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Metastable phase equilibria for the quaternary system containing potassium, magnesium, rubidium and chloride at 323.15 K

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ABSTRACT

By employing the method of isothermal evaporation, the metastable phase equilibria of the quaternary systems $KCl + RbCl + MgCl_2 + H_2O$ were researched at 323.15 K. In this paper, the solubilities and physicochemical properties, such as refractive indices and densities of the equilibrated solution, were determined. Through analysis of the experiments data, the metastable phase diagram, the water content diagram and physicochemical properties versus composition diagrams of the quaternary system were plotted. The study results indicated that in the metastable phase diagram, there were four invariant points (H_1, H_2, H_3, H_4), nine univariant curves, and six crystallization fields. And the six crystallization fields were magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$) and potassium chloride (KCl) and rubidium chloride (RbCl) and a rubidium and magnesium chloride double salt named carnallite ($RbCl{\cdot}MgCl_2{\cdot}6H_2O$) and a potassium and magnesium chloride double salt named carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) and a solid solution of potassium and rubidium chloride [(K, Rb)Cl]. The solid solution [(K, Rb)Cl] had the largest crystallization field. This showed that only by using evaporation and crystallization methods at 323.15 K, was it difficult to separate potassium from rubidium in chloride solution. The physicochemical properties of the quaternary system change regularly with the changes of composition in aqueous solutions.

1. Introduction

Rubidium is mainly occurs in natural carnallite, cesium lithium mica, feldspar and brine [1]. The Pingleba brine located in the Sichuan Basin is famous for concentrations high sodium, potassium, lithium, bromine, borate and rubidium in the world. The Pingleba brine resource is of excellent quality, the rubidium content is as high as 32.55 mg/L. Its rubidium content is 3.75 times of the industrial mined grade, which is far higher than other world's brine [2].

Underground brine is a complex water–salt coexisting system. Through studying the phase equilibrium of the corresponding brine system to explore the regular about the evaporation, concentration, and crystallization behavior of salts, we can obtain the necessary basic data for the comprehensive utilization of brine resources. Due to the lack of the phase equilibrium data of the containing rubidium salt water system, the development and utilization of Rubidium resources will be affected. In order to solve this problem, some scholars have carried out the study of the phase equilibrium for the partial containing rubidium brine system, and ternary $K_2SO_4 + Rb_2SO_4 + H_2O$ phase equilibrium for 298.15 K was studied by Kalink and Rumyantsev [3]; Merbach did on 298.15 K quaternary system of $KCl + RbCl + CsCl + H_2O$ and its sub system phase equilibrium [4,5]; D'Ans and Brsch did on 298.15 K quaternary system of $KCl + RbCl + (CsCl) + MgCl_2 + H_2O$ and its sub systems [6,7]; Zeng completed the study for 298.15 K quaternary system of $LiCl + KCl + RbCl + H_2O$ and its sub system phase equilibrium [8–10].

The quaternary system $KCl + RbCl + MgCl_2 + H_2O$ is an important subsystem for the complex multiple-system of Pingleba brine. So far the metastable equilibrium of the quaternary system $KCl + RbCl + MgCl_2 + H_2O$ at 323.15 K has not been reported. Zeng has completed the study of the ternary system $KCl + MgCl_2 + H_2O$, $KCl + RbCl + H_2O$ 323.15 K metastable phase equilibrium [11]. In this paper, the metastable phase equilibria of the system was presented and the solubilities, densities, and refractive index of the equilibrated solution in the systems were measured at 323.15 K.

2. Experimental

2.1. Reagents and apparatus

The chemicals used were analytical purity grade: potassium chloride (KCl; 99.5%), rubidium chloride (RbCl; 99.5%), and magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$; 98.0%). Deionized water

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with an electrical conductivity less than 1×10^{-4} S m^{-1} and pH ≈6.60, was used in the experiments.

A thermostatic evaporator (type SHH-250, Chongqing Inborn Instrument Corp., China) was used for metastable phase equilibrium experiments, the temperature precision is ±0.1 K. An inductively coupled plasma optical emission spectrometer (type 5300 V, Perkin-Elmer Instrument Corp., America) was used for the determination of the potassium and rubidium ion concentrations in solution. An Abbe refractometer (type 2WAJ, Shanghai Jingke Electronic Co., Ltd., China) was used for measuring the refractive index of the equilibrated solution with a precision of 0.0001. A standard analytical balance (type FA1204B, Shanghai Jingke Electronic Co., Ltd., China) of 110 g capacity and 0.0001 g resolution was used for determination of the density of solution. A Siemens D500 X-ray diffractometer with Ni-filtered Cu KR radiation and a Hitachi S-530 scanning electron microscope were used to analyze the crystalloid form of the solid phases and determining invariant points. The operating conditions of the X-ray diffractometer were 35 kV and 25 mA.

2.2. Analytical method

The Rb^+ and K^+ ion composition was analyzed by inductively coupled plasma optical emission spectrometry (precision: less than 0.06 mass %, type ICP-OES 5300 V). The Mg^{2+} ion concentration was determined by titration with EDTA stand solution in the presence of indicator of K–B with a precision of 0.5% [12]. The Cl^- concentration was measured by $AgNO_3$ titration in the presence of indicator K_2CrO_4 with a precision of 0.3% [13].

