



Phase Equilibria in the Ternary System $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and the Quaternary Systems $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

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Received: 6 September 2017 / Accepted: 25 April 2018 / Published online: 5 July 2018
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Abstract

The stable phase equilibria of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and the two quaternary systems $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K were investigated using an isothermal method. Based on the experimental results, the isothermal solubility diagram of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$, and the solubility diagrams and water content diagrams of the two quaternary systems were constructed. The results show that the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K belongs to the simple co-saturated type without complex salt or solid solution. There are two invariant points, three univariant curves and three crystallization fields corresponding to $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K is of the simple co-saturated type and no complex salt or solid solution are found. The phase diagram contains two invariant points, five univariant curves and four crystallization fields (where the solids are NaCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$). The system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K has a double salt named carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) without solid solution formation. The phase diagram contains three invariant points, seven univariant curves and five crystallization fields (where the solids are KCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Keywords Phase equilibrium · Solubility · Sodium chloride · Magnesium chloride · Strontium chloride

1 Introduction

China is a country with abundant underground brine resources that are distributed in many oil and gas bearing sedimentary basins. Due to the recharge of underground brine from multiple sources, and through sedimentary metamorphism during burial, most of the

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underground brine is at high temperature, high salinity, and under high pressure. Therefore, there are obvious distinctions in the chemical composition compared with the shallow groundwater, seawater and even saline lake brine. The underground brine in the Sichuan basin, whose brine salinity reaches $190\text{--}290\text{ g}\cdot\text{L}^{-1}$, is not only rich in Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- and other common elements, but also rich in Sr^{2+} , Br^- , I^- , Ba^{2+} and other minor components. The content of these components often can meet or exceed the industrial grade, and what's more, they are important or indispensable materials in light industry, the chemical industry, nuclear engineering, aerospace and other high-tech fields [1, 2]. Consequently, with the gradual depletion of solid mineral resources, the comprehensive utilization of underground brine has an economic value and broad social prospects that cannot be overestimated.

In the process of mineralization and the exploitation of mineral resources, there is a dynamic solid–liquid phase equilibrium. The comprehensive utilization of brine resources usually needs to be guided by the multi-temperature phase equilibrium, and it can be realized by a series of phase separation techniques, such as evaporation, crystallization, salting out, heating, cooling or dissolution [3, 4]. Therefore, the studies of the solid–liquid phase equilibria of the underground brine can reveal the metallogenic contents of the liquid mineral and guide the development and utilization of brine resources.

The underground brine of Sichuan basin, which is rich in the elements strontium and potassium, can be simplified to the multi-component system $\text{NaCl} + \text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{CaCl}_2 + \text{H}_2\text{O}$. The phase equilibria of the subsystems of this complex multi-component system at different temperatures have been investigated by many workers. The ternary systems $\text{NaCl} + \text{SrCl}_2 + \text{H}_2\text{O}$, $\text{KCl} + \text{SrCl}_2 + \text{H}_2\text{O}$ [5], $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ [6], $\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ [7], as well as the quaternary system $\text{NaCl} + \text{KCl} + \text{SrCl}_2 + \text{H}_2\text{O}$ and the multi-component systems $\text{NaCl} + \text{KCl} + \text{SrCl}_2 + \text{CaCl}_2 + \text{H}_2\text{O}$ [8] and $\text{NaCl} + \text{KCl} + \text{SrCl}_2 + \text{CaCl}_2 + \text{MgCl}_2 + \text{H}_2\text{O}$ [9] have been studied. The quaternary system $\text{KCl} + \text{CaCl}_2 + \text{MgCl}_2 + \text{H}_2\text{O}$ and the three ternary systems it embodies, at 273, 308 and 348 K, have also been studied [10–15]. The solubilities in the ternary systems $\text{NaCl} + \text{SrCl}_2 + \text{H}_2\text{O}$ [16], $\text{KCl} + \text{SrCl}_2 + \text{H}_2\text{O}$ [17], and $\text{CaCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ [18] at 298 K have been explored. Studies of some brine systems containing potassium and strontium have also been carried out by our group, they are the ternary systems $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$, $\text{NaCl} + \text{SrCl}_2 + \text{H}_2\text{O}$, $\text{KCl} + \text{SrCl}_2 + \text{H}_2\text{O}$ and quaternary system $\text{SrCl}_2 + \text{KCl} + \text{NaCl} + \text{H}_2\text{O}$ [19–21]. The purpose of this article is to report the solubilities and identify the equilibrium solid phases of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and the two quaternary systems $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K. The latter two systems have not been published yet. Although the phase equilibria on the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ had been reported [6], this study only presented the invariant point data, and there is very little solubility data in the literature. So, the present work is a continuation of the previous project. Simultaneously, our identification has promising application in exploiting the brine resources and understanding the geochemical behavior.

2 Experimental Section

2.1 Reagents and Instruments

2.1.1 Reagents

The starting materials NaCl, KCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ used in the experiment are all produced in Chengdu Kelong Chemical Reagent Factory, and they are all analytically pure agents. The purity of the reagents is more than 99.5%, with the exception of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, whose purity is not less than 98%. The water for preparation of sample solution and analytical water is deionized water, whose pH is nearly 6.6 and conductivity is less than $1 \times 10^{-5} \text{ S} \cdot \text{m}^{-1}$.

2.1.2 Experimental Instruments

A standard electronic balance of 110 g capacity made by the Mettler Toledo Instruments Co., Ltd., whose precision is 0.0001 g, was used to weigh the samples. An ultrapure water apparatus (UPT-II-20T) was used to produce deionized water.

The constant temperature oil bath oscillator (HZ-9613Y, $\pm 0.1 \text{ K}$) supplied by the Jintan Jieruier Instrument Co., Ltd. was used to control the equilibrium temperature.

X-ray diffraction (DX-2700) instrument manufactured by the Dandong Fangyuan Instrument Co., Ltd. was used to identify the solid phases.

