

Measurements and calculations of solid-liquid equilibria in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at (298 and 323) K

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ABSTRACT

Through using the isothermal dissolution equilibrium method, phase equilibria in the quaternary system KBr–CaBr₂–MgBr₂–H₂O were studied at (298 and 323) K. Based on the experimental data, the phase diagrams were obtained. It can be seen that two phase diagrams all contain complex salts. In quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K, there are two invariant points, five univariant curves, and four crystallization fields, corresponding to KBr, CaBr₂·6H₂O, MgBr₂·6H₂O and KBr·MgBr₂·6H₂O. At 323 K, a new double salt 2MgBr₂·CaBr₂·12H₂O could be found in this quaternary system. As a result, it has three invariant points, seven univariant curves, and five crystallization regions fields, corresponding to KBr, CaBr₂·4H₂O, MgBr₂·6H₂O, KBr·MgBr₂·6H₂O and 2MgBr₂·CaBr₂·12H₂O. Moreover, the phase diagrams for the quaternary system do not consist new precipitated solids at 298 K and 323 K in comparison with the phase diagrams for ternary subsystems. Using Pitzer theoretical and mathematical calculation tool, the solubilities of the quaternary system were calculated under the condition of (298 and 323) K. And make a comparison with the experimental data. It shows that the calculation results are in good agreement with experimental values.

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1. Introduction

Development of underground brine and Salt Lake resources will offer rich and required mineral resources [1]. There are abundant underground brine resources in Western Sichuan Basin of China. Compared with salt lake system in the Tibetan Plateau and seawater system, the chemical component in Sichuan Basin's underground brine is also rich in various useful components of boron, strontium, potassium, bromine, lithium and iodine in addition to the high concentration common elements of sodium chloride and calcium chloride [2,3].

Potassium salt is mainly used to manufacture potash fertilizer which is one of indispensable three fertilizers in agriculture. At present, the potash fertilizer used in China is severely insufficient, mainly depending on import. Potassium salt has been listed as one of nation's critical needed mineral species. It is necessary to exploit and develop potassium resources. The potassium content in multilayer underground brine is most between 7.18 and

25.95 g dm^{−3}, average in 18.86 g dm^{−3}, with the highest potassium contents reaching at 53.27 g dm^{−3} [2]. It is important liquid potassium resources in China.

Bromine is a rare element with strong dispersion with the wide application in industry field. It has no independent mineral in nature. Currently, the bromine in industry mainly comes from underground brine. The concentration of bromine in underground brine of Sichuan Basin is generally high. According to related study documents, the content of bromine in brine generally can reach above 300 g m^{−3} averagely (production-grade of separate exploiting). Its content is generally 1500–2000 g m^{−3} in the lower-middle Triassic brine, with the highest reaching 2533–2640 g m^{−3}, which is 8.4–8.8 times of separate exploiting production-grade [3]. It demonstrates that the underground brine resource in Sichuan Basin is important liquid mineral resources.

The phase diagram is used as a basis for describing the salting-out and mineralization regularity of brine. The graphical representation represents the relationship between phase equilibrium and thermodynamic variables of a material system. It is an important theoretical basis for chemical chemistry, materials science, metallurgy, petrology, mineralogy, ore deposit, geochemistry and other disciplines. Salt lake brine and underground brine are

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naturally occurred water, which is involved in salt co-exist in the multi-component complex system. The dissolution of salts and its solid-liquid phase equilibrium in the thermodynamics process from the aqueous solution is the study foundation of natural brine and salt mineral deposits. Consequently, the results of the phase equilibrium study of brine system can predict the crystallization of salt minerals and the symbiosis of minerals, demonstrating the evolution of brine, the formation of salt minerals, the brine elements and salt in the geochemical balance of minerals. Besides, it is also the basis for the comprehensive application of brine [4].

Regarding electrolyte solution model, Pitzer K.S [5,6], published a series of papers about electrolyte solution, and came up with a set of semi-empirical theory of statistical mechanics. It can be successfully applied to high concentrations of electrolyte solution. In recent decades, a number of theoretical studies on salt minerals and brine system have been carried out. Aiming at the seawater system, Harvie et al. carried out a series of research and extended the Pitzer ion-interaction model to Harvie–Weare (H–W) model in the prediction for the Na–K–Mg–Ca–H–Cl–SO₄–OH–HCO₃–CO₃–CO₂–H₂O system at 25 °C [7–9]. To increase the applicability to a number of diverse geochemical systems at higher or lower temperatures, additional work has focused on developing variable temperature models. Then, for the H–Na–K–Ca–OH–Cl–HSO₄–SO₄–H₂O system, model is valid from low to high concentration and from 0 to 250 °C [10–13]. In terms of natural waters Na–K–Ca–Mg–Cl–H₂O system, the model of Spenser et al. is valid for temperatures below 25 °C [14]. For the calcium and magnesium system, Christov also developed a thermodynamic model for the H–Mg–Ca–Cl–H₂O system at the T-variation from 0 to 100 °C [15,16]. For the bromide-bearing brine system, Christov and co-workers develop a well validated and fully consistent model for Li–Na–K–NH₄–Rb–Cs–Mg–Ca–Cl–Br–H₂O system at standard temperature [17–26]. Recently, Christov have conducted a series of research work for bromide-rich brine system Na–K–Mg–Ca–Br–SO₄–H₂O [27–32].

