, the supernatant was taken out to be analyzed every other day until the relative standard uncertainty between the results (mass fraction) at two times was within 0.003, it was considered that the equilibrium state of the studied systems had reached. Then the liquid phase was sampled for chemical analysis. The solid phases at the bottom were taken out for identifications through XRD method, and the solid phases in three ternary systems were also determined using the Schreinemakers residue method [17].

2.3. Analytical methods

The solubility of each salt in the solution was determined by chemical analysis [18] and Flame Atomic Absorption Spectrometry method. The bromide ion (Br^-) was titrated with $AgNO_3$ solution using potassium chromate as the indicator (with a maximum relative standard uncertainty of 0.003). When strontium ion (Sr^{2+}) simultaneously existed with magnesium ion (Mg^{2+}), the total amounts of Mg^{2+} and Sr^{2+} were measured by EDTA titration in the presence of Eriochrome black T as an indicator, Sr^{2+} was measured by Flame Atomic Absorption Spectrometry method (with a maximum relative standard uncertainty of 0.005), and Mg^{2+} were obtained by subtraction. When Sr^{2+} and Mg^{2+} were not together, Sr^{2+} was measured in the same way as when strontium and magnesium coexisted (with a maximum relative standard uncertainty of 0.005). Potassium ion (K^+) was obtained by volumetric analysis of sodium tetraphenylboron with a maximum relative standard uncertainty of 0.005. The content of Na^+ was obtained by ion balance subtraction method and Flame Atomic Absorption Spectrometry method (with a maximum relative standard uncertainty of 0.005).

Table 1
Chemical reagents.

Chemical name	CAS Reg. No.	Purity (mass fraction)	Source
NaBr	7647-15-6	$\geq$99.0%	Chengdu Kelong Chemical Reagent Manufactory, China
KBr	7758-02-3	$\geq$99.0%	Chengdu Kelong Chemical Reagent Manufactory, China
$MgBr_2 \cdot 6H_2O$	13446-53-2	$\geq$98%	Shanghai Aladdin Biochemical Technology Co. Ltd.
$SrBr_2 \cdot 6H_2O$	7789-53-9	$\geq$99.0%	Shanghai Aladdin Biochemical Technology Co. Ltd.

Table 2
Instruments.

Instrument name	Type	Manufacturing Company
Electronic balance	AL 104	Mettler Toledo Instruments Co., Ltd. (precision: 0.0001 g)
Ultrapure water machine	UPT-II-20T	Sichuan Youpu Ultrapure Technology Co. Ltd.
Incubator	SHH-250	Chongqing Yingbo Experimental Instrument Co. Ltd. (precision: ± 0.1 K)
Oscillator	HY-5	Jintan Kexi Instrument Co. Ltd.
X-ray diffraction analyzer	DX-2700	Dandong Fangyuan Instrument Co. Ltd.
Atomic absorption spectrometer	ICE 3300	Thermo Fisher Company

Table 3
The comparison data of invariant points in the binary subsystems at 273.15 K between this work and literatures.

Systems		Composition of solution $100 \cdot w(B)$	Equilibrium solid phases	Reference
$NaBr + H_2O$	NaBr	44.40	$NaBr \cdot 2H_2O$	[19]
		44.60		[20]
		44.58		this work
$KBr + H_2O$	KBr	35.00	KBr	[19]
		35.11		[21]
		34.73		[20]
		34.95		this work
$MgBr_2 + H_2O$	$MgBr_2$	49.30	$MgBr_2 \cdot 6H_2O$	[19]
		49.48		[20]
		49.56		this work
$SrBr_2 + H_2O$	$SrBr_2$	46.00	$SrBr_2 \cdot 6H_2O$	[19]
		46.04		this work

3. Results and discussion

The experimental solubilities for the binary subsystems $NaBr + H_2O$, $KBr + H_2O$, $MgBr_2 + H_2O$ and $SrBr_2 + H_2O$ have been reported in literatures [19–21]. The comparison data of invariant points for the binary subsystems between this work and literatures are listed in Table 3.

For the binary system $NaBr + H_2O$ at 273.15 K, the mass fraction of NaBr at the invariant point is 44.58% in this study, the data reported in the CRC Handbook of Chemistry and Physics [19] is 44.40% and that reported in the literature is 44.60% [20]. Similarly, the mass fraction of $SrBr_2$ at the invariant point of the binary system $SrBr_2 + H_2O$ at 273.15 K is 46.04% in this work, while that shown in the CRC Handbook of Chemistry and Physics [19] is 46.00%. We can see that all the solubilities for the binary subsystems in this work are well in agreement with the literature data. These results show that the experimental process and analytical results are reliable in this work.

3.1. Ternary system $NaBr + SrBr_2 + H_2O$

The solubility of each salt in the ternary system $NaBr + SrBr_2 + H_2O$ at 273.15 K was determined, and the experimental results (in mass fraction) were listed in Table 4. The equilibrium phase diagram was constructed in Fig. 1, and Fig. 2 is the XRD patterns of the equilibrium solid phases at the invariant point E_1.

In Fig. 1, A_1 and B_1 represent the invariant points of the binary systems $SrBr_2 + H_2O$, $NaBr + H_2O$ at 273.15 K, respectively. From Fig. 1 we can see that the phase diagram at 273.15 K contains one invariant point (E_1), two isothermal solubility curves (A_1E_1 and B_1E_1) and two crystallization fields, there is no formation of double salts or solid solution. Two hydrated salts $NaBr \cdot 2H_2O$ and $SrBr_2 \cdot 6H_2O$ reach co-saturation at the invariant point E_1, at which the solubilities of two salts in the mass fraction are $w(NaBr)=0.2112$, $w(SrBr_2)=0.2799$. According to the results of the Schreinemakers residue method (in Fig. 1) and the XRD method (in Fig. 2), both of them indicate that the equilibrium solid phases at the invariant point E_1 are $NaBr \cdot 2H_2O$ and $SrBr_2 \cdot 6H_2O$. The isothermal solubility curve A_1E_1 is saturated with $SrBr_2 \cdot 6H_2O$ and
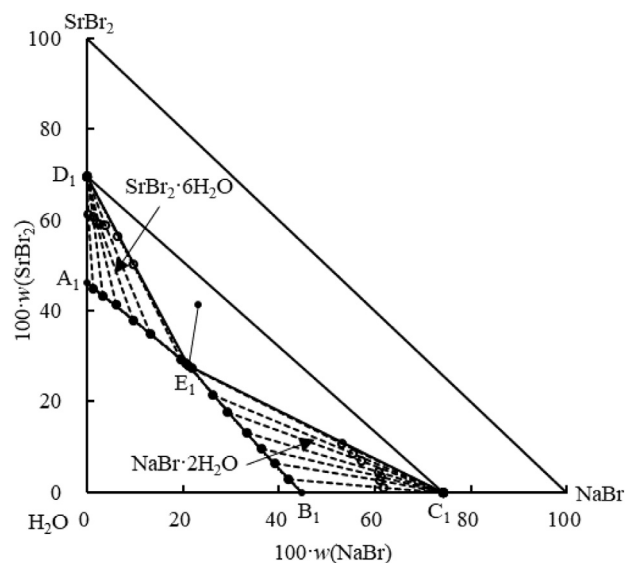

Fig. 1. Equilibrium phase diagram of the ternary system $NaBr + SrBr_2 + H_2O$ at 273.15 K ●, equilibrium liquid phase composition; ○, wet residue composition; −, isothermal solubility curve, wet residue line.