2.2 Experimental Method

The isothermal method [4] was adopted to study the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and quaternary systems $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$. Based on the solubility data of each single salt and the existing invariant point solubility in each ternary system, a certain proportion of blend salts and 30 mL water were mixed in the ground glass bottles (3 cm in diameter and 12 cm in height), the sealed bottles were placed in the constant temperature oil bath oscillator (HZ-9613Y). The oscillator was used to promote the establishment of equilibrium. The temperature was controlled at $373 \pm 0.1 \text{ K}$ for the isothermal dissolution equilibrium. All the samples were fully shaken for 3 days and then kept standing for 2–4 days at 373 K. The supernatant solution was taken out regularly for chemical analysis until the contents of the chemical components remained constant, which indicated that the samples had reached equilibrium. The required time for equilibration was found to be 5–7 days. Sampling correctly was the key to the success of the experiment. We only took the supernatant solution during the sampling, thus avoiding particles from entering the samples. Also the solid phases were large grains and precipitated at the bottom at 373 K in the experiment, the height of the solution is much larger than the diameter of the bottle, and it is also more than $2/3$ the height of the bottle, so that it can avoid solid phase entering the sampling pipette. The pipette was preheated, then it was inserted into the supernatant layer to suck up 2–3 mL of liquid quickly. The removed samples were put into weighing bottles with known, constant weight, and then the weighing bottles were accurately weighed and diluted with distilled water in a 100 mL volumetric flask and then analyzed. The mixtures of solids were taken out to be checked by X-ray diffraction.

2.3 Analytical Methods

The concentration of potassium ion (K^+) was analyzed by a sodium tetra-phenyl borate(STPB)–hexadecyltrimethyl ammonium bromide (CTAB) back titration (uncertainty of 0.5%). The concentration of magnesium ion (Mg^{2+}) was evaluated with an EDTA standard solution and eriochrome black T as the indicator. The strontium ion (Sr^{2+}) concentration was titrated in a strongly alkaline solution with an EDTA standard solution in the presence of the calcium indicator (uncertainty: 0.5%). The chloride ion (Cl^-) concentration was determined with Mohr's method using a silver nitrate standard solution (with a precision of 0.3%) in near neutral solution. The concentration of sodium ion (Na^+) was obtained according to the ion charge balance and assisted by atomic absorption spectrometry (uncertainty, 0.3%). Equilibrium solid phases were identified by a chemical reaction method combined with XRD (X-ray diffraction).

3 Results and Discussion

3.1 The Ternary System $MgCl_2 + SrCl_2 + H_2O$ at 373 K

The measured data of the ternary system $MgCl_2 + SrCl_2 + H_2O$ at 373 K are listed in Table 1, where the concentration of the liquid is expressed in mass fraction $w(B)$. The graphical representation shown in Fig. 1 is also plotted based on the determined data. As will be seen from Fig. 1, the isothermal solubility diagram contains two invariant points (E_1 and F_1) and three solubility curves: B_1F_1 , corresponding to the crystallization of $SrCl_2 \cdot 2H_2O$; F_1E_1 , corresponding to the crystallization of $SrCl_2 \cdot H_2O$; E_1A_1 , the $MgCl_2 \cdot 6H_2O$ curve. The invariant point F_1 is saturated with $SrCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot H_2O$ and the composition of the point is $w(MgCl_2) = 34.3\%$, $w(SrCl_2) = 6.40\%$. The other co-saturated point E_1 is saturated with $MgCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot H_2O$ and the composition of the point is $w(MgCl_2) = 41.68\%$, $w(SrCl_2) = 1.68\%$.

Figure 2 is the X-ray diffraction pattern at the invariant point E_1 , where equilibrium solids $MgCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot H_2O$ were identified. Figure 3 is the X-ray diffraction of the invariant point F_1 , at which $SrCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot H_2O$ coexist. The tie-lines joining the composition points of a solution and its corresponding “dry” residue meet at the composition points of the coexisting solid phase. At the same time, $MgCl_2$ acts as a salting-out agent with respect to $SrCl_2$. The strontium chloride dihydrate loses one molecule of water and is converted into strontium chloride monohydrate in the presence of the increasing amount of magnesium chloride hexahydrate.

The Swedish scholar Assarsson studied the solubility of the ternary system $MgCl_2 + SrCl_2 + H_2O$ at 291–373 K [6]. Their salt solubility data and the phase diagrams of this system at different temperatures are very few, and thus incomplete. For example, the compositions of each salt and each univariant curve are not given at 373 K [6]. In this paper, a complete study of this system at 373 K is carried out, and the solubility data and solid crystallization regions associated with the univariant curves that are missing in the literature are added.

Our team also carried out the solubility of the ternary system $MgCl_2 + SrCl_2 + H_2O$ at 348 and 323 K [19] earlier. The contrast chart at these three temperatures is shown in Fig. 4. It can be seen that the phase diagrams at 323 and 348 K are similar in shape, and

Table 1 Solubilities of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

| No | Composition of solution (100·w(b)) | | Composition of wet residue (100·w(b)) | | Equilibrium solids |
|--------------------|------------------------------------|----------------------|---------------------------------------|----------------------|--|
| | w(MgCl_2) | w(SrCl_2) | w(MgCl_2) | w(SrCl_2) | |
| 1, A ₁ | 42.29 | 0 | – | – | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 2 | 42.18 | 0.59 | – | – | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 3 | 41.87 | 1.15 | 44.98 | 0.50 | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4 | 41.98 | 1.43 | 44.68 | 0.80 | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 5 | 41.58 | 1.62 | – | – | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 6, E ₁ | 41.68 | 1.68 | – | – | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 7, B ₁ | 0 | 50.25 | – | – | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 8 | 6.27 | 41.52 | – | – | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 9 | 12.72 | 31.90 | – | – | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 10 | 18.52 | 24.05 | 8.83 | 55.18 | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 11 | 27.99 | 11.29 | 13.48 | 48.39 | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 12 | 31.07 | 7.87 | 15.53 | 44.85 | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 13 | 32.10 | 6.86 | – | – | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 14 | 32.37 | 6.75 | 13.35 | 51.84 | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ |
| 15, F ₁ | 34.30 | 6.40 | – | – | $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 16 | 33.80 | 5.89 | 18.83 | 42.58 | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 17 | 34.86 | 4.86 | 20.74 | 39.96 | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 18 | 35.20 | 4.40 | – | – | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 19 | 36.08 | 3.94 | 18.10 | 47.90 | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 20 | 39.70 | 2.44 | 22.60 | 41.34 | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 21 | 41.40 | 2.01 | 25.18 | 36.50 | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |
| 22 | 41.48 | 1.68 | – | – | $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ |

Standard uncertainty u are $u(T) = 0.1$ K, $u_r(w(\text{MgCl}_2)) = 0.003$, $u_r(w(\text{SrCl}_2)) = 0.005$

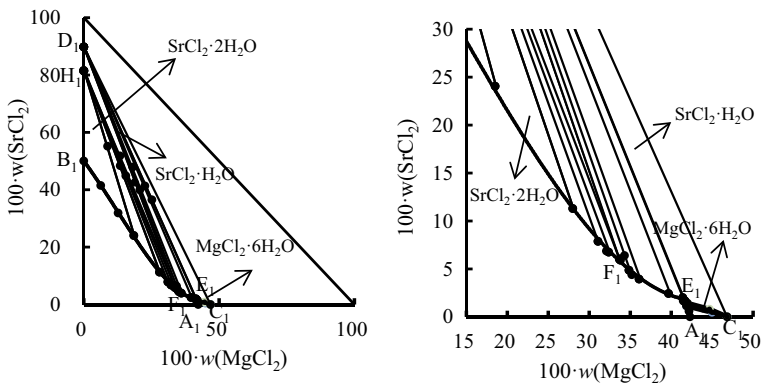


Fig. 1 Phase diagram of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and its enlarged diagram at 373 K

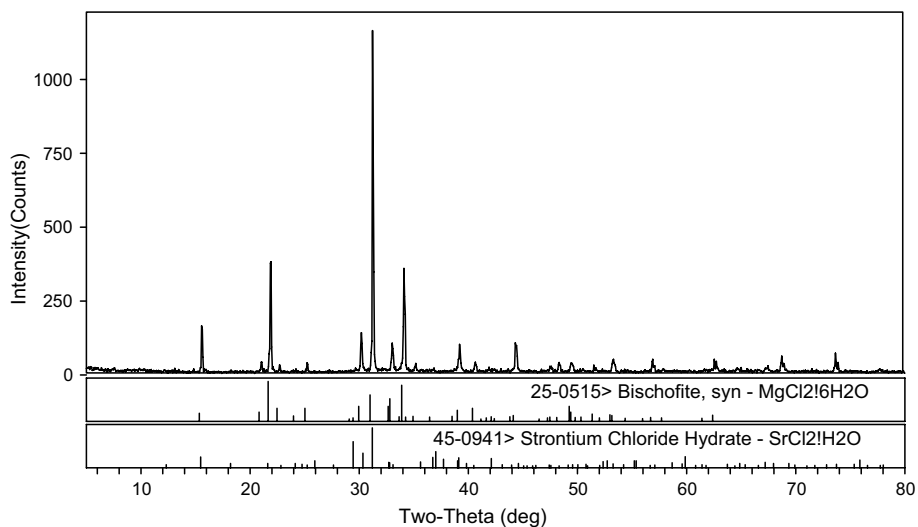


Fig. 2 X-ray diffraction photograph of the invariant point E_1 ($MgCl_2 \cdot 6H_2O + SrCl_2 \cdot H_2O$) in the ternary system $MgCl_2 + SrCl_2 + H_2O$ at 373 K

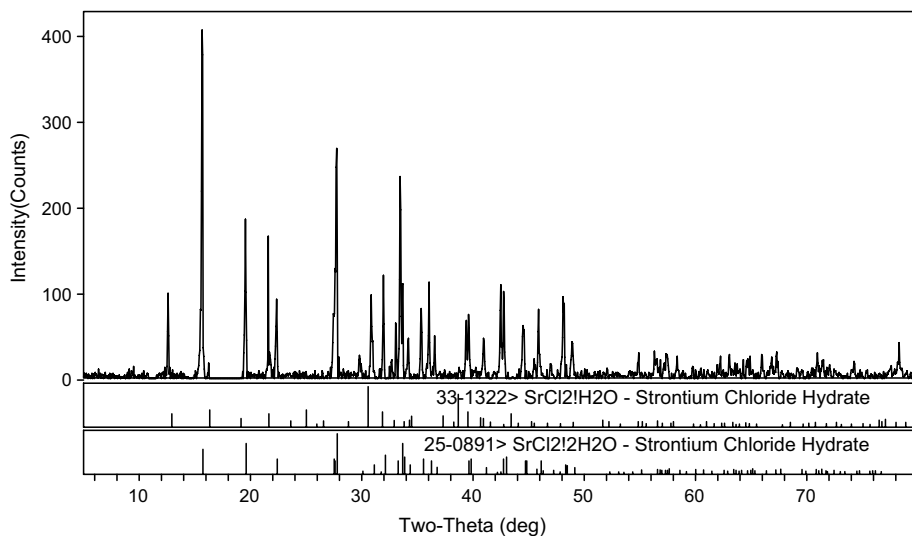
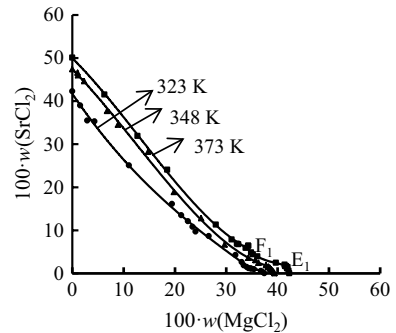


Fig. 3 X-ray diffraction photograph of the invariant point F_1 ($SrCl_2 \cdot H_2O + SrCl_2 \cdot 2H_2O$) in the ternary system $MgCl_2 + SrCl_2 + H_2O$ at 373 K

both contain two single variable curves, one invariant point and two crystalline regions, where $SrCl_2 \cdot 2H_2O$ has the larger crystallization region, and it reveals that the solubility of $SrCl_2$ in the equilibrium solution is very small. However, the phase diagram at 373 K consists of three single variable curves, two co-saturated points and three crystallization regions. The equilibrium solid phases at 323 and 348 K are $MgCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot 2H_2O$,

Fig. 4 Equilibrium phase diagram of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373, 348 and 323 K [19]



whereas when the temperature increases to 373 K, the equilibrium solids are $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot \text{H}_2\text{O}$. The mass fraction of MgCl_2 in the co-saturated liquid phase increases and the mass fraction of SrCl_2 increases slightly with the increase of temperature.

