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Experimental Study and Theoretical Simulation of Fluid Phase

Equilibrium in the Subsystems of Quinary System

NaBr–KBr–MgBr₂–SrBr₂–H₂O at 298 K

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Abstract: Underground brine known as one of special fluids existing in nature has been regarded as a kind of comprehensive mineral resource. After multi-step separation mining, it can realize the effective extraction and recovery of various mineral resources. Conducting a series of further studies on this kind of natural fluid, especially on the study of fluid phase equilibrium, will be of great significance to explore the rules of its geochemical evolution and formation, and to guide the follow-up fluid mineralization simulation. Based on the above considerations, stable phase equilibria and solubility data of unreported subsystems for quinary system NaBr–KBr–MgBr₂–SrBr₂–H₂O at 298 K were determined by the method of isothermal dissolution equilibrium aiming at the compositions of the underground brine in wetern Sichuan Basin. The research contents in this work include two ternary systems (NaBr–SrBr₂–H₂O, KBr–SrBr₂–H₂O) and three quaternary systems (NaBr–KBr–SrBr₂–H₂O, NaBr–MgBr₂–SrBr₂–H₂O, and KBr–MgBr₂–SrBr₂–H₂O). The phase diagrams of listed above systems were all drawn by experimental data. The experimental results show that there are no solid solutions as well as any complex salts in the three ternary systems. These phase diagrams all contain two solid phase regions of crystallization, two isothermal dissolution curves and only one isothermal-isobaric invariant point. At 298 K, quaternary systems NaBr–KBr–SrBr₂–H₂O belongs to a simple type, and the phase diagram consists of only one isothermal-isobaric invariant point, three isothermal dissolution curves and

three crystallization regions. In the phase diagram of quaternary system $\text{NaBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ at 298 K, there are two isothermal-isobaric invariant points, five isothermal dissolution curves, and four crystallization regions. In the quaternary systems $\text{KBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ at 298 K, it was found that one complex salt ($\text{KBr}\cdot\text{MgBr}_2\cdot 6\text{H}_2\text{O}$) formed and the phase diagram has two isothermal-isobaric invariant points, five isothermal dissolution curves, and four crystallization regions. The solubilities of the above subsystems at 298 K were predicted accurately by referring to Pitzer's electrolyte solution theory. It was found that the predicted results were coincided basically with the experimental data.

Keywords: Underground brine; Phase diagram; Solubility; Strontium; Pitzer model

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1. Introduction

As one of the important geological fluids on the surface and inside of the earth, the study on the physical and chemical properties of brine is of great significance for understanding the geochemical behavior of salt ores and the law of mineral enrichment^[1]. As a natural fluid, brine usually has complex chemical compositions, which is composed of massive dissoluble salts and trace elements, such as alkali metals, alkali-earth metals, halogens, and other salt-forming elements. And underground brine as an important component of the natural brine, its formation and evolution provide a natural research object for brine geochemistry^[2]. Because of the different compositions and contents of underground brine, geologists can study the mineral enrichment rule according to its occurrence state and formation conditions, thus providing an important reference for geological prospecting. Therefore, conducting the comprehensive research on underground brine can not only provide important guidance for the comprehensive development of brine resources, but also provide important theoretical basis for the formation and evolution rule of this type of

brine.

The comprehensive development and utilization of brine resources usually rely on the guidance of multi-temperature phase equilibrium and phase diagram, then using a series of phase separation technologies to realize^[3]. Up to now, researches in phase equilibrium and diagram of complex brine systems have greatly promoted the development of brine resources^[4].

In order to reveal the mechanism of water-salt interactions in underground brine of western Sichuan Basin and to realize the separation and extraction of various useful components, the experimental and theoretical studies of phase equilibrium are necessary. The underground brine in western Sichuan Basin can be described as a multi-component system $\text{Li-Na-K-Sr-Ca-Mg-Cl-Br-SO}_4\text{-B}_4\text{O}_7\text{-H}_2\text{O}$ according to its compositions. During the enrichment process of brine, sodium chloride is precipitated continuously, and the useful components such as strontium, potassium and bromine in the brine are further enriched^[5,6]. So aiming at the compositions of above enriched brine, it is necessary to conduct experimental and theoretical studies of stable phase equilibria of quinary systems $\text{NaBr-KBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ at 298 K. As it is the necessary process for building a prediction model aiming at describing thermodynamic properties of comprehensive brine system. But now, as for phase equilibria studies of strontium bromide-bearing system, only a small amount of literatures have reported such as $\text{NaBr-KBr-SrBr}_2\text{-H}_2\text{O}$, $\text{NaBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ and $\text{KBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ at 323 K^[7,8], so that it can not be effective to bulid a complete multi-temperature and multi-component system containing strontium bromide to guide industrial production and make a further theoretical research.