B_1E_1 is saturated with $NaBr \cdot 2H_2O$. For two crystallization fields ($NaBr \cdot 2H_2O$ and $SrBr_2 \cdot 6H_2O$) in the phase diagram, the crystallization area of $SrBr_2 \cdot 6H_2O$ is smaller than that of $NaBr \cdot 2H_2O$, but the difference between the two areas is not significant.

3.2. Ternary system $KBr + SrBr_2 + H_2O$

The solubility data of the ternary system $KBr + SrBr_2 + H_2O$ were shown in Table 5, the phase diagram was plotted in Fig. 3, and the identification results of the equilibrium solid phases were shown in Fig. 4. From two isothermal solubility curves A_2E_2 (saturated with $SrBr_2 \cdot 6H_2O$) and B_2E_2 (saturated with KBr), we can see that the solubility of potassium bromide decreases with the addition of strontium bromide. Potassium bromide cannot dissolve more when strontium bromide is saturated, so it can be

Table 4
The experimental solubility data in the ternary system $NaBr + SrBr_2 + H_2O$ at 273.15 K and 94.77 kPa [a].

No.	Composition of solution $100 \bullet w(B)$		Composition of wet residue $100 \bullet w(B)$		Equilibrium solid phases
	NaBr	$SrBr_2$	NaBr	$SrBr_2$	
1, A_1	0	46.04	–	–	$SrBr_2 \bullet 6H_2O$
2	1.13	44.93	0.34	61.22	$SrBr_2 \bullet 6H_2O$
3	3.29	43.32	1.21	60.65	$SrBr_2 \bullet 6H_2O$
4	6.13	41.19	2.09	59.19	$SrBr_2 \bullet 6H_2O$
5	9.61	37.86	2.58	59.03	$SrBr_2 \bullet 6H_2O$
6	13.07	34.76	3.85	58.88	$SrBr_2 \bullet 6H_2O$
7	19.50	29.25	9.68	50.25	$SrBr_2 \bullet 6H_2O$
8	20.63	28.45	6.27	56.48	$SrBr_2 \bullet 6H_2O$
9, E_1	21.12	27.99	–	–	$SrBr_2 \bullet 6H_2O + NaBr \bullet 2H_2O$
10	21.77	27.43	53.04	10.78	$NaBr \bullet 2H_2O$
11	26.18	21.32	55.29	8.41	$NaBr \bullet 2H_2O$
12	29.32	17.64	57.12	7.03	$NaBr \bullet 2H_2O$
13	33.18	13.15	60.81	4.43	$NaBr \bullet 2H_2O$
14	36.23	9.57	61.14	3.52	$NaBr \bullet 2H_2O$
15	39.01	6.50	60.92	2.55	$NaBr \bullet 2H_2O$
16	41.99	2.79	61.86	1.03	$NaBr \bullet 2H_2O$
17, B_1	44.58	0	–	–	$NaBr \bullet 2H_2O$

[a] Standard uncertainties are $u(T)$=0.1 K, $u(p)$=0.9 kPa. Maximum relative standard uncertainties for solubilities are $u_r[w(NaBr)]$=0.005, $u_r[w(SrBr_2)]$=0.005.

Table 5
The experimental solubility data in the ternary system $KBr + SrBr_2 + H_2O$ at 273.15 K and 94.77 kPa [a].

No.	Composition of solution $100 \bullet w(B)$		Composition of wet residue $100 \bullet w(B)$		Equilibrium solid phases
	KBr	$SrBr_2$	KBr	$SrBr_2$	
1, A_2	0	46.04	–	–	$SrBr_2 \bullet 6H_2O$
2	3.15	44.57	1.33	57.63	$SrBr_2 \bullet 6H_2O$
3	5.35	43.63	2.68	55.93	$SrBr_2 \bullet 6H_2O$
4, E_2	6.57	42.35	–	–	$SrBr_2 \bullet 6H_2O + KBr$
5	7.04	42.08	–	–	KBr
6	8.12	39.69	65.71	15.83	KBr
7	8.79	37.97	70.02	12.86	KBr
8	11.55	33.39	71.95	9.77	KBr
9	13.84	28.85	69.67	10.54	KBr
10	17.35	22.92	70.50	8.50	KBr
11	20.89	18.75	73.44	6.26	KBr
12	24.92	12.91	76.27	4.39	KBr
13	30.18	6.62	77.46	2.60	KBr
14, B_2	34.95	0	–	–	KBr

[a] Standard uncertainties are $u(T)$=0.1 K, $u(p)$=0.9 kPa. Maximum relative standard uncertainties for solubilities are $u_r[w(KBr)]$=0.005, $u_r[w(SrBr_2)]$=0.005.

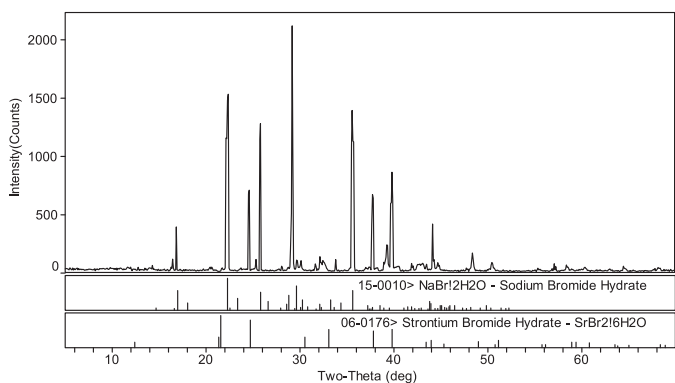**Fig. 2.** X-ray diffraction patterns of the invariant point E_1 ($SrBr_2 \bullet 6H_2O + NaBr \bullet 2H_2O$) in the ternary system $NaBr + SrBr_2 + H_2O$ at 273.15 K.

seen that strontium bromide will produce a strong salting-out effect on potassium bromide. Two salts reach co-saturation at the invariant point E_2, where the compositions are $w(KBr)$=0.0657, $w(SrBr_2)$=0.4235. According to the X-ray diffraction patterns of the equilibrium solid phases at the invariant point E_2 (in Fig. 4), the

positions of the main peaks of the characteristic peaks are basically the same as those of the standard cards. The results of the Schreinemakers residue method also confirm this, so the equilibrium solid phases at E_2 are KBr and $SrBr_2 \bullet 6H_2O$. The crystallization fields are KBr and $SrBr_2 \bullet 6H_2O$, and the crystallization area of KBr is bigger than that of $SrBr_2 \bullet 6H_2O$, indicating that the solubility of KBr is lower in the mixed solution, and KBr is easier to precipitate from the saturated solution.

3.3. Ternary system $MgBr_2 + SrBr_2 + H_2O$

The experimental values of this ternary system were shown in Table 6, the corresponding phase diagram was plotted in Fig. 5 and Fig. 6 shows the identification results of the equilibrium solid phases. It can be seen from the phase diagram that this ternary system is hydrate type I. The phase diagram has two isothermal solubility curves, which are saturated with hydrated salts $SrBr_2 \bullet 6H_2O$ and $MgBr_2 \bullet 6H_2O$, respectively. Two hydrated salts reach co-saturation at the only one invariant point E_3, and the corresponding compositions of the saturated solution are $w(MgBr_2)$=0.4941, $w(SrBr_2)$=0.0105. Two crystallization fields are strontium bromide hexahydrate and magnesium bromide hexahydrate, from the areas of the crystallization fields ($MgBr_2 \bullet 6H_2O$ > $SrBr_2 \bullet 6H_2O$), we can see that $MgBr_2$ has a strong salting-out effect

Table 6
The experimental solubility data in the ternary system $MgBr_2$ + $SrBr_2$ + H_2O at 273.15 K and 94.77 kPa [a].