3.2 The Quaternary System $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

The quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K was brought into equilibrium by the isothermal method. The liquid composition (mass percent) and the corresponding equilibrium solids are shown in Table 2 (J is the dry salt index of the quaternary system, $J(\text{NaCl}) + J(\text{MgCl}_2) + J(\text{SrCl}_2) = 100$). According to the experimental results, the corresponding phase diagram and water diagram are drawn (Figs. 5 and 6). As can be seen from Table 2 and Fig. 5, the quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K is a simple co-saturated phase diagram, no double salt formation or solid solution is formed, and there are two invariant points E_2 and F_2 . As can be seen from Figs. 7 and 8 XRD diffraction patterns that the position of the characteristic peaks present are in accordance with those of the reference compounds, hence the invariant points are saturated with salts $\text{NaCl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{NaCl} + \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$. The composition of the invariant point E_2 is $w(\text{NaCl}) = 0.13\%$, $w(\text{MgCl}_2) = 41.53\%$, $w(\text{SrCl}_2) = 1.51\%$, and that of the invariant point F_2 is $w(\text{NaCl}) = 1.04\%$, $w(\text{MgCl}_2) = 34.71\%$, $w(\text{SrCl}_2) = 6.68\%$.

Additionally, the quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K is composed of five univariate curves: A_2E_2 , B_2E_2 , C_2E_2 , D_2F_2 and E_2F_2 , four solid phase crystallization areas (where the solids are NaCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$). The crystalline zone of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is much smaller than those of NaCl , $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, indicating that the solubility of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is the largest and that it is difficult to crystallize from the solution. This quaternary system comprises three ternary systems, those are $\text{NaCl} + \text{MgCl}_2 + \text{H}_2\text{O}$, $\text{NaCl} + \text{SrCl}_2 + \text{H}_2\text{O}$ and $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$. Each invariant point of the ternary systems is reflected in the phase diagram. Point A_2 and D_2 are the invariant points of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$, point B_2 is the invariant point of the ternary system $\text{NaCl} + \text{MgCl}_2 + \text{H}_2\text{O}$, at the same time point C_2 is the invariant point of the ternary system $\text{NaCl} + \text{SrCl}_2 + \text{H}_2\text{O}$.

Figure 6 shows the relationship between the liquid water content $J(\text{H}_2\text{O})$ and the liquid composition $J(\text{NaCl})$. On the univariate curve F_2C_2 , the water content of the solution decreases with the increase of $J(\text{NaCl})$, however, the water content of the solution on the other curves does not change obviously with the increase of $J(\text{NaCl})$. Therefore, the water

Table 2 Solubilities of the quaternary system NaCl + MgCl₂ + SrCl₂ + H₂O at 373 K

| No | Composition of solution (100·w(b)) | | | Jänecke index J (g/100 g) | | | | Equilibrium solids |
|--------------------|---------------------------------------|-----------------------|-----------------------|--|--------------------|--------------------|-------------------------|--------------------|
| | | | | $J(\text{NaCl}) + J(\text{SrCl}_2) + J(\text{MgCl}_2) = 100$ g | | | | |
| | w(NaCl) | w(SrCl ₂) | w(MgCl ₂) | $J(\text{NaCl})$ | $J(\text{SrCl}_2)$ | $J(\text{MgCl}_2)$ | $J(\text{H}_2\text{O})$ | |
| 1, A ₂ | 0 | 1.68 | 41.68 | 0 | 3.85 | 96.15 | 130.77 | Bis + SC |
| 2 | 0.07 | 1.60 | 41.64 | 0.17 | 3.70 | 96.13 | 130.89 | Bis + SC |
| 3 | 0.08 | 1.59 | 41.61 | 0.19 | 3.68 | 96.13 | 131.03 | Bis + SC |
| 4 | 0.12 | 1.53 | 41.63 | 0.28 | 3.53 | 96.19 | 131.07 | Bis + SC |
| 5, E ₂ | 0.13 | 1.51 | 41.53 | 0.30 | 3.49 | 96.21 | 131.63 | Bis + SC + NC |
| 6, B ₂ | 0.15 | 0 | 42.10 | 0.35 | 0 | 99.65 | 136.69 | Bis + NC |
| 7 | 0.14 | 0.63 | 41.69 | 0.34 | 1.48 | 98.18 | 135.52 | Bis + NC |
| 8 | 0.13 | 1.03 | 41.53 | 0.31 | 2.41 | 97.28 | 134.22 | Bis + NC |
| 9 | 0.13 | 1.46 | 41.44 | 0.31 | 3.40 | 96.29 | 132.34 | Bis + NC |
| 10, C ₂ | 3.60 | 48.20 | 0 | 6.95 | 93.05 | 0 | 93.05 | NC + SCH |
| 11 | 3.18 | 41.16 | 5.89 | 6.33 | 81.95 | 11.72 | 99.11 | NC + SCH |
| 12 | 2.63 | 33.51 | 10.61 | 5.62 | 71.68 | 22.70 | 113.91 | NC + SCH |
| 13 | 2.14 | 27.00 | 15.99 | 4.74 | 59.84 | 35.42 | 121.60 | NC + SCH |
| 14 | 1.73 | 20.29 | 22.48 | 3.89 | 45.60 | 50.51 | 124.72 | NC + SCH |
| 15 | 1.39 | 14.75 | 27.28 | 3.19 | 33.98 | 62.83 | 130.32 | NC + SCH |
| 16, F ₂ | 1.04 | 6.68 | 34.71 | 2.44 | 15.75 | 81.81 | 135.69 | NC + SCH + SC |
| 17 | 0.43 | 3.67 | 38.70 | 1.00 | 8.58 | 90.42 | 133.63 | NC + SC |
| 18 | 0.16 | 1.55 | 41.06 | 0.38 | 3.61 | 96.00 | 133.83 | NC + SC |
| 19, D ₂ | 0 | 6.40 | 34.30 | 0 | 15.72 | 84.28 | 145.70 | SC + SCH |
| 20 | 0.09 | 6.42 | 34.33 | 0.22 | 15.71 | 84.06 | 144.84 | SC + SCH |
| 21 | 0.25 | 6.43 | 34.34 | 0.60 | 15.69 | 83.71 | 143.80 | SC + SCH |
| 22 | 0.50 | 6.46 | 34.40 | 1.22 | 15.63 | 83.15 | 141.74 | SC + SCH |
| 23 | 0.90 | 6.50 | 34.30 | 2.15 | 15.59 | 82.26 | 139.82 | SC + SCH |