In order to reveal the interaction mechanism between the water and salt about the mineral in the process of thermodynamic phase equilibrium, the study of phase equilibrium and phase diagram for the underground brine system in Sichuan Basin is of much significance. Targeting at its components, the brine system is a multi-component system of Na–K–Ca–Mg–Sr–Li–Cl–B₄O₇–Br–SO₄–I–H₂O. According to the constituent content in brine, it can be simplified into seven-element multi-component system of Na–K–Ca–Mg–Sr–Cl–Br–H₂O. Ternary system KBr–K₂B₄O₇–H₂O 298 K, 323 K, 348 K, and 373 K [33–36], quaternary systems NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O, KCl–K₂SO₄–K₂B₄O₇–H₂O and NaBr–KBr–CaBr₂–H₂O at 298 K [37–40], and quinary system Na⁺, K⁺/Cl[–], Br[–], SO₄^{2–}–H₂O at 373 K [41] of the multi-component system in Sichuan Basin have been carried out in a systematic research program by our group. The quaternary system KBr–CaBr₂–MgBr₂–H₂O is one subsystem of the brine-salt system in Western Sichuan Basin and this paper continues our series concerning the quaternary system at (298 and 323) K.

2. Experimental

2.1. Reagents and instruments

An HZS-H type thermostated vibrator with a precision ±0.1 K (Harbin DongLian electronic technology Co., Ltd.) and a standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, the Mettler Toledo Instruments Co., Ltd.) were used for the solid-liquid equilibrium measurements.

Distilled water (pH = 6.60 and conductivity ≤ 1.2 · 10^{–4} S m^{–1} at

indoor temperature) and the Chemical reagents used in experiment are analytic grade and are listed in Table 1.

2.2. Experimental method

The equilibrium experiments in this work were conducted through using isothermal solution saturation method. Another new salt at certain interval on the basis of the ternary subsystems invariant points was added and the prepared solution in the glass bottles with good leakproofness was put. Then, put them in water bath vibrator for continuous vibration until equilibrium, with unchanged chemical composition as the symbol of equilibrium, and keep temperature (298 ± 0.1) K or (323 ± 0.1) K in the process. According to the analysis, the time for equilibrium is about three weeks. Let it stand for 4–6 days after equilibrium, take supernatant, and determine its composition of materials based on chemical analysis method.

2.3. Analytical methods

In this paper, there are four kinds of ions (K⁺, Ca²⁺, Mg²⁺ and Br[–]) whose concentrations need to be measured. K⁺ ion concentration was determined by a sodium tetraphenylborate (STPB) – hexadecyl trimethyl ammonium bromide (CTAB) titration with an indicator of titan yellow (TY). Total quantifies of the Mg²⁺ ion concentration and Ca²⁺ ion concentration were determined by titration with EDTA standard solution with an indicator of Eriochrome Black-T. Then, added sodium hydroxide solution. The Ca²⁺ ion concentration was determined by titration with EDTA standard solution with an indicator of calconcarboxylic acid. The Mg²⁺ ion concentration was determined from the total concentration of Mg²⁺ ion and Ca²⁺ ion and the Ca²⁺ ion concentration. The bromide ion concentration (Br[–]): silver nitrate volumetry with an indicator of potassium chromate.

3. Results and discussion

The Br-bearing quaternary system KBr–CaBr₂–MgBr₂–H₂O consists of three ternary subsystems: (1) KBr–CaBr₂–H₂O, (2) KBr–MgBr₂–H₂O and (3) CaBr₂–MgBr₂–H₂O. The KBr–CaBr₂–H₂O ternary system at 298 K, 323 K and 348 K has been studied [29,42,43]. This ternary system is simple co-saturation type; it consists of only one invariant point, two univariant curves and two crystallization regions at three temperatures. In addition to KBr, another equilibrium solid is calcium bromide hydrates (CaBr₂ · 6H₂O at 298 K, CaBr₂ · 4H₂O at 323 K and CaBr₂ · 2H₂O at 348 K). The corresponding crystallization fields show a regular change at the three temperatures. As temperature increases, the crystallization field of calcium bromide hydrates becomes smaller because of the rapid increase in the solubility of calcium bromide with temperature. At 273 K, 298 K, 323 K and 348 K, the four phase diagrams of ternary system KBr–MgBr₂–H₂O have very similar shapes; the double salt KBr · MgBr₂ · 6H₂O was found, each of them having two invariant points, three univariant curves, and three crystallization regions (corresponding to two single salts KBr, MgBr₂ · 6H₂O and one double salt KBr · MgBr₂ · 6H₂O). In this system, every salt has the same crystallization form at the four temperatures [32,42,44]. In the phase diagrams of the ternary system CaBr₂–MgBr₂–H₂O at 273 K and 298 K, neither double salt nor solid solution was found. The saturated salts in the two crystallization fields are CaBr₂ · 6H₂O and MgBr₂ · 6H₂O [42]. At 323 K and 348 K, the double salt 2MgBr₂ · CaBr₂ · 12H₂O was found. The two phase diagrams all have two invariant points, three univariant curves and three crystallization fields. The solid phases in three crystallization fields are 2MgBr₂ · CaBr₂ · 12H₂O, MgBr₂ · 6H₂O, and CaBr₂ · 4H₂O at 323 K, and

Table 1
Chemical sample specifications.

Chemical name	source	Initial mass fraction purity	Purification method	Analysis method
KBr	Chengdu KeLong Chemical Reagent Factory	0.99	None	Titration
MgBr ₂ ·6H ₂ O	Tianjin guangfu Fine Chemical Research Institute	0.99	None	Titration
CaBr ₂ ·6H ₂ O	Tianjin guangfu Fine Chemical Research Institute	0.99	None	Titration

those at 348 K are 2MgBr₂·CaBr₂·12H₂O, MgBr₂·6H₂O, and CaBr₂·2H₂O [42,45].