No.	Composition of solution $100 \cdot w(B)$		Composition of wet residue $100 \cdot w(B)$		Equilibrium solid phases
	$MgBr_2$	$SrBr_2$	$MgBr_2$	$SrBr_2$	
1, A_3	0	46.04	–	–	S6
2	4.43	41.46	–	–	S6
3	9.73	35.82	3.00	57.73	S6
4	11.63	33.25	–	–	S6
5	12.90	31.06	5.99	53.08	S6
6	17.94	26.91	7.56	52.27	S6
7	21.55	21.99	–	–	S6
8	25.66	18.06	–	–	S6
9	29.00	14.66	10.91	50.8	S6
10	32.36	11.94	14.18	45.98	S6
11	37.17	7.11	13.02	46.8	S6
12	41.95	3.77	15.62	47.21	S6
13	43.47	2.92	16.63	45.31	S6
14,	48.32	1.15	15.92	45.98	S6
15, E_3	49.41	1.05	–	–	S6+M6
16	49.45	1.03	–	–	M6
17, B_3	49.56	0	–	–	M6

[a] Standard uncertainties are $u(T)$=0.1 K, $u(p)$=0.9 kPa. Maximum relative standard uncertainties for solubilities are $u_r[w(MgBr_2)]$=0.005, $u_r[w(SrBr_2)]$=0.005. Abbreviations: M6=$MgBr_2 \cdot 6H_2O$, S6=$SrBr_2 \cdot 6H_2O$.

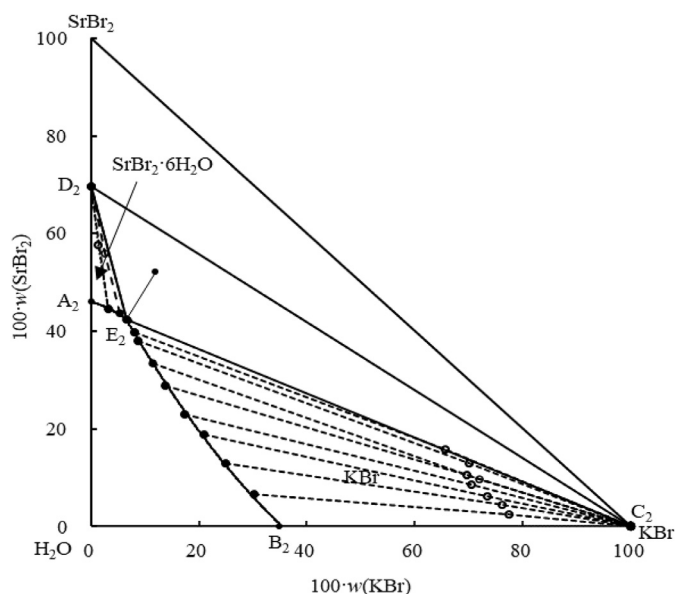**Fig. 3.** Equilibrium phase diagram of the ternary system KBr + SrBr2 + H2O at 273.15 K, •, equilibrium liquid phase composition; ○, wet residue composition; −, isothermal solubility curve, wet residue line.
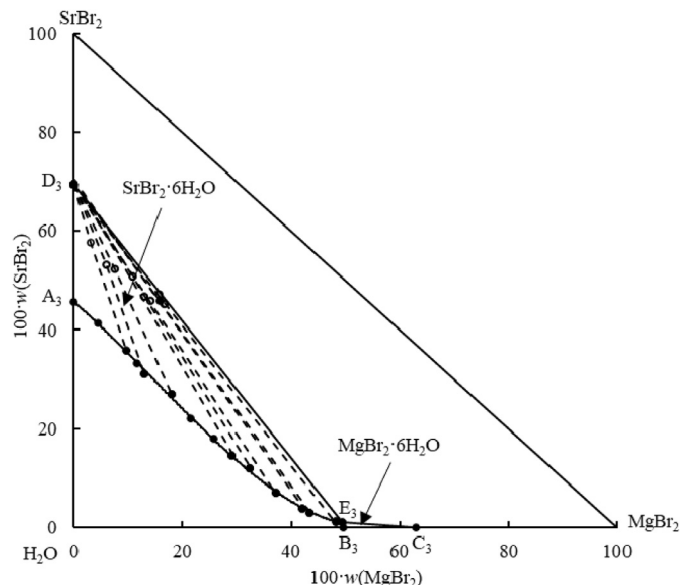

Fig. 5. Equilibrium phase diagram of the ternary system $MgBr_2$ + $SrBr_2$ + H_2O at 273.15 K, •, equilibrium liquid phase composition; ○, wet residue composition; −, isothermal solubility curve, wet residue line.

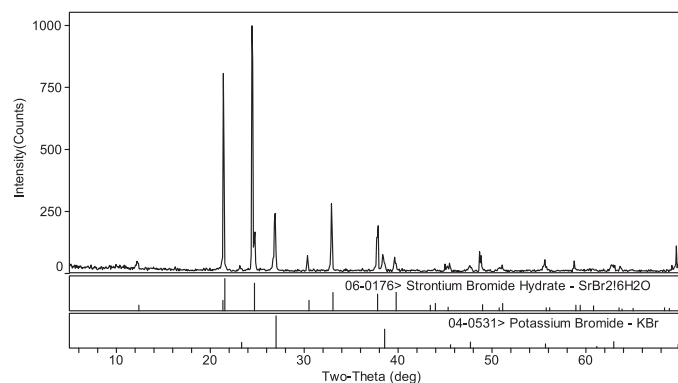**Fig. 4.** X-ray diffraction patterns of the invariant point E_2 ($SrBr_2 \cdot 6H_2O$ + KBr) in the ternary system KBr + $SrBr_2$ + H_2O at 273.15 K.
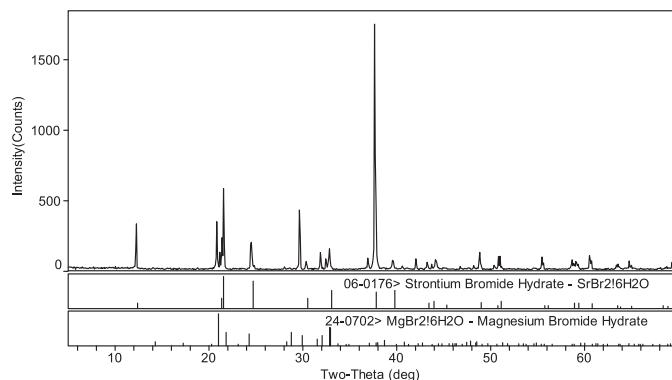
Fig. 6. X-ray diffraction patterns of the invariant point E_3 ($SrBr_2 \cdot 6H_2O$ + $MgBr_2 \cdot 6H_2O$) in the ternary system $MgBr_2$ + $SrBr_2$ + H_2O at 273.15 K.