NC: NaCl, Bis: MgCl₂·6H₂O, SC: SrCl₂·H₂O, SCH: SrCl₂·2H₂O. Standard uncertainty u are $u(T)=0.1$ K, $u_r(w(\text{MgCl}_2))=0.003$, $u_r(w(\text{SrCl}_2))=0.005$, $u_r(w(\text{NaCl}))=0.003$

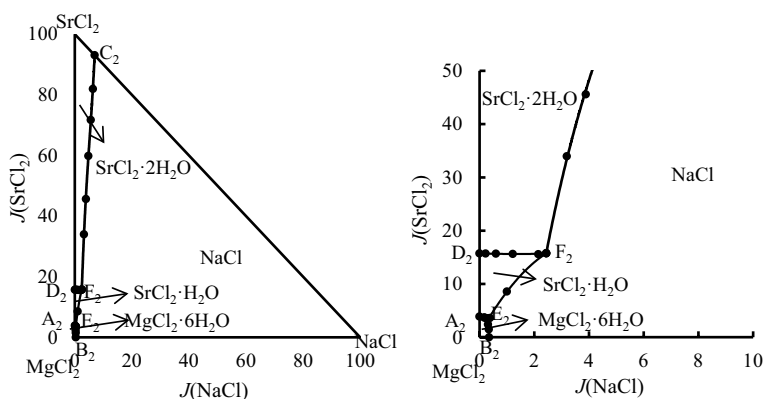


Fig. 5 Dry salt diagram of the quaternary system NaCl + MgCl₂ + SrCl₂ + H₂O and its enlarged diagram at 373 K

Fig. 6 Water content diagram of the quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

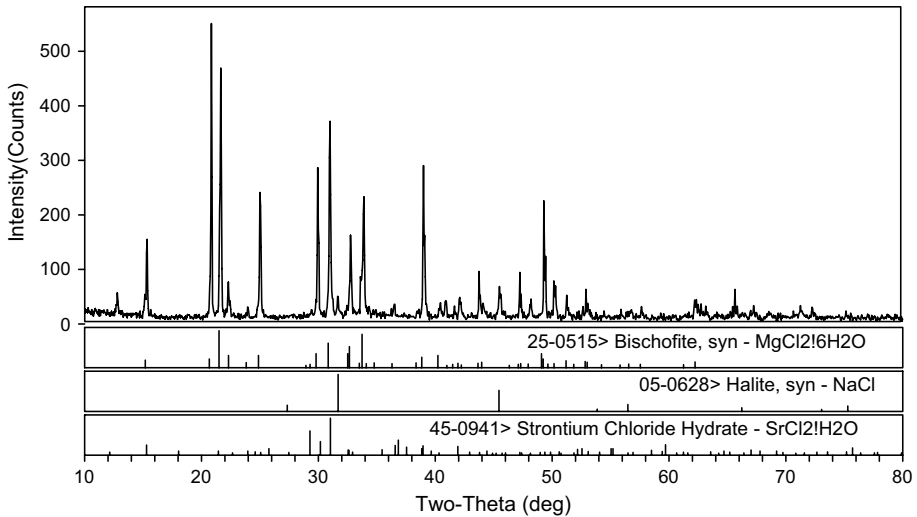
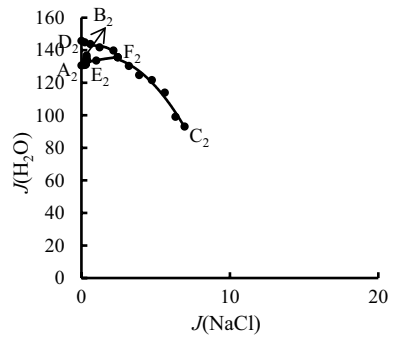


Fig. 7 X-ray diffraction photograph of the invariant point E_2 ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaCl} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$) in the quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

content reaches its minimum at the point C_2 ($J=93.05$), which indicates that the total salt concentration reaches its maximum at the point C_2 .