3.1. The KBr–CaBr₂–MgBr₂–H₂O system at 298 K

The experimental results of solubilities and equilibrium solids of the equilibrated solution in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K are shown in Table 2. On the basis of Jänecke index values ($J(\text{KBr}) + J(\text{CaBr}_2) + J(\text{MgBr}_2) = 100$ g), the phase diagram was constructed, and is shown in Fig. 1. The respective ion Jänecke dry-salt indices $J(\text{KBr})$, $J(\text{CaBr}_2)$, $J(\text{MgBr}_2)$ and $J(\text{H}_2\text{O})$ were calculated as follows:

$$J(\text{B}) = 100 \frac{w(\text{B})}{ws}$$

$$J(\text{H}_2\text{O}) = 100 \frac{w(\text{H}_2\text{O})}{ws}$$

$$ws = w(\text{KBr}) + w(\text{CaBr}_2) + w(\text{MgBr}_2)$$

where subscript “S” means “salts”, and component B can be KBr, MgBr₂ or CaBr₂.

It is seen from Table 2 and Fig. 1 that the phase diagram of the quaternary system consists of two invariant points, five univariant

curves, and four regions of crystallization.

Points A1 and B1 are the invariant points of ternary subsystem KBr–MgBr₂–H₂O at 298 K; A1 is saturated with MgBr₂·6H₂O and KBr·MgBr₂·6H₂O [$w(\text{KBr}) = 0.0025$, $w(\text{MgBr}_2) = 0.5018$], and B1 is saturated with KBr and KBr·MgBr₂·6H₂O [$w(\text{KBr}) = 0.0330$, $w(\text{MgBr}_2) = 0.4285$]. Points C1 is the invariant point of ternary subsystem CaBr₂–MgBr₂–H₂O at 298 K, which is saturated with CaBr₂·6H₂O and MgBr₂·6H₂O [$w(\text{CaBr}_2) = 0.5571$, $w(\text{MgBr}_2) = 0.0496$]. Point D1 is the invariant point of the ternary subsystem KBr–CaBr₂–H₂O of this quaternary system at 298 K, which is saturated with KBr and CaBr₂·6H₂O [$w(\text{KBr}) = 0.0081$, $w(\text{CaBr}_2) = 0.5914$]. It showed that the equilibrium solids and liquid compositions of each invariant point in ternary subsystems are consistent with reference experimental data at 298 K [42].

The four crystallization regions correspond to three single salts KBr, CaBr₂·6H₂O, MgBr₂·6H₂O and one double salt KBr·MgBr₂·6H₂O. The crystallization region of CaBr₂·6H₂O is the smallest, it indicates that the CaBr₂·6H₂O is more difficult crystallize than the other salts from solution at 298 K. Five univariant curves are A1E1, C1E1, D1F1, B1F1 and E1F1, and two invariant points in this system are named as E1 and F1. Point E1 is saturated with salts MgBr₂·6H₂O + KBr·MgBr₂·6H₂O + CaBr₂·6H₂O, and the mass fraction composition of the corresponding liquid phase is $w(\text{KBr}) = 0.0014$, $w(\text{CaBr}_2) = 0.5521$, $w(\text{MgBr}_2) = 0.0473$. Point F1 is saturated with salts KBr + KBr·MgBr₂·6H₂O + CaBr₂·6H₂O, and the

Table 2
Solubilities of solution in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K and 0.09477 MPa.

No.	Composition of solution $w(\text{B}) \times 100$			Jänecke index $J/(\text{g}/100 \text{ g})$				Equilibrium solids
				$J(\text{KBr})+J(\text{CaBr}_2)+J(\text{MgBr}_2) = 100 \text{ g}$				
	$w(\text{KBr})$	$w(\text{CaBr}_2)$	$w(\text{MgBr}_2)$	$J(\text{KBr})$	$J(\text{CaBr}_2)$	$J(\text{MgBr}_2)$	$J(\text{H}_2\text{O})$	
1, B1	3.30	0.00	42.85	7.14	0.00	92.86	116.71	KB + KMB
2	3.22	3.63	41.23	6.69	7.55	85.76	108.00	KB + KMB
3	3.15	10.52	37.74	6.13	20.46	73.41	94.49	KB + KMB
4	2.71	24.86	26.66	4.99	45.85	49.17	84.40	KB + KMB
5	2.17	39.58	15.97	3.76	68.57	27.67	73.25	KB + KMB
6	1.20	52.56	5.58	2.03	88.57	9.40	68.52	KB + KMB
7, F1	0.61	56.05	4.66	0.99	91.41	7.61	63.08	KB + KMB + CB6
8, A1	0.25	0.00	50.18	0.49	0.00	99.51	98.30	MB + KMB
9	0.23	2.31	49.06	0.45	4.48	95.08	93.79	MB + KMB
10	0.23	4.46	48.69	0.43	8.35	91.22	87.35	MB + KMB
11	0.22	12.76	41.99	0.40	23.21	76.39	81.92	MB + KMB
12	0.22	17.66	37.25	0.40	32.03	67.57	81.42	MB + KMB
13	0.20	28.77	27.92	0.36	50.57	49.07	75.77	MB + KMB
14	0.18	33.40	22.57	0.32	59.48	40.20	78.10	MB + KMB
15	0.18	40.23	16.71	0.32	70.42	29.26	75.06	MB + KMB
16	0.15	48.97	9.41	0.25	83.68	16.07	70.88	MB + KMB
17, E1	0.14	55.21	4.73	0.24	91.89	7.87	66.44	MB + KMB + CB6
18, D1	0.81	59.14	0.00	1.35	98.65	0.00	66.80	KB + CB6
19	0.79	58.93	0.58	1.32	97.72	0.96	65.83	KB + CB6
20	0.76	58.05	0.99	1.27	97.06	1.66	67.22	KB + CB6
21	0.72	57.80	2.63	1.18	94.52	4.30	63.53	KB + CB6
22	0.68	57.19	4.52	1.08	91.67	7.24	60.29	KB + CB6
23, C1	0.00	55.71	4.96	0.00	91.82	8.18	64.82	CB6 + MB
24	0.09	55.58	4.82	0.15	91.88	7.97	65.33	CB6 + MB
25	0.28	55.52	4.77	0.46	91.66	7.88	65.08	CB6 + KMB
26	0.45	55.37	4.68	0.74	91.52	7.74	65.28	CB6 + KMB