Table 7
The experimental solubility data in the quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O at 273.15 K and 94.77 kPa [a].

No.	Composition of solution 100•w(B)			Dry salt composition J (g/100 g) J(NaBr) + J(KBr) + J(SrBr$_2$)=100 g				Equilibrium solid phases
	NaBr	KBr	SrBr$_2$	NaBr	KBr	SrBr$_2$	H$_2$O	
1, A$_4$	0	6.57	42.35	0	13.43	86.57	104.42	S6 + K
2	3.07	6.36	40.43	6.16	12.76	81.09	100.57	S6 + K
3	5.36	6.19	38.28	10.75	12.42	76.83	100.70	S6 + K
4	10.31	5.82	34.02	20.55	11.61	67.84	99.41	S6 + K
5	16.36	5.35	29.33	32.05	10.49	57.47	95.93	S6 + K
6	19.70	4.97	26.56	38.45	9.70	51.85	95.20	S6 + K
7	19.85	4.90	26.69	38.59	9.52	51.89	94.39	S6 + K
8, B$_4$	21.12	0	27.99	43.01	0	56.99	103.62	S6 + N2
9	20.99	1.30	27.84	41.87	2.59	55.54	99.48	S6 + N2
10	20.52	3.75	26.98	40.04	7.32	52.64	95.12	S6 + N2
11, E$_4$	20.08	4.83	26.60	38.98	9.38	51.64	94.14	S6 + N2 + K
12, C$_4$	40.68	7.05	0	85.23	14.77	0	109.54	N2 + K
13	38.32	6.99	2.50	80.15	14.63	5.23	109.15	N2 + K
14	36.88	6.84	4.22	76.92	14.27	8.81	108.56	N2 + K
15	35.30	6.64	6.20	73.32	13.79	12.88	107.71	N2 + K
16	33.59	6.48	8.40	69.31	13.36	17.33	106.34	N2 + K
17	32.12	6.22	10.37	65.94	12.77	21.29	105.29	N2 + K
18	30.70	6.13	11.86	63.05	12.58	24.36	105.38	N2 + K
19	27.24	5.79	16.30	55.23	11.73	33.04	102.74	N2 + K
20	24.15	5.50	20.51	48.15	10.97	40.88	99.33	N2 + K
21	21.11	5.13	24.81	41.36	10.04	48.60	95.91	N2 + K
22	20.26	4.97	26.42	39.23	9.62	51.15	93.62	N2 + K
23	20.19	4.86	26.74	38.98	9.39	51.63	93.10	N2 + K

[a] Standard uncertainties are u(T)=0.1 K, u(p)=0.9 kPa. Maximum relative standard uncertainties for solubilities are $u_r[w(NaBr)]$=0.005, $u_r[w(KBr)]$=0.005, $u_r[w(SrBr_2)]$=0.005. Abbreviations: N2=NaBr•2H$_2$O, K=KBr, S6=SrBr$_2$•6H$_2$O.
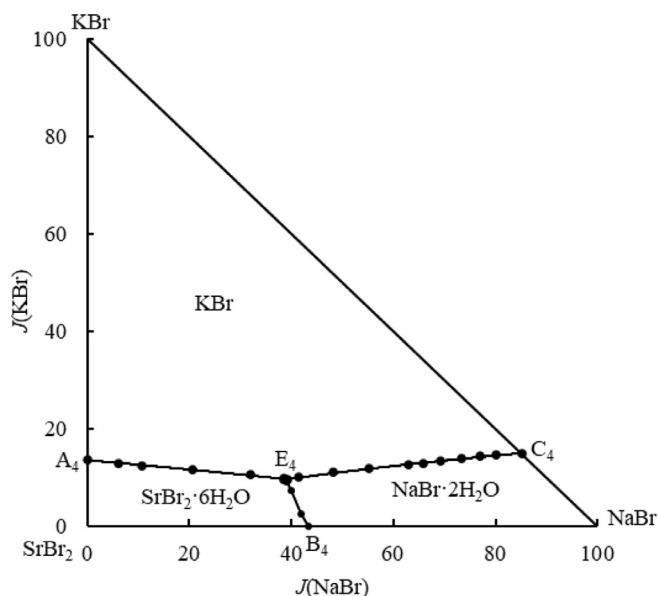

Fig. 7. Dry salt phase diagram of the quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O at 273.15 K, •, equilibrium liquid phase composition; −, isothermal solubility curve.

on SrBr$_2$, which makes SrBr$_2$•6H$_2$O more likely to crystallize out from saturated solution.

3.4. Quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O

The measured results of this quaternary system were listed in Table 7, the equilibrium phase diagram and water content diagram were drawn according to the results and shown in Figs. 7 and 8. The results of the identifications on the solid phases at the invariant point are shown in Fig. 9. The dry salt compositions (the Jänecke index) in Table 7 were calculated through the following formulas:
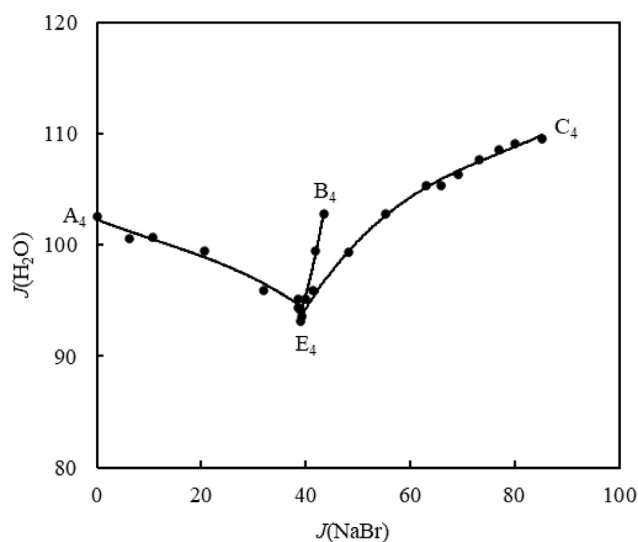

Fig. 8. Water content diagram of the quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O at 273.15 K.

$$w_{total} = w(NaBr) + w(KBr) + w(SrBr_2) \tag{1}$$

$$J(B) = \frac{100gw(B)}{w_{total}} (B = salt\ or\ H_2O) \tag{2}$$

Table 7 and Fig. 7 show that there is no new salt formation in this quaternary system compared with the subsystems at 273.15 K. The dry salt phase diagram is composed of one invariant point, three isothermal solubility curves and three crystallization fields. A$_4$, B$_4$, C$_4$ represent the invariant points of the ternary systems KBr + SrBr$_2$ + H$_2$O, NaBr + SrBr$_2$ + H$_2$O and NaBr + KBr + H$_2$O, respectively. Three isothermal solubility curves A$_4$E$_4$ (saturated with KBr and SrBr$_2$•6H$_2$O), B$_4$E$_4$ (saturated with NaBr•2H$_2$O and SrBr$_2$•6H$_2$O) and C$_4$E$_4$ (saturated with

Table 8
The experimental solubility data in the quaternary system NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O at 273.15 K and 94.77 kPa [a].