2.3. Experimental method

The metastable phase equilibria of the quaternary systems were studied at 323.15 K using the isothermal evaporation method. Depending on the solubility of salts in aqueous solution and the invariant point in the ternary subsystem at 323.15 K, the appropriate quantities of salts and deionized water were calculated and mixed into clean polyethylene containers. After salts completely dissolved, the container was placed in a thermostatic evaporator (SHH-250 type) for isothermal evaporation. The experimental conditions were a relative humidity of (20–30%) and evaporation rate of (4.0–5.5) mm d^{-1}. The temperature was controlled to [(323.15 ± 0.1) K] measured by a thermal resistance. When enough solid phases appeared, the solid were separated from the solution. For further identification, the salts were dried at 323.15 K and then analyzed by X-ray diffraction (XRD; Siemens D500 X-ray diffractometer) to determine the crystalloid form of the solid phase and determining invariant points. Meanwhile, a 5.0 mL sample of the clarified solution was taken from the liquid phase through a pipette and then diluted to a 100 mL final volume in a volumetric flask filled with deionized water to analyze the liquid-phase compositions. The densities of solution were measured with specific gravity bottle method with a precision of 0.0002 g cm^{-3} [14], the refractive index of equilibrated solution was determined by a 2WAJ. The remainder of the solution continued to be evaporated to reach the next measuring point. The same procedure was repeated until the solution was completely evaporated.

3. Results and discussion

The experimental results and the physicochemical property values such as densities and refractive indices of the quaternary system at 323.15 K are listed in Table 1. The ion concentration values of the metastable equilibrated solution were expressed both in mass fraction *w* (b) and Jänecke index *J* (b). According to the experimental data in Table 1, the experimental metastable phase diagram of the system at 323.15 K was constructed in Fig. 1. Fig. 2 is a partial enlarged diagram of Fig. 1. Fig. 3 is the relevant water diagram of the system at 323.15 K. In Figs. 1 and 2, points A, B, C, D, E and F are invariant points of the three ternary systems. Points S_1, S_2, S_3 and S_4 are invariant points of the quaternary system. The phase diagram consists of six crystallization fields, nine univariant curves, and four invariant points.

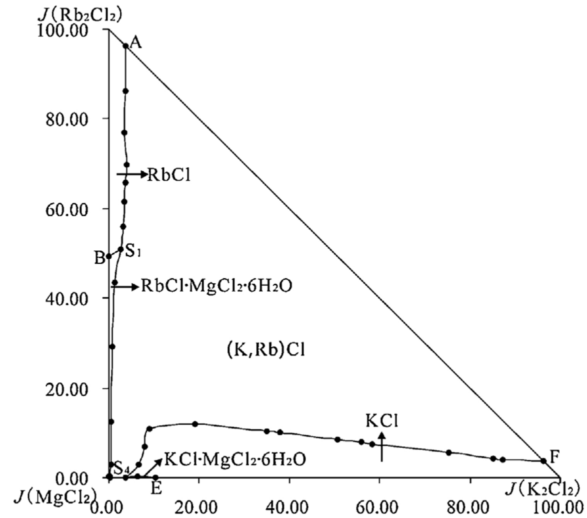

Fig. 1. Metastable phase diagram of the quaternary system KCl + RbCl + $MgCl_2$ + H_2O at 323 K.

The six crystallization fields correspond to single salts KCl, RbCl, $MgCl_2 \cdot 6H_2O$, and double salt $KCl \cdot MgCl_2 \cdot 6H_2O$, $RbCl \cdot MgCl_2 \cdot 6H_2O$ and the solid solution [(K, Rb)Cl]. The salt's crystallization region decreases in the order of KCl, RbCl, $RbCl \cdot MgCl_2 \cdot 6H_2O$, $KCl \cdot MgCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$. The solid solution [(K, Rb)Cl] has the largest crystallization field almost occupies the entire phase region, the salt $MgCl_2 \cdot 6H_2O$ has the smallest crystallization field, which shows that it is difficult to separate potassium from rubidium in chloride solution by only using evaporation and crystallization methods at 323 K. Four invariant points in this system are noted as S_1, S_2, S_3 and S_4. Point S_1 is a commensurate invariant point, cosaturated with three salts RbCl, $RbCl \cdot MgCl_2 \cdot 6H_2O$ and [(K, Rb)Cl]. The composition of the corresponding equilibrated solution is *w*(KCl) = 1.02%, *w*($MgCl_2$) = 11.97%, *w*(RbCl) = 30.01%. Point S_2 is a commensurate invariant point, cosaturated with

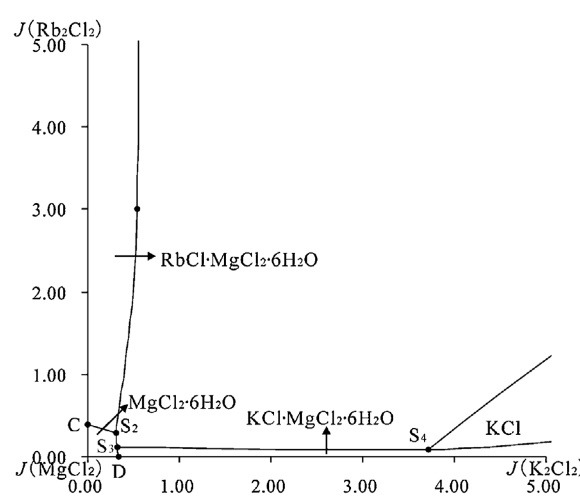

Fig. 2. Partial enlarged diagram of Fig. 1.