Abbreviations: KB = KBr, CB6 = CaBr₂·6H₂O, MB = MgBr₂·6H₂O, KMB = KBr·MgBr₂·6H₂O.

Standard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(K^+) = 0.005$, $u(\text{Ca}^{2+}) = 0.003$, $u(\text{Mg}^{2+}) = 0.005$, $u(\text{Br}^-) = 0.003$.

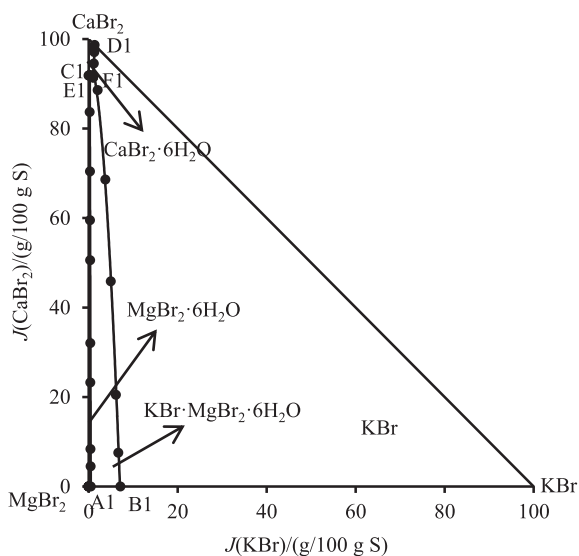


Fig. 1. Equilibrium phase diagram and partial enlarged diagram of the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K.

mass fraction composition of the corresponding liquid phase is $w(\text{KBr}) = 0.0061$, $w(\text{CaBr}_2) = 0.5605$, $w(\text{MgBr}_2) = 0.0466$.

Fig. 2 presents the water content diagram of this quaternary system at 298 K showing that Jänecke index of water of the quaternary system is changed regularly by the content change of potassium bromide. It reaches the maximum value at the point B1 and gets to the minimum value at the point F1.

3.2. The KBr–CaBr₂–MgBr₂–H₂O system at 323 K

The experimental solubilities and equilibrium solids of quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K are shown in Table 3. Using the Jänecke index values ($J(\text{KBr}) + J(\text{CaBr}_2) + J(\text{MgBr}_2) = 100$ g), the phase equilibrium diagram of the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K was plotted in Fig. 3. It is seen from Table 3 and Fig. 3 that the phase diagram of the quaternary system consists of three invariant points,

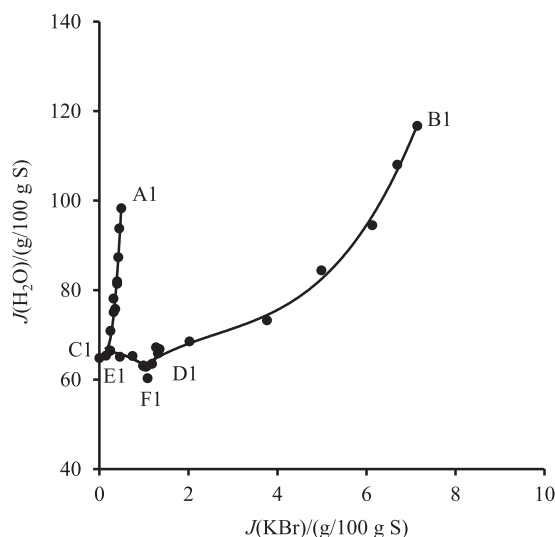


Fig. 2. Water contents of saturated solutions in quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K.

seven univariant curves, and five crystallization regions fields. No solid solution is found in this system. In addition to three simple salts KBr, CaBr₂·4H₂O, MgBr₂·6H₂O and one complex salt KBr·MgBr₂·6H₂O, the complex salt 2MgBr₂·CaBr₂·12H₂O also crystallizes from the saturated solutions. The crystallization region of calcium bromide tetrahydrate is the smallest, it indicates that it is more difficult to crystallize than the other salts from solution at 323 K.

Points A2 and B2 are the two invariant points of the ternary subsystems KBr–MgBr₂–H₂O of this quaternary system at 323 K. At point A2 [$w(\text{KBr}) = 0.0080$, $w(\text{MgBr}_2) = 0.5180$], the solution is saturated with single salt MgBr₂·6H₂O and double salt KBr·MgBr₂·6H₂O. At point B2 [$w(\text{KBr}) = 0.0488$, $w(\text{MgBr}_2) = 0.4433$], the solution is saturated with single salt KBr and double salt KBr·MgBr₂·6H₂O. Points C2 and J2 are the two invariant points of the ternary subsystems CaBr₂–MgBr₂–H₂O at 323 K. At point C2 [$w(\text{CaBr}_2) = 0.6923$, $w(\text{MgBr}_2) = 0.0193$], the solution is saturated with single salt CaBr₂·4H₂O and double salt 2MgBr₂·CaBr₂·12H₂O. At point J2 [$w(\text{CaBr}_2) = 0.5351$, $w(\text{MgBr}_2) = 0.1201$], the solution is saturated with single salt MgBr₂·6H₂O and double salt 2MgBr₂·CaBr₂·12H₂O. Points D2 are the invariant point of the ternary subsystems KBr–CaBr₂–H₂O of this quaternary system at 323 K. At point A2 [$w(\text{KBr}) = 0.0065$, $w(\text{CaBr}_2) = 0.7049$], the solution is saturated with two single salts CaBr₂·4H₂O and KBr. For each invariant point of ternary subsystems, the corresponding equilibrium solids have a good agreement with reference values, and the experimental data on the liquid composition is also basically in line with the experimental results reported in literatures.