3.3 The Quaternary System $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

The method for the identification of the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K is the same as above. All the measured values are given in Table 3. The dry salt phase diagram is plotted based on the experimental results in Fig. 9. As shown in Fig. 9, the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ embodies three ternary systems, which are as follow: $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$, $\text{KCl} + \text{MgCl}_2 + \text{H}_2\text{O}$ and $\text{KCl} + \text{SrCl}_2 + \text{H}_2\text{O}$. A_3 and H_2 are the invariant points of the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$, B_3 and C_3 are the invariant points of the ternary system $\text{KCl} + \text{MgCl}_2 + \text{H}_2\text{O}$, and D_3 is the invariant point of the ternary system $\text{KCl} + \text{SrCl}_2 + \text{H}_2\text{O}$. This quaternary system that generates a potassium and magnesium

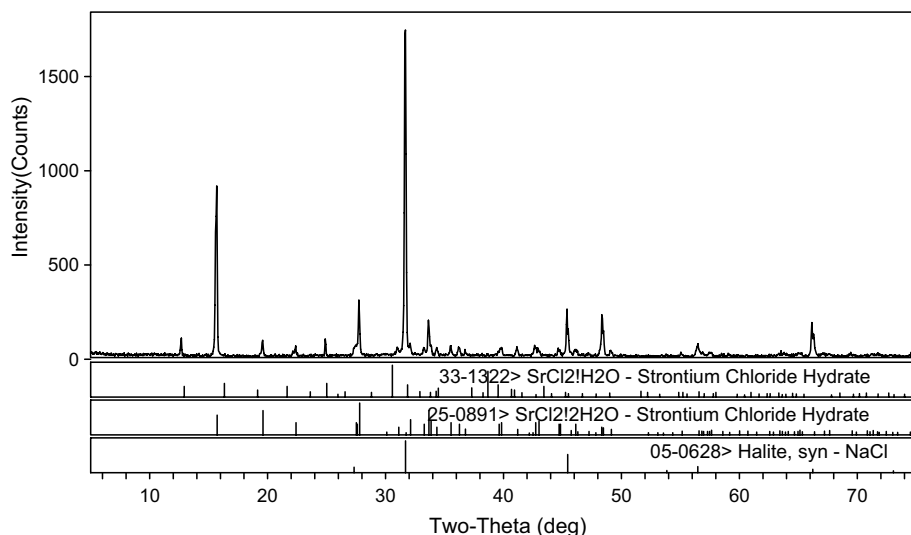


Fig. 8 X-ray diffraction photograph of the invariant point F_2 ($\text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{NaCl}$) in the quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

chloride double salt named carnallite (Car), is made up of three invariant points (E_3 , F_3 and G), seven univariant curves and five crystallizing fields. The invariant point E_3 is saturated with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and the content of the saturated solution is $w(\text{KCl}) = 0.52\%$, $w(\text{SrCl}_2) = 1.36\%$, $w(\text{MgCl}_2) = 41.40\%$. The invariant point F_3 is saturated with $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and the composition of the equilibrium solution is $w(\text{KCl}) = 4.54\%$, $w(\text{SrCl}_2) = 6.47\%$, $w(\text{MgCl}_2) = 33.53\%$. The last invariant point G is at $w(\text{KCl}) = 6.18\%$, $w(\text{SrCl}_2) = 10.85\%$, $w(\text{MgCl}_2) = 29.76\%$, where KCl , $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ coexist. The seven univariant curves are namely A_3E_3 , B_3E_3 , C_3G , D_3G , H_2F_3 , E_3F_3 , and F_3G . The five crystallization zones are $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and KCl , respectively. As can be seen from Fig. 9, the crystalline region of KCl is the largest, however, that of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is the smallest, which indicate that KCl has the lowest solubility and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ has the largest.

The water content diagram of the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K is constructed in Fig. 10. It illustrates the relationship between the water content $J(\text{H}_2\text{O})$ and the liquid composition $J(\text{KCl})$. On the univariant curve GC_3 , the water content of the solution increases with increasing $J(\text{KCl})$ and reaches its maximum at the point C_3 , which shows that the total salts concentration reaches its minimum at the point C_3 . On the contrary, the relationship on curve GD_3 is opposite to that of the curve GC_3 , hence the total salts concentration at the point D_3 reaches its maximum.

Figure 11 is the X-ray diffraction pattern of the saturated point E_3 , where the equilibrium solids $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are all identified. Figure 12 shows that the invariant point F_3 is saturated with solid phases $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Table 3 Solubilities of the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