2. Experimental

The isothermal dissolution equilibrium method was used to determine the solubilities in this work. All the samples were prepared by the chemical reagents and ultrapure water, and the specific chemicals used in this work were given in Table 1. The resistivity of ultrapure water after multiple filtration was greater than 17 $\text{M}\Omega\cdot\text{cm}$.

Another new salt was added in a gradient manner by referring to the

compositions of isothermal-isobaric invariant points of the subsystems. Each sample was placed in a rigid plastic bottle and kept at (298 ± 0.1) K by using a constant temperature water bath oscillator (the HZS-H with an accuracy of 0.1 K) to remain constant. The mixtures in rigid plastic bottles were stirred for over two weeks, and then left standing for about 6~7 days under the conditions of constant temperature. And then the supernatant liquids were taken out periodically to analyze until the concentration of any single ion did not change anymore, indicating the thermodynamic equilibrium was established in the system. After reaching final solid-liquid phase equilibrium, the solid and the liquid phases were taken out for analyzing, respectively. The solid phase compositions were identified by the X-ray diffractometer (DX-2700, China).

The details of analytical methods for each ion could be introduced as follows: (1) Br^- , the silver nitrate capacity method (potassium dichromate as an indicator); (2) K^+ , the sodium tetraphenylboron method (Titan Yellow as an indicator); (3) Mg^{2+} , the EDTA volumetric method (Eriochrome Black T used as an indicator); (4) Sr^{2+} , the EDTA volumetric method (K-B indicator used as an indicator); (5) Na^+ , the ion balance subtraction method. It's worth noting when Mg^{2+} and Sr^{2+} coexisted, sodium hydroxide was initially added to precipitate Mg^{2+} as $\text{Mg}(\text{OH})_2$, and the free Sr^{2+} was titrated as described above. Once the complexation of Sr^{2+} with EDTA was complete, hydrochloric acid (1:1) was added to solubilize the precipitated Mg^{2+} . Using Eriochrome black T as an indicator, free Mg^{2+} was titrated with a standard EDTA solution.

3 Results and Discussions

The quinary system $\text{NaBr-KBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ consists of six ternary subsystems and four quaternary systems. Four ternary systems ($\text{NaBr-KBr-H}_2\text{O}$, $\text{NaBr-MgBr}_2\text{-H}_2\text{O}$, $\text{KBr-MgBr}_2\text{-H}_2\text{O}$ and $\text{MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$) and one quaternary system ($\text{NaBr-KBr-MgBr}_2\text{-H}_2\text{O}$) of these at 298 K have been reported ^[9-11]. A well validated and fully consistent model for these systems was developed and the relevant Pitzer parameters and standard chemical potentials could be taken from the literature ^[12-14]. Among these systems, $\text{NaBr-KBr-H}_2\text{O}$ and $\text{MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ all

belong to the type I hydrate. Their phase diagrams contain only one isothermal-isobaric invariant point, two crystallization regions and two dissolution equilibrium curves. It was found that in addition to two hydrous salts $\text{NaBr} \cdot 2\text{H}_2\text{O}$ and $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, one anhydrous salt NaBr also crystallized from the saturated solutions in ternary system $\text{NaBr}-\text{MgBr}_2-\text{H}_2\text{O}$. In the phase diagrams of $\text{KBr}-\text{MgBr}_2-\text{H}_2\text{O}$ and $\text{NaBr}-\text{KBr}-\text{MgBr}_2-\text{H}_2\text{O}$, the double salt $\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ was found. On the base of the previous research results in the literatures, the relevant unreported subsystems of the quinary system were studied in this paper.