Seven univariant curves are A2K2, J2K2, K2E2, B2E2, E2F2, D2F2, C2F2, and three invariant points in this system are named as E2, F2 and J2.

Point E2 is saturated with salts 2MgBr₂·CaBr₂·12H₂O + KBr·MgBr₂·6H₂O + KBr, and the mass fraction composition of the corresponding liquid phase is $w(\text{KBr}) = 0.0049$, $w(\text{CaBr}_2) = 0.6185$, $w(\text{MgBr}_2) = 0.0716$.

Point F2 is saturated with salts 2MgBr₂·CaBr₂·12H₂O + KBr + CaBr₂·4H₂O, and the mass fraction composition of the corresponding liquid phase is $w(\text{KBr}) = 0.0052$, $w(\text{CaBr}_2) = 0.6339$, $w(\text{MgBr}_2) = 0.0326$.

Point K2 is saturated with salts 2MgBr₂·CaBr₂·12H₂O + KBr·MgBr₂·6H₂O + MgBr₂·6H₂O, and the

Table 3
Solubilities of solution in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K and 0.09477 MPa.

No.	Composition of solution w(B) × 100			Jänecke index J/(g/100 g)				Equilibrium solids
				J(KBr)+J(CaBr ₂)+J(MgBr ₂) = 100 g				
	w(KBr)	w(CaBr ₂)	w(MgBr ₂)	J(KBr)	J(CaBr ₂)	J(MgBr ₂)	J(H ₂ O)	
1, B2	4.88	0.00	44.33	9.91	0.00	90.09	103.22	KB + KMB
2	4.65	8.64	37.36	9.19	17.07	73.75	97.41	KB + KMB
3	4.07	20.40	29.20	7.59	38.01	54.40	86.31	KB + KMB
4	3.62	28.61	23.81	6.46	51.05	42.48	78.45	KB + KMB
5	2.92	37.39	17.70	5.04	64.45	30.51	72.37	KB + KMB
6	1.89	51.37	12.18	2.89	78.50	18.61	52.82	KB + KMB
7	1.15	57.94	9.22	1.69	84.82	13.50	46.38	KB + KMB
8, E2	0.49	61.85	7.16	0.70	88.99	10.30	43.89	KB + KMB + MCB
9, A2	0.80	0.00	51.80	1.53	0.00	98.47	90.09	MB + KMB
10	0.73	4.03	48.57	1.37	7.55	91.07	87.50	MB + KMB
11	0.60	11.50	41.90	1.11	21.29	77.60	85.20	MB + KMB
12	0.39	27.51	27.93	0.70	49.27	50.03	79.11	MB + KMB
13	0.26	37.23	20.20	0.45	64.53	35.02	73.34	MB + KMB
14, K2	0.17	53.40	12.29	0.26	81.08	18.66	51.83	MB + KMB + MCB
15	0.37	58.61	9.50	0.54	85.59	13.87	46.02	KMB + MCB
16, C2	0.00	69.23	1.93	0.00	97.29	2.71	40.52	CB4 + MCB
17	0.24	65.65	2.45	0.36	96.05	3.59	46.31	CB4 + MCB
18, F2	0.52	63.39	3.26	0.77	94.37	4.86	48.87	CB4 + MCB + KB
19, D2	0.65	70.49	0.00	0.91	99.09	0.00	40.57	KB + CB4
20	0.59	67.64	2.05	0.84	96.25	2.91	42.29	KB + CB4
21, J2	0.00	53.51	12.01	0.00	81.67	18.33	52.61	MB + MCB

Abbreviations: KB = KBr, CB4 = CaBr₂·4H₂O, MB = MgBr₂·6H₂O, KMB = KBr·MgBr₂·6H₂O, MCB = 2MgBr₂·CaBr₂·12H₂O. Standard uncertainties u are u(T) = 0.1 K, u(K⁺) = 0.005, u(Ca²⁺) = 0.003, u(Mg²⁺) = 0.005, u(Br[−]) = 0.003.

mass fraction composition of the corresponding liquid phase is w(KBr) = 0.0017, w(CaBr₂) = 0.5340, w(MgBr₂) = 0.1229.

The water content diagram of the quaternary system at 323 K is constructed in Fig. 4, which demonstrates that the water content increases regularly with an increase of the Jänecke index values of J(KBr) at univariant curves K2 A2, E2B2, and researches the maximum value at the point B2.

Compared with the two phase diagrams at different temperatures (298 K and 323 K), the result shows that the two phase diagrams have similar shapes and the shape of each crystallization region is almost identical. The crystallization region of KBr is all largest while other crystallization regions are very narrow. In addition, it also indicates that the solubility of KBr is the lowest among the salts. The double salt all forms and no solid solution forms in the quaternary system at two different temperatures. However, the numbers of invariant points, crystallization fields, and univariant curves are different. The phase diagram at 298 K includes two invariant points, five univariant curves, and four regions of crystallization (three single salts KBr, CaBr₂·6H₂O, MgBr₂·6H₂O and one double salt KBr·MgBr₂·6H₂O). At 323 K, the double salt 2MgBr₂·CaBr₂·12H₂O has been formed. Besides, the phase diagram contains three invariant points, seven univariant curves, and five crystallization regions fields (three simple salts KBr, CaBr₂·4H₂O, MgBr₂·6H₂O, two double salts KBr·MgBr₂·6H₂O and 2MgBr₂·CaBr₂·12H₂O). For calcium bromide hydrates, the number of crystal water is six at 298 K, which becomes four at 323 K.