| No | Composition of solution (100-w(b)) | | | Jänecke index J (g/100 g) | | | | Equilibrium solids |
|-----------|---------------------------------------|--------------------|--------------------|---|--------------------|--------------------|-------------------------|--------------------|
| | | | | $J(\text{KCl}) + J(\text{SrCl}_2) + J(\text{MgCl}_2) = 100$ g | | | | |
| | $w(\text{KCl})$ | $w(\text{SrCl}_2)$ | $w(\text{MgCl}_2)$ | $J(\text{KCl})$ | $J(\text{SrCl}_2)$ | $J(\text{MgCl}_2)$ | $J(\text{H}_2\text{O})$ | |
| 1, A_3 | 0 | 1.68 | 41.68 | 0 | 3.87 | 96.13 | 130.63 | SC + Bis |
| 2 | 0.17 | 1.64 | 41.61 | 0.40 | 3.78 | 95.82 | 130.29 | SC + Bis |
| 3 | 0.30 | 1.47 | 41.49 | 0.69 | 3.41 | 95.90 | 131.15 | SC + Bis |
| 4 | 0.41 | 1.37 | 41.38 | 0.95 | 3.18 | 95.87 | 131.69 | SC + Bis |
| 5, E_3 | 0.52 | 1.36 | 41.40 | 1.19 | 3.14 | 95.67 | 131.10 | SC + Bis + Car |
| 6, B_3 | 0.50 | 0 | 42.00 | 1.18 | 0 | 98.82 | 135.32 | Car + Bis |
| 7 | 0.55 | 0.58 | 41.89 | 1.27 | 1.34 | 97.39 | 132.47 | Car + Bis |
| 8 | 0.57 | 0.94 | 41.53 | 1.33 | 2.17 | 96.50 | 132.35 | Car + Bis |
| 9 | 0.56 | 1.19 | 41.34 | 1.29 | 2.77 | 95.94 | 132.05 | Car + Bis |
| 10 | 0.58 | 1.31 | 41.46 | 1.33 | 3.02 | 95.65 | 130.73 | Car + Bis |
| 11, C_3 | 6.40 | 0 | 31.30 | 16.98 | 0 | 83.02 | 165.22 | KC + Car |
| 12 | 6.37 | 1.48 | 31.09 | 16.35 | 3.80 | 79.85 | 156.84 | KC + Car |
| 13 | 6.41 | 2.64 | 30.79 | 16.10 | 6.62 | 77.28 | 150.96 | KC + Car |
| 14 | 6.46 | 4.23 | 30.22 | 15.79 | 10.33 | 73.87 | 144.49 | KC + Car |
| 15 | 6.43 | 6.11 | 29.77 | 15.19 | 14.45 | 70.36 | 136.32 | KC + Car |
| 16 | 6.47 | 10.35 | 29.38 | 14.00 | 22.41 | 63.59 | 116.45 | KC + Car |
| 17, D_3 | 10.80 | 46.70 | 0 | 18.78 | 81.22 | 0 | 73.90 | KC + SCH |
| 18 | 9.53 | 39.62 | 4.92 | 17.63 | 73.28 | 9.09 | 84.93 | KC + SCH |
| 19 | 8.51 | 32.31 | 11.10 | 16.40 | 62.23 | 21.37 | 92.59 | KC + SCH |
| 20 | 7.66 | 22.35 | 19.68 | 15.43 | 44.97 | 39.60 | 101.27 | KC + SCH |
| 21 | 6.86 | 16.79 | 24.39 | 14.28 | 34.95 | 50.77 | 108.14 | KC + SCH |
| 22, G | 6.18 | 10.85 | 29.76 | 13.21 | 23.19 | 63.60 | 113.69 | KC + Car + SCH |
| 23 | 5.51 | 9.30 | 31.05 | 12.02 | 20.28 | 67.70 | 118.07 | Car + SCH |
| 24 | 4.47 | 6.49 | 33.79 | 9.98 | 14.51 | 75.51 | 123.45 | Car + SCH |
| 25 | 3.53 | 4.48 | 37.04 | 7.84 | 9.95 | 82.21 | 121.96 | Car + SC |
| 26 | 2.63 | 3.04 | 38.24 | 6.00 | 6.92 | 87.08 | 127.74 | Car + SC |
| 27 | 1.14 | 2.06 | 40.00 | 2.63 | 4.77 | 92.60 | 131.49 | Car + SC |
| 28 | 0.57 | 1.50 | 41.21 | 1.31 | 3.47 | 95.23 | 131.06 | Car + SC |
| 29, H_2 | 0 | 6.40 | 34.30 | 0 | 15.72 | 84.28 | 145.70 | SC + SCH |
| 30 | 1.11 | 6.42 | 34.17 | 2.66 | 15.39 | 81.95 | 139.84 | SC + SCH |
| 31 | 1.71 | 6.39 | 34.07 | 4.05 | 15.15 | 80.81 | 137.18 | SC + SCH |
| 32 | 2.48 | 6.42 | 33.94 | 5.78 | 14.98 | 79.23 | 133.47 | SC + SCH |
| 33 | 3.29 | 6.37 | 33.10 | 7.70 | 14.89 | 77.41 | 133.88 | SC + SCH |
| 34, F_3 | 4.54 | 6.47 | 33.53 | 10.19 | 14.53 | 75.27 | 124.52 | SC + SCH + Car |

KC: KCl, Bis: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, SC: $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, SCH: $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, Car: $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Standard uncertainty u are $u(T) = 0.1$ K, $u_r(w(\text{MgCl}_2)) = 0.003$, $u_r(w(\text{KCl})) = 0.005$, $u_r(w(\text{SrCl}_2)) = 0.005$

3.4 Method Verification

The isothermal method is a classical method which has been used to study isothermal phase diagrams for a long time. The reliability and repeatability of the experimental results

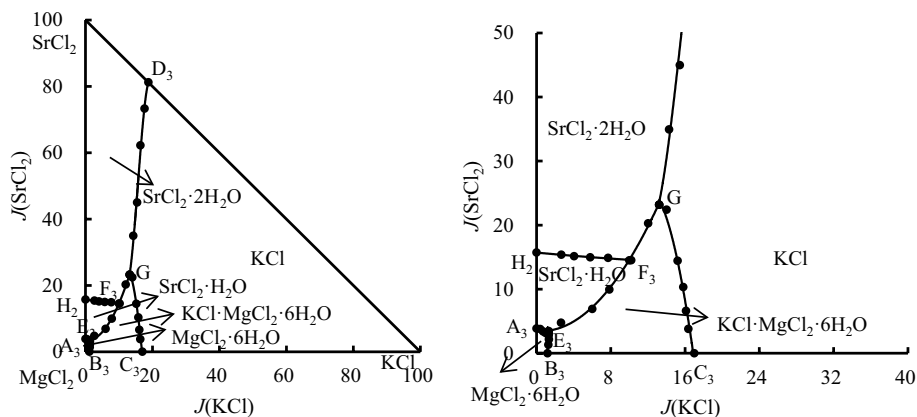


Fig. 9 Dry salt diagram of the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and its enlarged diagram at 373 K

Fig. 10 Water content diagram of the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

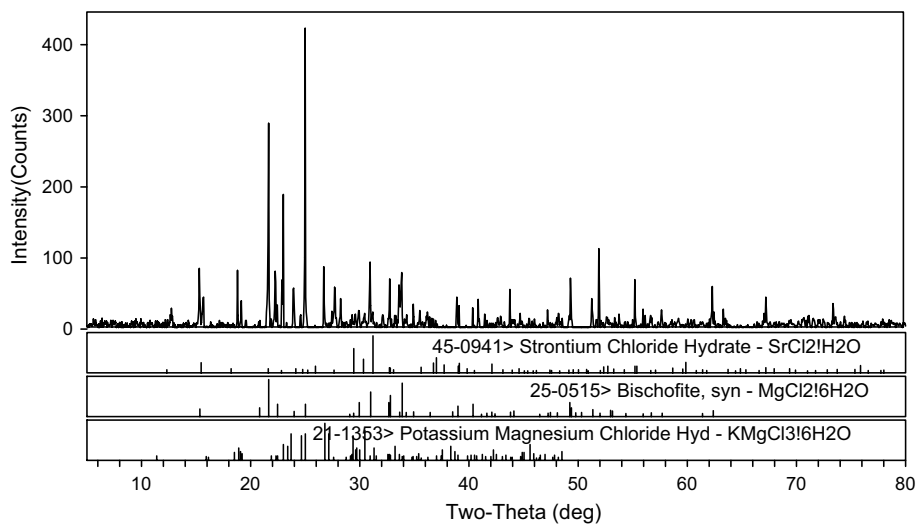
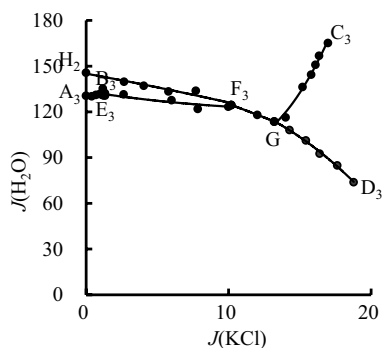