3.1 The ternary system $\text{NaBr}-\text{SrBr}_2-\text{H}_2\text{O}$

The experimental data expressed in mass percent of $\text{NaBr}-\text{SrBr}_2-\text{H}_2\text{O}$ system at 298 K were listed in Table 2. The stable phase diagram of this system at 298 K (Figure 1) was plotted in Table 2. Figure 2 is X-ray diffraction pattern of the isothermal-isobaric invariant point of this system. The points of the liquid phase composition and the corresponding wet residue were then connected to form a straight line which was extended, and the solid point could be found according to the lever rule. As Figure 1 shows, the phase diagram consists of two crystallization regions: strontium bromide hexahydrate and sodium bromide dihydrate. At 298 K, there is only one isothermal-isobaric invariant point in $\text{NaBr}-\text{SrBr}_2-\text{H}_2\text{O}$ system. It is denoted as point E1, which is saturated with two single salts $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NaBr} \cdot 2\text{H}_2\text{O}$ with $w(\text{SrBr}_2) = 0.3302$ and $w(\text{NaBr}) = 0.2164$. In Figure 1, point A and point B represent the isothermal-isobaric invariant point of the single salts SrBr_2 and NaBr , respectively. Two curves AE1 and BE1 are isothermal dissolution curves in this system.

3.2 The ternary system $\text{KBr}-\text{SrBr}_2-\text{H}_2\text{O}$

The solubility data of $\text{KBr}-\text{SrBr}_2-\text{H}_2\text{O}$ system at 298 K measured in experiment were listed in Table 3. Using these data, the phase diagram of the ternary system at 298 K was plotted, which was shown in Figure 3. Figure 4 is X-ray diffraction pattern of the isothermal-isobaric invariant point in this system. It can be seen that there are two crystallization regions (KBr and $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$), two isothermal dissolution curves (AE2 and CE2), and one isothermal-isobaric invariant point (E2) in Figure 3. According to Figure 4, two saturated salts are $\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{KBr}$ for point E2, and the

composition of liquid phase is $w(\text{KBr}) = 0.0668$, $w(\text{SrBr}_2) = 0.4700$. In this system, the crystallization region of strontium bromide hexahydrate is smaller, whereas that of potassium bromide is larger. And the strontium bromide hexahydrate has obvious salting-out effect on potassium bromide in the solutions.

3.3 The quaternary system $\text{NaBr-KBr-SrBr}_2\text{-H}_2\text{O}$

The results from the solubility measurements for $\text{NaBr-KBr-SrBr}_2\text{-H}_2\text{O}$ system at 298 K were given in Table 4. The corresponding phase diagram (Figure 5) and water content diagram (Figure 6) of this system were drawn using Jänecke dry-salt indexes. Figure 7 is X-ray diffraction pattern of the isothermal-isobaric invariant point F1 in this system. The specific calculation formulas are as follows:

$$J(\text{NaBr}) = \frac{w(\text{NaBr})}{w(\text{NaBr}) + w(\text{KBr}) + w(\text{SrBr}_2)} \times 100 \quad (3-1)$$

$$J(\text{KBr}) = \frac{w(\text{KBr})}{w(\text{NaBr}) + w(\text{KBr}) + w(\text{SrBr}_2)} \times 100 \quad (3-2)$$

$$J(\text{SrBr}_2) = \frac{w(\text{SrBr}_2)}{w(\text{NaBr}) + w(\text{KBr}) + w(\text{SrBr}_2)} \times 100 \quad (3-3)$$

$$J(\text{H}_2\text{O}) = \frac{w(\text{H}_2\text{O})}{w(\text{NaBr}) + w(\text{KBr}) + w(\text{SrBr}_2)} \times 100 \quad (3-4)$$

It can be seen from Figure 5, there are three isothermal dissolution curves (curves E1F1, E2F1 and E5F1), one isothermal-isobaric invariant point (point F1) and three crystallization regions corresponding to three single salts: $\text{NaBr} \cdot 2\text{H}_2\text{O}$, KBr and $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ in phase diagram of this quaternary system.

The area size of crystallization region follows $\text{KBr} > \text{NaBr} \cdot 2\text{H}_2\text{O} > \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$. It means that single salt KBr has the smaller solubility than others, and crystallization of KBr becomes easier from solutions in this system. At the isothermal-isobaric invariant point F1 of this system, the composition of its equilibrium liquid phase is as follow: $w(\text{NaBr}) = 0.2177$, $w(\text{KBr}) = 0.0492$, $w(\text{SrBr}_2) = 0.3109$, and the corresponding equilibrium solid phases are $\text{NaBr} \cdot 2\text{H}_2\text{O}$, KBr and $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, respectively.

The diagram of water-content vs composition (Figure 6) of $\text{NaBr-KBr-SrBr}_2\text{-H}_2\text{O}$ system at 298 K shows that the water content changes regularly with $J(\text{NaBr})$. It decreases at the isothermal dissolution curve E2F1, and

reaches the minimum value at the point F1. Then it increases at the isothermal dissolution curve E5F1.