No.	Composition of solution 100•w(B)			Dry salt composition J (g/100 g) J(NaBr) + J(MgBr$_2$) + J(SrBr$_2$)=100 g				Equilibrium solid phases
	NaBr	MgBr$_2$	SrBr$_2$	NaBr	MgBr$_2$	SrBr$_2$	H$_2$O	
1, A$_5$	0	49.41	1.05	0	97.92	2.08	98.18	M6 + S6
2	1.37	47.71	0.98	2.74	95.29	1.96	99.76	M6 + S6
3	3.08	46.80	1.07	6.05	91.84	2.11	96.23	M6 + S6
4	3.22	46.68	1.09	6.31	91.55	2.14	96.15	M6 + S6
5, B$_5$	3.46	47.45	0	6.80	93.20	0	96.43	N2 + M6
6	3.43	47.08	0.44	6.73	92.40	0.87	96.27	N2 + M6
7	3.40	46.55	0.89	6.69	91.56	1.76	96.70	N2 + M6
8, E$_5$	3.29	46.39	1.14	6.48	91.28	2.24	96.78	N2 + M6 + S6
9, C$_5$	21.12	0	27.99	43.01	0	56.99	103.62	N2 + S6
10	20.25	3.42	25.79	40.94	6.92	52.14	102.15	N2 + S6
11	17.95	8.11	21.92	37.40	16.91	45.69	108.40	N2 + S6
12	16.00	12.58	19.05	33.59	26.41	40.00	109.97	N2 + S6
13	13.60	18.31	14.62	29.24	39.35	31.41	114.91	N2 + S6
14	12.24	21.09	12.36	26.79	46.15	27.05	118.81	N2 + S6
15	8.29	30.25	7.87	17.86	65.19	16.96	115.47	N2 + S6
16	6.11	35.74	4.70	13.13	76.78	10.09	114.80	N2 + S6
17	4.67	40.94	2.43	9.71	85.22	5.07	108.16	N2 + S6
18	3.40	46.22	1.19	6.69	90.97	2.34	96.84	N2 + S6

[a] Standard uncertainties are $u(T)$=0.1 K, $u(p)$=0.9 kPa. Maximum relative standard uncertainties for solubilities are $u_r[w(\text{NaBr})]$=0.005, $u_r[w(\text{MgBr}_2)]$=0.005, $u_r[w(\text{SrBr}_2)]$=0.005. Abbreviations: N2=NaBr•2H$_2$O, M6=MgBr$_2$•6H$_2$O, S6=SrBr$_2$•6H$_2$O.
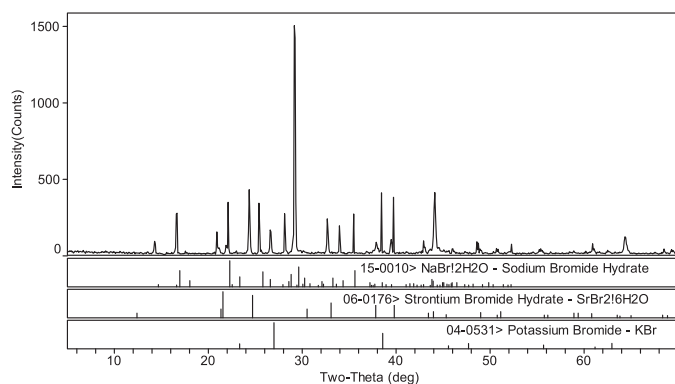

Fig. 9. X-ray diffraction patterns of the invariant point E$_4$ (NaBr•2H$_2$O + KBr + SrBr$_2$•6H$_2$O) in the quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O at 273.15 K.

Fig. 10. Dry salt phase diagram of the quaternary system NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O at 273.15 K, ●, equilibrium liquid phase composition; −, isothermal solubility curve.

KBr and NaBr•2H$_2$O) reach co-saturation at the invariant point E$_4$. So three salts KBr, NaBr•2H$_2$O and SrBr$_2$•6H$_2$O coexist at point E$_4$, and the compositions of the liquid phase are w(NaBr)=0.2008, w(KBr)=0.0483, w(SrBr$_2$)=0.2660. The identifications of the solid phases in Fig. 9 confirm that the equilibrium salts at E$_4$ are KBr, NaBr•2H$_2$O and SrBr$_2$•6H$_2$O. The order of the area size of three crystallization fields is KBr > NaBr•2H$_2$O > SrBr$_2$•6H$_2$O, so we can conclude that the solubility of KBr is the smallest, and that of SrBr$_2$•6H$_2$O is the biggest, strontium bromide has a salting-out effect on potassium bromide and sodium bromide. KBr is the easiest to be separated from the mixed solution.

From the water content diagram in Fig. 8, we can see that on the isothermal solubility curves A$_4$E$_4$, B$_4$E$_4$ and C$_4$E$_4$, the water content J(H$_2$O) decreases with the addition of the third salt from the invariant points of three ternary systems. The water content decreases to its minimum value (94.14) at the invariant point E$_4$, where the dry salt content reaches its maximum value.

3.5. Quaternary system NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O

In the quaternary system NaBr + MgBr$_2$ + SrBr$_2$ + H$_2$O, the solubility values and dry salt compositions were calculated in the same way as above and shown in Table 8, the phase diagram and water content diagram were constructed in Figs. 10 and 11, Fig. 12
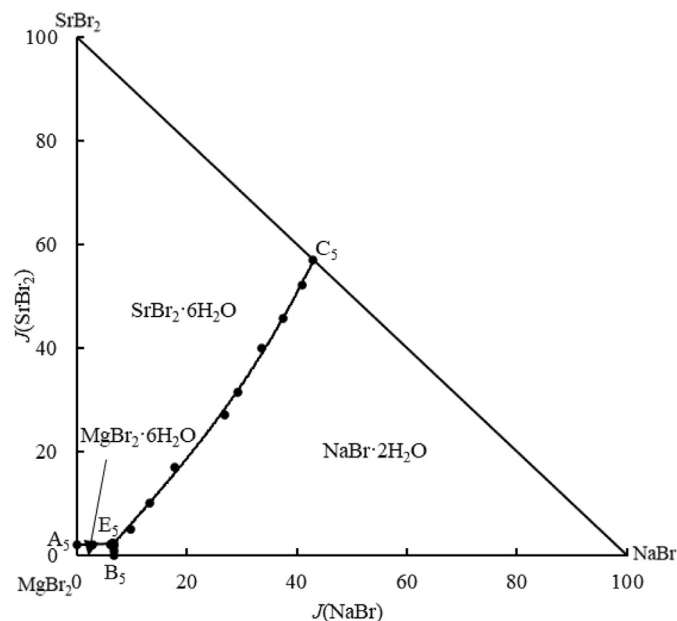
displays the patterns of the identification results of the equilibrium solid phases.

From the phase diagram in Fig. 10, we can see that this phase diagram is composed of one invariant point (E$_5$), three isothermal solubility curves and three crystallization fields. Three crystallization fields are NaBr•2H$_2$O, MgBr$_2$•6H$_2$O and SrBr$_2$•6H$_2$O, respectively, and the order of whose area size is NaBr•2H$_2$O > SrBr$_2$•6H$_2$O > MgBr$_2$•6H$_2$O, this indicates that the solubility of MgBr$_2$•6H$_2$O is the biggest among three salts. At the invariant point E$_5$, where the compositions in the saturated solutions are w(NaBr)=0.0329, w(MgBr$_2$)=0.4639, w(SrBr$_2$)=0.0114, three solid phases NaBr•2H$_2$O, MgBr$_2$•6H$_2$O and SrBr$_2$•6H$_2$O simultaneously reach saturation, which are confirmed by the identification results of the equilibrium solid phases in Fig. 12.