Fig. 11 X-ray diffraction photograph of the invariant point E_3 ($\text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

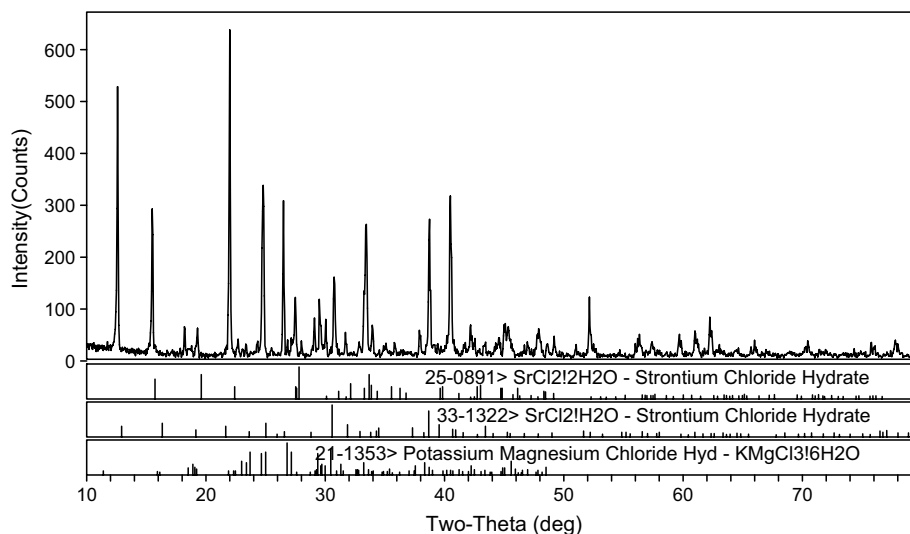


Fig. 12 X-ray diffraction photograph of the invariant point F_3 ($\text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in the quaternary system $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ at 373 K

have been verified by a large number of related studies, which ensure the reliability of the experimental data. In the process of the experiments, we selected at least three groups of parallel samples to verify the repeatability of the experiment, especially the boundary points and the invariant points. For example, in the first point (A_1) of Table 1, the mass fraction of MgCl_2 measured is 42.29%, while that reported in the literature [4] is 42.2%, the standard deviation of these two results is 0.064%. And the mass fraction of SrCl_2 measured in the seventh point (B_1) is 50.25%, while that in literature [5] is 50.8%, the standard deviation of these two results is 0.39%. The results of the determination and the results reported in the literature agree within the experimental error.

Some other systems at 373 K had also been carried out by our group using the isothermal method, such as the ternary system $\text{KCl} + \text{KBr} + \text{H}_2\text{O}$ [22], where the mass fraction of KCl measured in the boundary point is 36.04%, while that reported in the literature [4] is 35.90% and in the ternary $\text{NaCl} + \text{ZnCl}_2 + \text{H}_2\text{O}$ [23], the mass fraction of NaCl measured in the boundary point is 28.25%, while that reported in the literature [4] is 28.20%. In addition, the invariant point data of the ternary system $\text{NaCl} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ at 373 K [24] studied by another group are $w(\text{NaCl}) = 26.19\%$, $w(\text{Na}_2\text{SO}_4) = 4.38\%$, while that reported in the literature [4] are $w(\text{NaCl}) = 25.9\%$, $w(\text{Na}_2\text{SO}_4) = 4.40\%$. These data agree within the experimental error. Therefore, our experimental method at 373 K is reliable.

4 Conclusions

The ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and quaternary systems $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and $\text{KCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ were brought into equilibrium at 373 K by means of the isothermal method. Solubilities and the corresponding solid phases were determined. The results show that the ternary system $\text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ and quaternary system $\text{NaCl} + \text{MgCl}_2 + \text{SrCl}_2 + \text{H}_2\text{O}$ belong to simple co-saturated systems; however, there is a

complex salt $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ in the quaternary system $\text{KCl}+\text{MgCl}_2+\text{SrCl}_2+\text{H}_2\text{O}$. The ternary system $\text{MgCl}_2+\text{SrCl}_2+\text{H}_2\text{O}$ at 373 K has two invariant points, three univariant curves and three crystallization areas ($\text{SrCl}_2\cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2\cdot\text{H}_2\text{O}$ and $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$). The quaternary system $\text{NaCl}+\text{MgCl}_2+\text{SrCl}_2+\text{H}_2\text{O}$ at 373 K contains two co-saturated points, five univariant curves and four crystallization regions corresponding to NaCl , $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2\cdot\text{H}_2\text{O}$ and $\text{SrCl}_2\cdot 2\text{H}_2\text{O}$. The quaternary system $\text{KCl}+\text{MgCl}_2+\text{SrCl}_2+\text{H}_2\text{O}$ at 373 K is made of three invariant points, seven univariant curves and five crystallization fields, which are KCl , $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2\cdot\text{H}_2\text{O}$, $\text{SrCl}_2\cdot 2\text{H}_2\text{O}$ and $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, respectively.

Acknowledgements This project was supported by the National Natural Science Foundation of China (41373062, U1407108) and scientific research and innovation team in Universities of Sichuan Provincial Department of Education (15TD0009).

Compliance with Ethical Standards

Conflict of interest The authors declare no competing financial interest.

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