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# Measurements and calculations of solid-liquid equilibria in the quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ at $T = 348$ K

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ABSTRACT

Using an isothermal dissolution equilibrium method, solid-liquid equilibria in the quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ were studied at $T = 348$ K. The phase diagram, water diagram and the density-composition diagram were plotted according to the experiment results. One double salt $Na_2SO_4 \cdot 3K_2SO_4$ was found in the quaternary system at $T = 348$ K. There are five areas of crystallization, seven univariant solubility curves, and three invariant points. Respectively, the five crystallization regions are $Na_2SO_4 \cdot 3K_2SO_4$, NaBr, KBr, $Na_2SO_4$ and $K_2SO_4$. Based on the chemical model of Pitzer's electrolyte solution theory, the solubilities of the quaternary systems $NaCl-KCl-Na_2SO_4-K_2SO_4-H_2O$, $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ have been calculated at $T = 348$ K. The calculation diagrams were plotted. Comparing experimental measurement with calculation, the results showed that the calculated results are in accordance with experiments.



## 1. Introduction

Underground brine is rich and widespread in western Sichuan Basin which contains high concentration of potassium and borate. In addition to $K^+$, $B^{3+}$, the brine still has some useful components such as $Br^-$, $I^-$, $Li^+$, $Sr^{2+}$, etc, and all of them can reach or exceed the industrial index. Potassium concentration reaches up to 53.3 g $L^{-1}$, and the bromine concentration is also as high as 2533 mg $L^{-1}$. The brine is the world's rare liquid mineral resource. And it will reap full social and economic benefits by development and utilization the underground brine resources [1,2].

For the Western Sichuan Basin brine-salt resources, it could be simplified as $Na-K-B_4O_7-Br-Cl-SO_4-H_2O$ complex multi-component system. Aiming at this system, our research work has made a series of studies from 298 K to 373 K. Such as ternary system $KBr-K_2B_4O_7-H_2O$ at $T = (298, 323, 348, \text{and } 373)$ K [3–6], quaternary systems $NaBr-Na_2SO_4-KBr-K_2SO_4-H_2O$ at $T = 323$ K [7,8], $NaBr-KBr-CaBr_2-H_2O$ at $T = 298$ K [9], and quinary system $Na^+$, $K^+//Cl^-$, $Br^-$, $SO_4^{2-}-H_2O$ at $T = 373$ K [10] have been carried out by our group.

The $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ system is one of quaternary subsystems for the underground brine in western Sichuan Basin, and so far the phase equilibrium study of the system at $T = 348$ K has not been reported. In this paper, study involves four parts: (1) Measurement of solubilities and densities of solutions in the quaternary system at $T = 348$ K and plotting the experimental phase diagram. (2) In order to prove if the same algorithm could be used to predict phase equilibria of the actual quaternary system, calculation of the solubilities in $NaCl-KCl-Na_2SO_4-K_2SO_4-H_2O$ quaternary system at $T = 348$ K based on the chemical model of Pitzer's electrolyte solution theory and corresponding parameters. (3) Fitting the corresponding ion-interaction mix parameters $\Psi_{Na,Br,SO4}$ and $\Psi_{K,Br,SO4}$ derived from ternary subsystems. (4) Calculation of the solubilities of $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ quaternary system at $T = 348$ K and comparison of experimental and calculated data.

## 2. Experimental

### 2.1. Reagents and instruments

The water used was distilled water (pH = 6.60 and conductivity ≤ 1.2 · $10^{-4}$ S $m^{-1}$at indoor temperature). The Chemical reagents used in experiment are analytic grade and are listed in Table 1.

Instruments used in this experiment were showed as follows:

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**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 |
| NaBr | Chengdu KeLong Chemical Reagent Factory | 0.99 | None | Titration |
| $K_2SO_4$ | Chengdu KeLong Chemical Reagent Factory | 0.99 | None | Titration |
| $Na_2SO_4$ | Chengdu KeLong Chemical Reagent Factory | 0.99 | None | Titration |

(1) an AL104 type standard analytical balance of 110 g capacity from Mettler Toledo Instruments Co., Ltd. (an uncertainty of 0.0001 g); (2) an SHA-GW type oil bath thermostated vibrator from Jintan Guowang Instrument Factory (an uncertainty of 0.1 K by using precision thermometer calibration); (3) a Siemens D500 X-ray diffractometer with Ni-filtered Cu Kα radiation and a Hitachi S-530 scanning electron microscope (the operating conditions of the X-ray diffractometer were 35 kV and 25 mA).

### 2.2. Experimental method

In this study, the isothermal dissolution equilibrium method has been used. According to the composition of the invariant points of its ternary subsystems NaBr–KBr–$H_2O$, NaBr–$Na_2SO_4$–$H_2O$, KBr–$K_2SO_4$–$H_2O$ and $Na_2SO_4$–$K_2SO_4$–$H_2O$ at $T = 348$ K, appropriate quantity of salts were calculated, and the third salt was added. The salts and 50 mL distilled water were put into a number of airtight glass bottles. The bottles have been placed in the oil bath thermostated vibrator (SHA-GW type) to vibrate, and always maintain the temperature at $T = (348 \pm 0.1)$ K. The solid–liquid mixtures were shaken for over a week to accelerate the establishment of equilibrium states. Then, the clarification of the solutions required about 5 days. The upper clear liquids of samples were taken regularly to analyze the concentration. When the chemical composition remained constant, the equilibrium was reached. After the equilibrium is reached, liquid phases (5 mL liquid from per glass bottle) were removed and diluted to 100 mL volumetric flask immediately to measure the composition. Solid phases were taken out and analyzed by X-ray diffraction to ascertain the crystalloid form. The method for density measurement is pycnometer method with accuracy to 0.0002 g $cm^{-3}$.