3.4 The quaternary NaBr–MgBr₂–SrBr₂–H₂O

The results obtained from phase equilibrium experiments for NaBr–MgBr₂–SrBr₂–H₂O system at 298 K were summarized in Table 5. Then the corresponding equilibrium phase diagram (Figure 8) was drawn by the data in Table 5. Figure 9 and Figure 10 are the X-ray diffraction pattern of two isothermal-isobaric invariant points (F2, F3) in this system, respectively.

In NaBr–MgBr₂–SrBr₂–H₂O system, just like its subsystem NaBr–MgBr₂–H₂O, the solids hydrated salt NaBr·2H₂O and the corresponding anhydrous salt NaBr exist simultaneously with neither solid solution nor double salt. It belongs to a type II hydrate. The isothermal dissolution curve E7F3 in Figure 8 is the co-saturated solubility curve of NaBr·2H₂O + NaBr, and the X-ray diffraction pattern at a point on the curve is given in Figure 11. In the diagram, there are two isothermal-isobaric invariant points, four regions of crystallization and five isothermal dissolution curves. The four crystallization regions are corresponding to SrBr₂·6H₂O, NaBr, NaBr·2H₂O and MgBr₂·6H₂O, respectively. The region of crystallization of NaBr·2H₂O is larger, and that of MgBr₂·6H₂O is smaller. It means that the single salt NaBr·2H₂O has smaller solubility in the equilibrium liquid phase, whereas the MgBr₂·6H₂O has larger solubility. At isothermal-isobaric invariant point F2 ($w(\text{NaBr}) = 0.0351$, $w(\text{MgBr}_2) = 0.4389$, $w(\text{SrBr}_2) = 0.0538$), the solution is saturated with MgBr₂·6H₂O, SrBr₂·6H₂O and NaBr. At isothermal-isobaric invariant point F3 ($w(\text{NaBr}) = 0.0718$, $w(\text{MgBr}_2) = 0.3491$, $w(\text{SrBr}_2) = 0.1128$), the solution is saturated with NaBr, SrBr₂·6H₂O and NaBr·2H₂O.

Figure 12 is the diagram of water-content vs composition of the NaBr–MgBr₂–SrBr₂–H₂O system at 298 K. As the $J(\text{NaBr})$ increases, the water content decreases regularly at isothermal dissolution curves E4F2, F2F3 and F3E1, and achieves a minimum at point E1.

3.5 The quaternary system KBr–MgBr₂–SrBr₂–H₂O

The experimental results of phase equilibria in KBr–MgBr₂–SrBr₂–H₂O system

at 298 K were given in Table 6. On the basis of Jänecke index values ($J(\text{KBr}) + J(\text{MgBr}_2) + J(\text{SrBr}_2) = 100 \text{ g}$), the phase diagram was plotted, as shown in Figure 13.

At 298 K, the quaternary system belongs to a complex type with the double salt $\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ found. This diagram in Figure 13 is composed of four crystallization regions ($\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ and KBr), two isothermal-isobaric invariant points (F4 and F5) and five isothermal dissolution curves (E4F4, F4F5, E8F4, E9F5 and E2F5). The regions of crystallization of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ is very close to the vertical axis and it is the smallest. It indicates that the $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ is more difficult to crystallize than the other salts in this system at 298 K. The corresponding equilibrium solid phases and the liquid compositions of the two isothermal-isobaric invariant points are as follows:

Point F4 ($\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O} + \text{MgBr}_2 \cdot 6\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$): $w(\text{SrBr}_2) = 0.0602$, $w(\text{MgBr}_2) = 0.4593$, $w(\text{KBr}) = 0.0023$;

Point F5 ($\text{SrBr}_2 \cdot 6\text{H}_2\text{O} + \text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O} + \text{KBr}$): $w(\text{SrBr}_2) = 0.0602$, $w(\text{MgBr}_2) = 0.4593$, $w(\text{KBr}) = 0.0023$.

The diagram of water-content vs composition of the system (Figure 14) at 298 K was drawn according to the value of $J(\text{NaCl})$ and $J(\text{H}_2\text{O})$. As it can be seen from the Figure 14, Jänecke index of water of the quaternary system $\text{KBr}-\text{MgBr}_2-\text{SrBr}_2-\text{H}_2\text{O}$ can vary with the content change of potassium bromide and reach the maximum at the point E9.