Table 9
The comparison data of invariant points in the ternary subsystems at 273.15 K between this work and literatures.

Systems	Composition of solution $100 \cdot w(B)$			Equilibrium solid phases	Reference
	NaBr	KBr	$MgBr_2$		
$NaBr + KBr + H_2O$	41.05	4.86		$NaBr \cdot 2H_2O + KBr$	[20]
	40.68	7.05		$NaBr \cdot 2H_2O + KBr$	this work
$NaBr + MgBr_2 + H_2O$	3.52		44.61	$NaBr \cdot 2H_2O + MgBr_2 \cdot 6H_2O$	[20]
	3.46		47.45	$NaBr \cdot 2H_2O + MgBr_2 \cdot 6H_2O$	this work
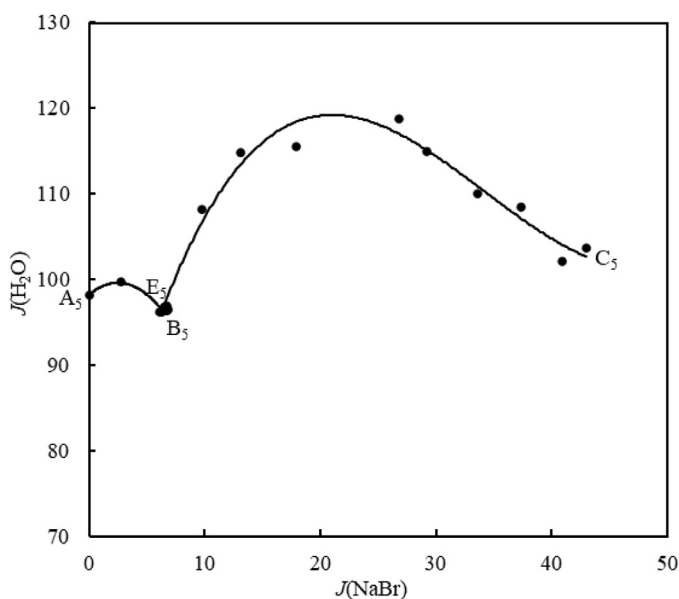
Fig. 11. Water content diagram of the quaternary system $NaBr + MgBr_2 + SrBr_2 + H_2O$ at 273.15 K.
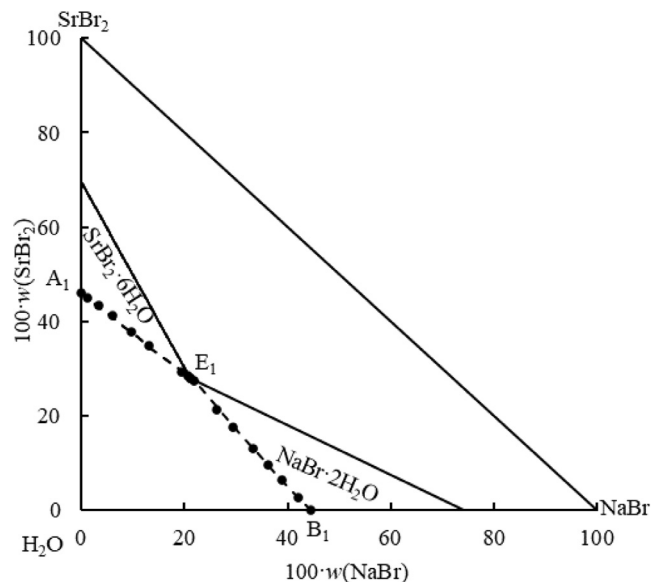
Fig. 13. Calculated and experimental phase diagram of the ternary system $NaBr + SrBr_2 + H_2O$ at 273.15 K, •, experimental result, calculated result.
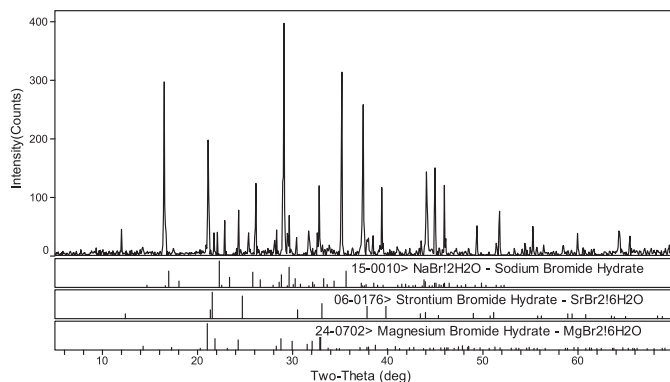
Fig. 12. X-ray diffraction patterns of the invariant point E_5 ($NaBr \cdot 2H_2O + MgBr_2 \cdot 6H_2O + SrBr_2 \cdot 6H_2O$) in the quaternary system $NaBr + MgBr_2 + SrBr_2 + H_2O$ at 273.15 K.

Table 10
Single-salt parameters of the systems in this paper at 273.15 K.

| Salt	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference
NaBr	0.10617	0.073762	-0.0009152	[5]
KBr	0.034492	0.32184	0.0011678	[5]
$MgBr_2$	0.35457	2.42653	0.010150	[7]
$SrBr_2$	0.36046	1.52115	-0.0037175	[30]

4. Solubility prediction

The solubility data of single and multiple components in water-salt systems are measured by phase equilibrium experiments mainly. However, it is a heavy work to determine the solubilities of multi-component water-salt systems by experiment, and the quantitative analysis conditions are limited, which bring difficulties to the process of salt production in the industry by using phase diagrams of multi-component water-salt systems. The phase equilibrium process of salts dissolve in water is subject to the basic rule of chemical thermodynamics, as is the chemical reaction equilibrium. Since 1973, Pitzer and other scientists have proposed the ionic interaction model. This semi-empirical statistical mechanical model can describe and predict electrolyte solutions ranging from very dilute to high concentrations [22–29]. This model is mainly used to study the solubilities of minerals and the solubilities of gases in saline solution. The solubility predictions of multi-component water-salt systems are of great value in the chemical industry, especially in the research of brine chemistry.

In the water content diagram (Fig. 11), on the isothermal solubility curves A_5E_5, B_5E_5 and C_5E_5, when the third salt is added, the dry salt content increases and the water content reaches its minimum value (96.78) at the invariant point E_5.

Among above two quaternary systems, the solubility data of the ternary subsystems $NaBr + KBr + H_2O$ and $NaBr + MgBr_2 + H_2O$ were also reported in literature [20], and the comparisons of the solubilities at the invariant points were listed in Table 9. It is shown that the solubility data of $MgBr_2$ and KBr measured in this work are higher than those in the literature, the solubilities of NaBr in two equilibrium systems are very close to those reported in the literature.