4. Prediction of solubility

The mixing ion-interaction parameters of $\psi_{K,Ca,Cl}$, $\psi_{K,Mg,Cl}$ and $\psi_{Ca,Mg,Cl}$ at 298 K and 323 K are evaluated based on experimental values in ternary systems KCl–CaCl₂–H₂O, KCl–MgCl₂–H₂O and CaCl₂–MgCl₂–H₂O [13,15,18,20]. Through using the equilibrium solubilities data of ternary subsystems KBr–CaBr₂–H₂O, KBr–MgBr₂–H₂O and CaBr₂–MgBr₂–H₂O at (273.15–323.15) K [29,32,42], the mixing ion-interaction parameters of $\psi_{K,Ca,Br}$, $\psi_{K,Mg,Br}$ and $\psi_{Ca,Mg,Br}$ at corresponding temperature were acquired.

In this paper, all required binary parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ), mixing ion-interaction parameters (θ_{ij} and Ψ_{ijk}), and solubility product values ($\ln K_{sp}$) for all sub-systems are taken from the previously published in literatures [11,13,15,18,28,29,32], adapted here to 298 K and 323 K conditions (see Tables 4–6). The solubilities of the three ternary systems have been calculated at different temperature in literatures [28,29,32], and the calculated results were in accordance with the experimental data showing that the parameters are reasonable and reliable.

The fundamental Pitzer equations are described and widely discussed in relevant literatures [7–9,17–26]. It is able to calculate solubility data after obtaining parameters. Heavy molar concentration is used for Pitzer equation calculation. The heavy molar concentration is defined as the molar percent of solutes in 1 kg solvent water. When processing computing phase equilibrium solubility data of solution with Pitzer electrolyte solution theory model, it needs to solve nonlinear multivariable equations.

Particle Swarm Optimization (PSO) algorithm was adopted in this paper. For the calculation of invariant point, it only needs to establish phase equilibrium state at the point and corresponding target equation. When it comes to univariate curve, change the size of certain ions with isometry to determine the change data of other ions and then obtain the required univariate curve. On the basis of the Pitzer equations and the H-W equations [5–9], the solubility data in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at (298 and 323) K were calculated using Particle Swarm Optimization (PSO) algorithm. Comparison between the calculated results and the experimental data of boundary points and invariant points can be found in Tables 7 and 8. According to the experimental and calculated solubilities, the comparison phase diagrams of the quaternary system at (298 and 323) K were plotted and are given in Figs. 5 and 6 showing that the theoretical value is consistent to experimental value. With the theoretical model to conduct the theoretical simulation calculation of phase equilibrium, it can not only verify the experimental data, but also complement and perfect the experimental data.

Phase equilibrium theory calculation results show that

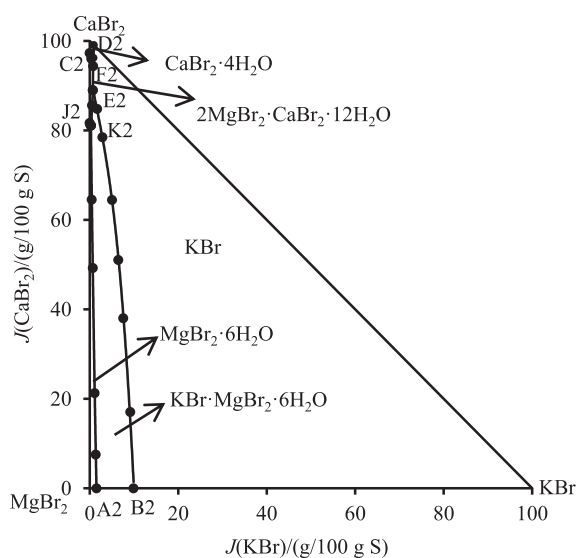


Fig. 3. Equilibrium phase diagram and partial enlarged diagram of the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K.

theoretical calculation data are close to the experimental data and the theoretical phase diagram is basically coincided with the experimental phase diagram, indicating that Pitzer theory model is suitable for theory calculation of phase equilibrium solubility of the quaternary system. The error in the process of prediction is mainly embodied in the following aspects:

- (1) Parameters fitting of Pitzer equation generally adopt activity coefficient and osmotic coefficient fitting with high precision, and less solubility data are used. Activity coefficient and osmotic coefficient data more accurately describe the non-ideality of electrolyte solution. In this paper, the all used parameters have been published in literatures. Some parameters containing bromide were obtained from osmotic coefficients and solubility data of ternary subsystems. Regarding some ternary subsystems, there are only solubility

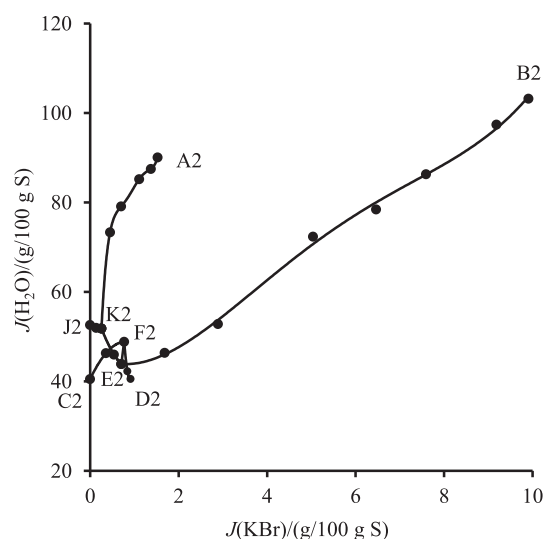


Fig. 4. Water contents of saturated solutions in quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K.

data and lack of the data of activity coefficient or osmotic coefficient. In this paper, although the fitting parameters, to a certain extent, can meet the theoretical calculation of solubility, its precision is a process of gradual improvement.