4 Prediction of Solubility

Brine, as one of the important geological fluids, is a naturally occurring concentrated electrolyte solution. Its formation, evolution and migration are often closely related to various geological processes. Therefore, building precise models to describe the thermodynamic properties of brine system will be the necessary for geologists. As it not only describes the thermodynamic properties of brine system more broadly, but also makes precise theoretical predictions, so as to avoid a lot of experimental works that are difficult to realize at present ^[2]. In this work, we used the Pitzer ion-interaction model that is known as more successful to describe the

thermodynamic properties of brine systems ^[15]. Pitzer's model is a semi-empirical statistical mechanics model that uses a series of parameters derived from experimental thermodynamic data to calculate thermodynamic properties of solutions that vary in concentration from very dilute through high or even saturated concentrations ^[16, 17]. Based on original Pitzer's model, Harvie and Weare derived a more convenient formula (referred to as the HW formula) for calculating the theoretical permeability coefficient and ion activity coefficients in solutions of electrolytes by rearranging the Pitzer formula ^[18-20]. It can be used to predict the solid-liquid equilibrium solubility data. In addition, many scholars including Pitzer have continuously improved the initial Pitzer model so that it can work for conditions other than one atmosphere and 298 K ^[21-23].

4.1 Model parameterization

Aiming at the research system of this work, the key issues for calculating the solubility of each electrolyte in a mixed electrolyte solution using the Pitzer electrolyte solution theory is to obtain each parameter in corresponding temperature and concentration range. The parameters for the Pitzer equation primarily include: binary parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ ; mixed ion interaction parameters θ_{ij} (parameters for two ions, two cations or two anions) and Ψ_{ijk} (the parameter of three ions, either two cations with one anion or one anion with two cations); and the dissolution equilibrium constant $\ln K_{sp}$ of various salts. These parameters are related to the structure, properties, ionic interaction and temperature of the electrolyte solution.

In this paper, the fitting range of the parameters should be extended to the saturated solution molalities for quinary system. The models for the Na–K–Ca–Cl–SO₄–H₂O ^[21,22] and Na–K–Mg–Ca–Br–H₂O ^[12-14, 24, 25] systems have been built based on extensive data such as activity and permeability coefficients and can be used to calculate mineral solubilities to high concentration and temperature within experimental accuracy. The Pitzer binary parameters for NaBr–H₂O and KBr–H₂O, correlated mixing ion-interaction parameters and solubility product are taken from temperature variable models of Christov ^[12-14] for bromide system, as well as from 298 K model of Harvie et al. ^[20].

In the current study, there are no parameters of a higher concentration range, as we still use the parameters given by Kim and Frederick^[26], which are bound to lead to a deviation in the calculation process. However, we believe the deviation is still within the acceptable range, and the calculated results are basically in agreement with the experimental results. Other Pitzer mixed ion interaction parameters ($\theta_{\text{Mg,Sr}}$, $\Psi_{\text{Na,Sr,Br}}$, $\Psi_{\text{K,Sr,Br}}$ and $\Psi_{\text{Mg,Sr,Br}}$) as well as the dissolution equilibrium constant $\ln K_{\text{sp}}$ of strontium bromide hexahydrate at 298 K were obtained by the experimental solubility data of NaBr–SrBr₂–H₂O, KBr–SrBr₂–H₂O and MgBr₂–SrBr₂–H₂O systems at 298 K. All parameters are given in Tables 7, 8 and 9.

4.3 Calculated solubility

After obtaining all the required Pitzer parameters, the theoretical calculations of phase equilibria at 298 K for three ternary systems (NaBr–SrBr₂–H₂O, KBr–SrBr₂–H₂O and MgBr₂–SrBr₂–H₂O) and three quaternary systems (NaBr–KBr–SrBr₂–H₂O, NaBr–MgBr₂–SrBr₂–H₂O and KBr–MgBr₂–SrBr₂–H₂O) were carried out. The calculated results are expressed as mass molar concentrations and converted to the Jänecke index. The calculated and experimental phase diagrams are plotted from experimental and calculation results and are shown in Figure 15 to Figure 20 (the solid lines and points correspond to the experimental results while the dashed lines and hollow points correspond to the calculated results). In order to further compare the theoretical data with the experimental data, the experimental values and calculation results of the isothermal-isobaric invariant points of each system were selected for analysis and are listed in Table 10 (for the sake of comparison, the mass percentages are used uniformly). From a comparison of the data in Table 10, the experimental results and the calculated results of the isothermal-isobaric invariant points of each system are in good agreement. Figures 15 to 20 show the similarity between the experimental and computational results of each isothermal dissolution curve and each isothermal-isobaric invariant point. In addition, the experimental phase diagrams are basically consistent with the calculated phase diagrams, meanwhile the results show the applicability of the fitting parameters utilized in this paper.