Table 11
Mixing ion-interaction parameters of the systems in this paper at 273.15 K.

| Parameters	$\theta_{Na, K}$	$\theta_{Na, Sr}$	$\theta_{K, Sr}$	$\theta_{Na, Mg}$	$\theta_{Mg, Sr}$
Values	0.0011007	-0.087189	-0.0048231	0.07	0.11911
Reference	[5]	[31]	[31]	[9]	this work
Parameters	$\Psi_{Na, K, Br}$	$\Psi_{Na, Sr, Br}$	$\Psi_{K, Sr, Br}$	$\Psi_{Na, Mg, Br}$	$\Psi_{Mg, Sr, Br}$
Values	-0.0030697	0.016178	-0.023296	-0.010837	-0.017982
Reference	[5]	this work	this work	[9]	this work
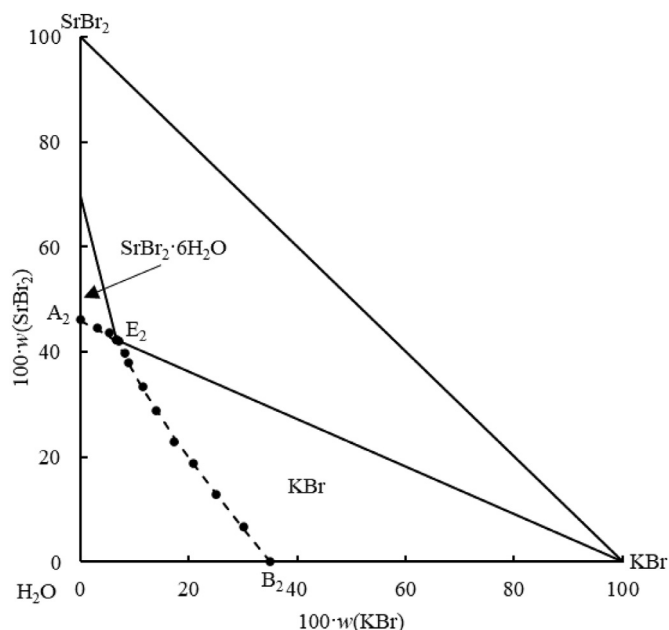
Fig. 14. Calculated and experimental phase diagram of the ternary system KBr + SrBr$_2$ + H$_2$O at 273.15 K, •, experimental result, calculated result.

Table 12
Values of Debye-Hückel constant (A^ϕ) and solubility equilibrium constants (ln$K$sp) of solid phases for the systems in this paper at 273.15 K.

Parameters	A^ϕ	NaBr	KBr	MgBr$_2$•6H$_2$O	SrBr$_2$•6H$_2$O
Values	0.37670	4.13696	2.004032	11.30535	5.92054
Reference	[28]	[5]	[5]	[7]	this work

4.1. Parameterization

Based on the Pitzer ionic interaction model, the systems studied in this paper were calculated through the Pitzer parameters. The Pitzer ionic interaction model is characterized by the fact that all parameters (single salt parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ, and the solubility equilibrium constant K_{sp}) can be measured by a single electrolyte and binary solution containing the same ions. For more complex mixed solutions, the solubilities can be predicted by adding binary interaction parameters θ_{ij} (the interaction of two identical ions) and ternary interaction parameters Ψ_{ijk} (the interaction between two identical and one different ions) without the need for new parameters, which is of great significance to the studies of multi-component in natural water.

The single salt parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ) and solubility equilibrium constant (K_{sp}) of NaBr, MgBr$_2$ and KBr, and the Debye-Hückel constant A^ϕ at 273.15 K were calculated according to the temperature-dependent equations in the literatures [5,7,28]. The single salt parameters of SrBr$_2$ were reported by Roy et al. [30]. The ionic strength of SrBr$_2$ reported was extended to 3 mol/kg, so the single salt parameters of SrBr$_2$ were based on the solubility
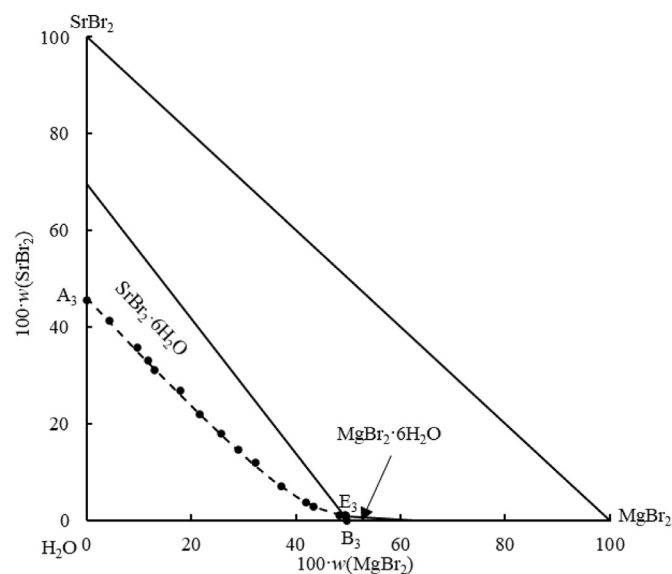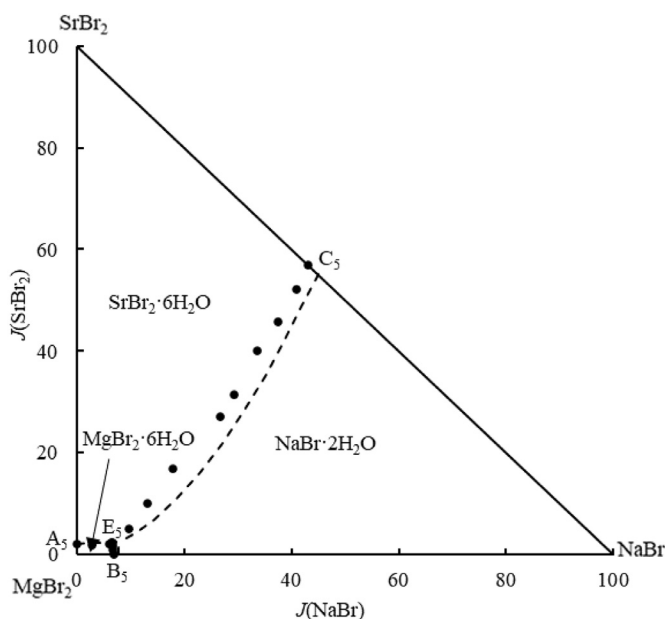

Fig. 15. Calculated and experimental phase diagram of the ternary system MgBr$_2$ + SrBr$_2$ + H$_2$O at 273.15 K, •, experimental result, calculated result.
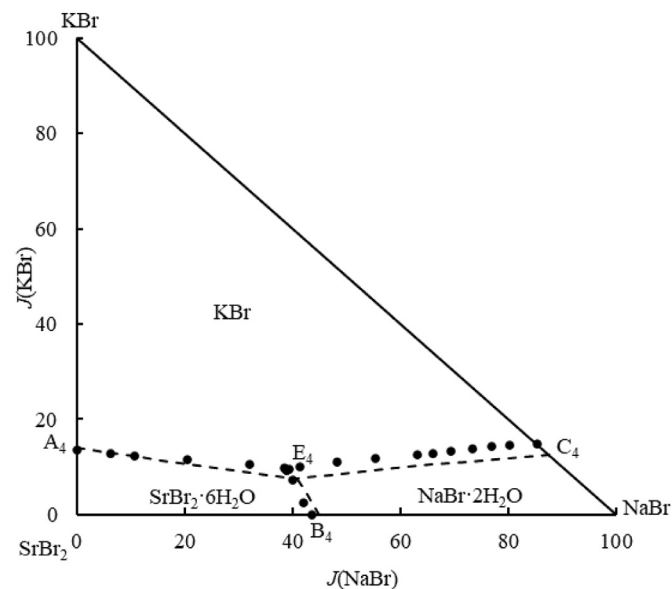
Fig. 16. Calculated and experimental phase diagram of the quaternary system NaBr + KBr + SrBr$_2$ + H$_2$O at 273.15 K, •, experimental result, calculated result.

data extending to 1 mol/kg. Although the concentration range of the fitted parameters is not very high, the parameters obtained can still obtain relatively satisfactory calculation results. It was also extrapolated from unsaturated solution to saturated solution to fit single salt parameters, mixing parameters and to calculate Ksp in the references [22–24], and the Pitzer model equations ap-
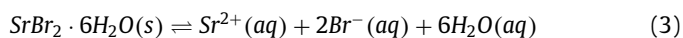
Table 13

Comparisons of calculated and experimental results at the invariant points of the systems studied in this paper at 273.15 K.