- (2) The quaternary system in this paper are composed of complex high component and high concentration, with strong non-ideality, which thus increases the difficulty of theoretical simulation, showing no high precision of simulation.
- (3) Programming realizes the error caused by the mathematical method which is used in computer calculation. As the principle used for realizing computer calculation is numerical calculation, the objective function value is the optimal value, and such calculation process will lead to errors.

5. Conclusions

The isothermal dissolution equilibrium method has been used to investigate the solid-liquid equilibria of quaternary system KBr–CaBr₂–MgBr₂–H₂O at (298 and 323) K. Through using the reported parameters and relevant model, the solubility data in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at (298 and 323) K were calculated.

Three ternary subsystems KBr–CaBr₂–H₂O, KBr–MgBr₂–H₂O and CaBr₂–MgBr₂–H₂O of the quaternary system have been studied at (298 and 323) K. The KBr–CaBr₂–H₂O ternary system at 298 K, 323 K and 348 K has been investigated [29,32,42]. According to the phase diagrams for three ternary subsystems [28,29,32], the KBr–CaBr₂–H₂O and CaBr₂–MgBr₂–H₂O systems at 298 K all belong to simple co-saturation type, and only one invariant point, two univariant curves and two crystallization regions in each system. The equilibrium solid phases in the ternary system KBr–CaBr₂–H₂O are KBr and CaBr₂·6H₂O, and those in the ternary system CaBr₂–MgBr₂–H₂O are CaBr₂·6H₂O and MgBr₂·6H₂O. In these phase diagram of the ternary system KBr–MgBr₂–H₂O at 298 K, there are two invariant points, three univariant curves and three regions of crystallization corresponding to KBr, MgBr₂·6H₂O and KBr·MgBr₂·6H₂O.

Table 4

Single-salt parameters in the solution of the quaternary system in this paper at (298 and 323) K.

salt	$\beta^{(0)}$		$\beta^{(1)}$		C^ϕ		Reference source
	298 K	323 K	298 K	323 K	298 K	323 K	
KBr	0.0518449	0.0746	0.2767664	0.2798	−0.000868	−0.0034	[27]
MgBr ₂	0.434520	0.462569	1.734634	1.534848	0.002684	−0.001301	[29]
CaBr ₂	0.3357135	0.3623529	2.9061559	2.1884234	0.0089749	0.0015618	[28]

Table 5Values of Debye-Hückel constant (A^ϕ) and mixing ion-interaction parameters in the solution of the quaternary system in this paper at (298 and 323) K.

	$\theta_{K,Ca}$	$\theta_{K,Mg}$	$\theta_{Ca,Mg}$	$\Psi_{K,Mg,Br}$	$\Psi_{Ca,Mg,Br}$	$\Psi_{K,Ca,Br}$	A^ϕ
298 K	0.1156	0	0.007	−0.0245	0.00088	−0.04224	0.3914752
323 K	0.1156	0	0.007	−0.03041	−0.00637	−0.028	0.4333
Reference	[13]	[18,20]	[15]	[29]	[32]	[32]	[11]

Table 6

Solubility product constants of salts of the quaternary system in this paper at (298 and 323) K.

Salt	$\ln K_{sp}$		Reference source
	298 K	323 K	
KBr	2.6271912	3.0893892	[27]
CaBr ₂ ·6H ₂ O	13.19653	—	[28]
CaBr ₂ ·4H ₂ O	—	19.36726	[28]
MgBr ₂ ·6H ₂ O	12.20095	12.49865	[29]
KBr·MgBr ₂ ·6H ₂ O	12.65277	14.04988	[29]
2CaBr ₂ ·MgBr ₂ ·12H ₂ O	73.65897	53.73992	[32]

At the 323 K, in the phase diagrams of ternary systems KBr–MgBr₂–H₂O and CaBr₂–MgBr₂–H₂O, the double salt was found in each system, consisting of three univariant curves, two invariant points and three crystallization regions. In the first

system, the solids are KBr, MgBr₂·6H₂O and KBr·MgBr₂·6H₂O, and in the second system, the solids are CaBr₂·6H₂O, MgBr₂·6H₂O and 2MgBr₂·CaBr₂·12H₂O. The ternary system KBr–CaBr₂–H₂O at 323 K belongs to a simple type and its solubility diagram has only one invariant point, two univariant curves and two crystallization regions (KBr and CaBr₂·4H₂O). In comparison with the ternary subsystems, no solid was found in quaternary system KBr–CaBr₂–MgBr₂–H₂O at two temperatures.

The quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K contained complex salt KBr·MgBr₂·6H₂O, and there was no solid solution formed in the process of experiment. The isothermal phase diagram is consisted of five univariant curves, four fields of crystallization and two invariant points of the quaternary system. The equilibrium solid phases of the four crystallization fields were KBr, CaBr₂·6H₂O, MgBr₂·6H₂O and KBr·MgBr₂·6H₂O. Calculations indicated that simulation calculation values of solubility are well

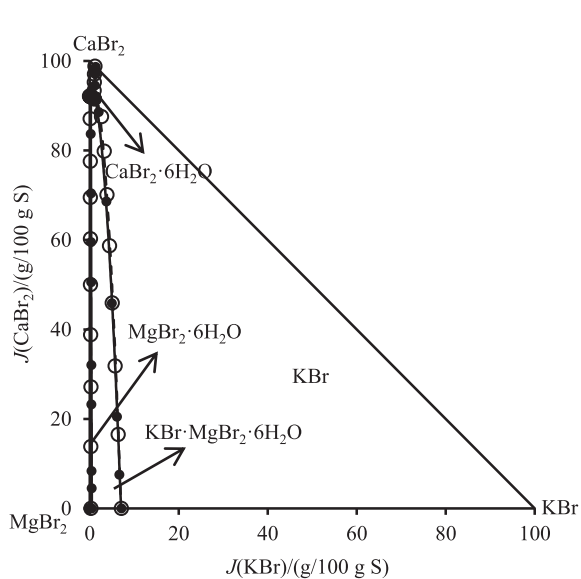
Table 7Calculated and partly experimental solubilities in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K.

	Experimental composition of liquid phase 100·w(B)			Calculated composition of liquid phase 100·w(B)			Relative deviation 100·w(B)	Equilibrium
	w(KBr)	w(CaBr ₂)	w(MgBr ₂)	w(KBr)	w(CaBr ₂)	w(MgBr ₂)		
Point A1	0.25	0.00	50.18	0.15	0.00	50.41	0.46	MB + KMB
Point B1	3.30	0.00	42.85	3.29	0.00	42.67	0.42	KB + KMB
Point C1	0.00	55.71	4.96	0.00	55.69	4.75	4.23	CB6 + MB
Point D1	0.81	59.14	0.00	0.73	59.90	0.00	0.00	KB + CB6
Point E1	0.14	55.21	4.73	0.63	56.22	4.55	3.81	MB + KMB + CB6
Point F1	0.61	56.05	4.66	0.08	55.69	4.74	1.72	KB + KMB + CB6

Abbreviations: KB = KBr, CB6 = CaBr₂·6H₂O, MB = MgBr₂·6H₂O, KMB = KBr·MgBr₂·6H₂O.**Table 8**Calculated and partly experimental solubilities in the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K.

	Experimental composition of liquid phase 100·w(B)			Calculated composition of liquid phase 100·w(B)			Relative deviation 100·w(B)	Equilibrium
	w(KBr)	w(CaBr ₂)	w(MgBr ₂)	w(KBr)	w(CaBr ₂)	w(MgBr ₂)		
Point A2	0.80	0.00	51.80	0.62	0.00	51.84	0.00	MB + KMB
Point B2	4.88	0.00	44.33	4.88	0.00	45.06	0.00	KB + KMB
Point C2	0.00	69.23	1.93	0.00	69.15	1.43	0.12	CB4 + MCB
Point D2	0.65	70.49	0.00	0.40	70.28	0.00	0.30	KB + CB4
Point E2	0.49	61.85	7.16	0.44	68.88	1.44	11.37	KB + KMB + MCB
Point F2	0.52	63.39	3.26	0.38	65.00	3.00	2.54	CB4 + MCB + KB
Point K2	0.17	53.40	12.29	0.11	53.21	12.36	0.36	MB + KMB + MCB
Point J2	0.00	53.51	12.01	0.00	53.28	12.26	0.43	MB + CMB

Abbreviations: KB = KBr, CB4 = CaBr₂·4H₂O, MB = MgBr₂·6H₂O, KMB = KBr·MgBr₂·6H₂O, MCB = 2MgBr₂·CaBr₂·12H₂O.



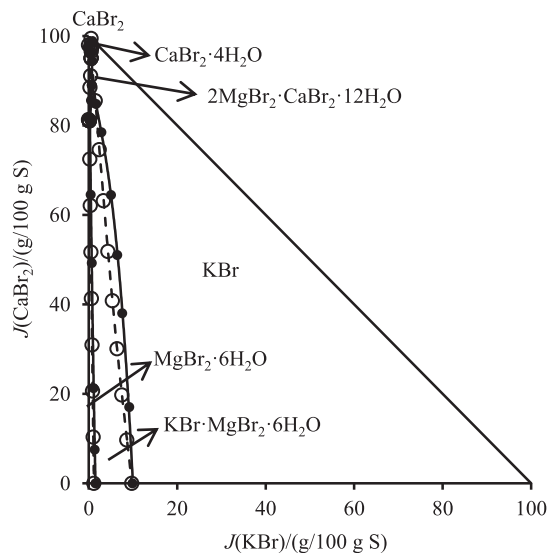
—, experimental isotherm curve; - - -, calculated isotherm curve;

●, experimental data; ○, calculated data

Fig. 5. The experimental and calculated phase diagram of the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 298 K.

coincided with the experimental values.

The quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K has two double salts and no solid solution is found. In the phase diagram, it has three invariant points, seven univariant curves, and five crystallization regions fields corresponding to three salts KBr, CaBr₂·4H₂O, MgBr₂·6H₂O and two double salts KBr·MgBr₂·6H₂O and 2MgBr₂·CaBr₂·12H₂O. Through contrastively analyzing the experimental measurement data with the theoretical calculation data analysis, it indicates the applicability of the proposed algorithm and the reliability of the experimental data.



—, experimental isotherm curve; - - -, calculated isotherm curve;

●, experimental data; ○, calculated data

Fig. 6. The experimental and calculated phase diagram of the quaternary system KBr–CaBr₂–MgBr₂–H₂O at 323 K.

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