4.4 Calculation error analysis

The solubility of salts in nine systems in this paper has been calculated. The calculated results are similar to the experimental data, and the relative error is small. However, there are still some deviations in the prediction process, which are mainly reflected in the following aspects:

In this paper, for the binary parameters of SrBr_2 , due to the lack of parameters for the saturation solubility range, we used the parameters given by Kim et al.^[26], whose maximum applicable range is only $m = 2$, and less than the solubility of SrBr_2 at 298 K. Although the calculation results were basically consistent with the experimental results, it would inevitably lead to deviations in the calculation process.

In general, when the experimental data are sufficient and accurate, the accuracy of the fitting parameters can be guaranteed by using solubility data only. In the fitting process, using solubility data, the permeability coefficient and activity coefficient together can often ensure a higher accuracy of parameters. Some of the parameters needed to be calculated in this paper have not been reported in the literature and can only be obtained by fitting the solubility data of the relevant ternary subsystems in the absence of the correlation coefficient and the permeability coefficient under relevant conditions. Since the existing experimental data samples are not sufficient, the accuracy of the regression parameters should be further improved.

5 Conclusions

In order to exploit and take advantage of brine resources comprehensively, guide the design process of separation and purification of inorganic salts, and provide a theoretical basis for describing salt precipitation and metallogenic regularity of brine that occurs in the underground strontium-rich brine resources in Sichuan Basin, the phase equilibria in subsystems of system $\text{NaBr-KBr-MgBr}_2\text{-SrBr}_2\text{-H}_2\text{O}$ at 298 K were studied by isothermal dissolution method. The solubility of salts in each system was determined and corresponding phase diagrams were drawn. Here were several conclusions drawn from this study:

- (1) At 298 K, $\text{NaBr-SrBr}_2\text{-H}_2\text{O}$, $\text{KBr-SrBr}_2\text{-H}_2\text{O}$ and $\text{NaBr-KBr-SrBr}_2\text{-H}_2\text{O}$

systems all belong to type I hydrate; due to crystallization fields of NaBr and NaBr·2H₂O were found in the phase diagram of NaBr–MgBr₂–SrBr₂–H₂O system, it is of a type II hydrate; KBr–MgBr₂–SrBr₂–H₂O system belongs to a complex type as the double salt formed in the quaternary system.

(2) By using the experimental solubility data in ternary systems, the Pitzer parameters $\theta_{\text{Mg,Sr}}$, $\psi_{\text{Na,Sr,Br}}$, $\psi_{\text{K,Sr,Br}}$, $\psi_{\text{Mg,Sr,Br}}$ and $\ln K(\text{SrBr}_2 \cdot 6\text{H}_2\text{O})$ at 298 K were fitted.

(3) Based on the parameters in the literature and the parameters determined during this study, the phase equilibrium solubility of nine strontium-bearing systems including three ternary systems (NaBr–SrBr₂–H₂O, KBr–SrBr₂–H₂O and MgBr₂–SrBr₂–H₂O) and three quaternary systems (NaBr–KBr–SrBr₂–H₂O, NaBr–MgBr₂–SrBr₂–H₂O and KBr–MgBr₂–SrBr₂–H₂O) at 298 K were calculated and their corresponding experimental and calculated phase diagrams were plotted. The theoretical phase diagrams generally agree with the experimental phase diagrams and causes of error were analyzed.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

Guo-Liang Nie: Writing-Original draft preparation, Methodology, Software.

Shi-Hua Sang: Supervision, Conceptualization.

Rui-Zhi Cui: Data curation, Writing-Reviewing and Editing, Validation.

Zhong-Zhong Wu: Formal analysis.

Chao Ye: Resources, Project administration.

Research highlights:

1. Fluid phase equilibrium study aiming at underground brine.
2. Stable phase equilibria of subsystems for quinary system Na–K–Mg–Sr–Br–H₂O.
3. Using Pitzer electrolyte solution theory to predict the experimental results.
4. Playing a fundamental role to bulid a thermodynamic framework.