Ternary system NaBr + SrBr₂ + H₂O						
Point	Experimental result 100•w(B)		Calculated result 100•w(B)			Equilibrium solid phases
	NaBr	SrBr₂	NaBr	SrBr₂		
E_1	21.12	27.99	22.23	27.19		N2 + S6
Ternary system KBr + SrBr₂ + H₂O						
Point	Experimental result 100•w(B)		Calculated result 100•w(B)			Equilibrium solid phases
	KBr	SrBr₂	KBr	SrBr₂		
E_2	6.57	42.35	6.91	41.90		K + S6
Ternary system MgBr₂ + SrBr₂ + H₂O						
Point	Experimental result 100•w(B)		Calculated result 100•w(B)			Equilibrium solid phases
	MgBr₂	SrBr₂	MgBr₂	SrBr₂		
E_3	49.41	1.05	48.66	1.18		M6 + S6
Quaternary system NaBr + KBr + SrBr₂ + H₂O						
Point	Experimental result 100•w(B)			Calculated result 100•w(B)		Equilibrium solid phases
	NaBr	KBr	SrBr₂	NaBr	KBr	SrBr₂
E_4	20.08	4.83	26.60	20.66	3.89	26.28	N2 + K + S6
Quaternary system NaBr + MgBr₂ + SrBr₂ + H₂O						
Point	Experimental result 100•w(B)			Calculated result 100•w(B)		Equilibrium solid phases
	NaBr	MgBr₂	SrBr₂	NaBr	MgBr₂	SrBr₂
E_5	3.29	46.39	1.14	3.99	45.60	1.25	N2 + M6 + S6

Abbreviations: N2=NaBr•2H₂O, K=KBr, M6=MgBr₂•6H₂O, S6=SrBr₂•6H₂O.

Fig. 17. Calculated and experimental phase diagram of the quaternary system NaBr + MgBr₂ + SrBr₂ + H₂O at 273.15 K, •, experimental result, calculated result.

pear to yield accurate predictions of properties of mixed aqueous electrolytes. Their approach has been adopted by many workers and has been successfully applied to a broad range of geochemical systems, which give good agreement with the high concentration solubility data. According to solubility data and thermodynamic model, the solubility equilibrium constant of strontium bromide hexahydrate is expressed as follows:

$$SrBr_2 \cdot 6H_2O(s) \rightleftharpoons Sr^{2+}(aq) + 2Br^-(aq) + 6H_2O(aq) \quad (3)$$

$$lnK_{sp} = ln(m_{Sr} \cdot \gamma_{Sr}) + 2ln(m_{Br} \cdot \gamma_{Br}) + 6lna_w = lnm_{Sr}$$
$$+ 2lnm_{Br} + ln\gamma_{Sr} + 2ln\gamma_{Br} + 6lna_w \quad (4)$$

In the equation, the activity coefficient (γ_{Sr} and γ_{Br}) and water activity (a_w) can be obtained based on the Pitzer ionic interaction model. Then the solubility equilibrium constant of strontium

bromide hexahydrate can be obtained using the m(sat)=3.4487 mol/kg of binary system SrBr₂ + H₂O. The mixing ion-interaction parameters $\theta_{Na, K}$, $\theta_{Na, Mg}$, $\theta_{Na, Sr}$, $\theta_{K, Sr}$, $\Psi_{Na, Mg, Br}$ and $\Psi_{Na, K, Br}$ were from the literatures [5,9,28,31]. While other mixing ion-interaction parameters $\theta_{Mg, Sr}$, $\Psi_{Mg, Sr, Br}$, $\Psi_{Na, Sr, Br}$ and $\Psi_{K, Sr, Br}$ have not been reported in the literatures, so they were obtained by fitting solubility data of the ternary systems MgBr₂ + SrBr₂ + H₂O, NaBr + SrBr₂ + H₂O and KBr + SrBr₂ + H₂O. All the related parameters are listed in Tables 10–12.

4.2. Calculated solubility

With all the required Pitzer parameters, the solubilities of three ternary systems (NaBr + SrBr₂ + H₂O, KBr + SrBr₂ + H₂O and MgBr₂ + SrBr₂ + H₂O) and two quaternary systems (NaBr + KBr + SrBr₂ + H₂O and NaBr + MgBr₂ + SrBr₂ + H₂O) were predicted. The unit used in the calculation is molality, which is the amount of solute contained in each kilogram of water. And then molality was converted to mass fraction and the Jänecke index. To compare the calculated and experimental values, the calculated and experimental results at the invariant point of each system are shown in Table 13. At the same time, the comparisons of phase diagrams between the calculated and experimental values at 273.15 K were drawn in Figs. 13–17. The results show that the calculated values are in accordance with the experimental data, and the applicability of the parameters fitted in this paper is verified.

5. Conclusions

Because of the occurrence of various mineral elements in underground brine in Sichuan Basin of China and to rationally develop and utilize the bromine brine resources, the phase equilibria of the quaternary systems NaBr + KBr + SrBr₂ + H₂O, NaBr + MgBr₂ + SrBr₂ + H₂O and their subsystems at 273.15 K were studied in this work. The solubilities of salts in every system were measured, and the respective diagram was constructed. The conclusions are summarized below.

The phase diagrams of five systems all belong to hydrate type I, and there is one invariant point in them. Three ternary systems NaBr + SrBr₂ + H₂O, KBr + SrBr₂ + H₂O and MgBr₂ + SrBr₂ + H₂O contain two isothermal solubility curves and two crystallization fields. And there are three isothermal solubility curves and three crystallization fields in two quaternary systems NaBr + KBr + SrBr₂ + H₂O and NaBr + MgBr₂ + SrBr₂ + H₂O.

Based on the experimental solubility data of three ternary systems, the unreported mixing ion-interaction parameters ($\theta_{Mg, Sr}$, $\Psi_{Mg, Sr, Br}$ $\Psi_{Na, Sr, Br}$ and $\Psi_{K, Sr, Br}$) were fitted. The Pitzer ionic interaction model and the corresponding required parameters were employed to calculate the solubilities of five systems studied in this work, and the comparisons of phase diagrams between the calculated and experimental values were drawn. The calculated values are in accordance with the experimental data, which verify the reliability of the parameters.

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Declaration of Competing Interest

None.

CRediT authorship contribution statement

Yun-Yun Gao: Investigation, Data curation, Formal analysis, Writing - original draft. **Xiao-Yun Qi:** Resources, Software. **Shi-Hua Sang:** Funding acquisition, Project administration, Validation, Writing - review & editing. **Chao Ye:** Supervision, Validation. **Lan-Rong Zhao:** Methodology, Visualization.

Acknowledgments

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