### 2.3. Analytical methods

In NaBr–KBr–$Na_2SO_4$–$K_2SO_4$–$H_2O$ quaternary system, here are four kinds of ions ($Na^+$, $K^+$, $Br^-$ and $SO_4^{2-}$) whose concentrations need to be measured. The definite means are as follows, the potassium ion ($K^+$) concentration: a sodium tetraphenylborate (STPB) – hexadecyl trimethyl ammonium bromide (CTAB) titration with an indicator of titan yellow (TY), the bromide ion ($Br^-$) concentration: silver nitrate volumetry with an indicator of potassium chromate, the sulfate ion ($SO_4^{2-}$) concentration: a method of alizarin red S volumetry with an indicator of S volumetry, and the sodium ion ($Na^+$) concentrationwas calculated by ionic balance.

## 3. Results and discussion

The measured results in the NaBr–KBr–$Na_2SO_4$–$K_2SO_4$–$H_2O$ quaternary system at $T = 348$ K were listed in Table 2. Using the experimental values from Table 2, the equilibrium phase diagram at $T = 348$ K was plotted by Jänecke dry-salt index values, with $J(2K^+) + J(2Na^+) = J(2Br^-) + J(SO_4^{2-}) = 100$ mol in Fig. 1. The respective ion Jänecke dry-salt indices $J(2Na^+)$, $J(2K^+)$, $J(2Br^-)$ and $J(SO_4^{2-})$ were calculated as follows:

$$\text{Letting } [\mathrm{B}] = \frac{w(\mathrm{Na^+})}{2\mathrm{M_{Na}}} + \frac{w(\mathrm{K^+})}{2\mathrm{M_K}} = \frac{w(\mathrm{Br^-})}{2\mathrm{M_{Br}}} + \frac{w\left(\mathrm{SO_4^{2-}}\right)}{\mathrm{M_{SO_4}}} \text{ mol} \quad (1)$$

$$J\left(2\mathrm{Na^+}\right) = 100\frac{\frac{w(\mathrm{Na^+})}{2\mathrm{M_{Na}}}}{[\mathrm{B}]} \quad (2)$$

$$J\left(2\mathrm{K^+}\right) = 100\frac{\frac{w(\mathrm{K^+})}{2\mathrm{M_K}}}{[\mathrm{B}]} \quad (3)$$

$$J(2\mathrm{Br^-}) = 100\frac{\frac{w(\mathrm{Br^-})}{2\mathrm{M_{Br}}}}{[\mathrm{B}]} \quad (4)$$

$$J\left(\mathrm{SO_4^{2-}}\right) = 100\frac{\frac{w(\mathrm{SO_4^{2-}})}{\mathrm{M_{SO_4}}}}{[\mathrm{B}]} \quad (5)$$

$$J(\mathrm{H_2O}) = 100\frac{\frac{w(\mathrm{H_2O})}{\mathrm{M_{H_2O}}}}{[\mathrm{B}]} \quad (6)$$

Where $w$(ion) and $w(H_2O)$ are the mass of the ion and water in grams per 100 g of solution; $J$(ion) and $J(H_2O)$ are the Jänecke dry-salt index values of the *ion* and water; and $M_{ion}$ is the molar weight of the *ion*.

It showed that the double salt $Na_2SO_4 \cdot 3K_2SO_4$ was found and no solid solution was found. In Fig. 1, the phase diagram has three invariant points, seven univariant solubility curves, and five crystallization fields. Saturated salts in the five crystallization fields are four single salts NaBr, KBr, $Na_2SO_4$, $K_2SO_4$ and one double salt, $Na_2SO_4 \cdot 3K_2SO_4$. The crystallization fields of double salt $Na_2SO_4 \cdot 3K_2SO_4$ and sulfates ($Na_2SO_4$ and $K_2SO_4$) are larger, whereas the crystallization fields of simple bromide salts (NaBr and KBr) are smaller. The solubility of NaBr is the highest and that of double salt $Na_2SO_4 \cdot 3K_2SO_4$ is the lowest among the salts. Therefore, the double salt $Na_2SO_4 \cdot 3K_2SO_4$ in this quaternary system is easy to crystallize.

Seven-univariant solubility isotherm curves of this quaternary system are $A_1E_1$, $D_1E_1$, $E_1F_1$, $F_1G_1$, $H_1F_1$, $B_1G_1$ and $C_1G_1$. Three invariant points are named as $E_1$, $F_1$ and $G_1$. The X-ray diffraction photographs of three invariant points are given in Figs. 2–4. Regarding the invariant points, the saturated salts and the primary percent contents are specifically as follows:

Invariant $E_1$, saturated with salts $Na_2SO_4 \cdot 3K_2SO_4$ + KBr + $K_2SO_4$, with $w(Na^+) = 0.0185$, $w(K^+) = 0.1367$, $w(Br^-) = 0.3238$, $w(SO_4^{2-}) = 0.0118$;

Invariant $F_1$, saturated with salts $Na_2SO_4 \cdot 3K_2SO_4$ + KBr + $Na_2SO_4$, with $w(Na^+) = 0.0729$, $w(K^+) = 0.0709$, $w(Br^-) = 0.3743$, $w(SO_4^{2-}) = 0.0143$;

Invariant $G_1$, saturated with salts $Na_2SO_4$ + NaBr + KBr, with $w(Na^+) = 0.1071$, $w(K^+) = 0.0384$, $w(Br^-) = 0.4447$, $w(SO_4^{2-}) = 0.0036$.

Figs. 5 and 6 are the water content diagram and density plot of