Metastable Phase Equilibria in the Aqueous Ternary Systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O at 323.15 K

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The metastable phase equilibria in the ternary systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O were studied at 323.15 K using an isothermal evaporation method. The solubilities, densities, and refractive indices of the equilibrated solution were measured. The crystalloid forms of the solid phase were determined using chemical analysis and an X-ray diffraction method. On the basis of the experimental data, the metastable equilibrium phase diagrams and the physicochemical properties vs composition in the ternary systems at 323.15 K were plotted. In the metastable phase diagram of the ternary system KCl + $MgCl_2$ + H_2O at 323.15 K, there are two invariant points, three univariant curves, and three crystallization fields, corresponding to potassium chloride (KCl), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), and a potassium and magnesium chloride double salt named carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). The salt KCl has the largest crystallization field and can be easily separated from the mixed aqueous solution containing potassium and magnesium chloride using an evaporation method. In the metastable phase diagram of the ternary system KCl + RbCl + H_2O, there are two invariant points and three crystallization fields, corresponding to the single salts potassium chloride (KCl) and rubidium chloride (RbCl) and a solid solution of potassium and rubidium chloride [(K, Rb)Cl]. The crystallization field of the solid solution (K, Rb)Cl almost occupies all the phase region; thus, it is difficult to separate potassium from rubidium in chloride solution by only using evaporation and crystallization methods at 323.15 K.

Introduction

Besides salt lake brines, underground brines are another kind of basilic liquid mineral resource. The underground brine, widely distributed in the Sichuan Basin, is famous for its high concentrations of sodium, potassium, lithium, borate, magnesium, and the rare alkali elements rubidium and cesium, especially the underground brine in Pingluoba.[1] The Pingluoba underground brine belongs to the marine sedimentary deep brine, with distinguishing features of deep buried depth (over 4500 m), high pressure (about 97 MPa), high temperature (about 393 K), and high salinity (over 420 $g \cdot L^{-1}$).[1] The Pingluoba underground brine is of the chloride type, and its main components can be described as the complex system $Li^+ + K^+ + Na^+ + Rb^+ + Mg^{2+} + Cl^-$ + bromine + borate + H_2O. After the brine is exploited, the salt NaCl is supersaturated, precipitated, and borated, and the bromine can be enriched and separated by means of acidification and an extraction method; thus, the main component of the brine can be simplified as the quinary system $Li^+ + K^+ + Rb^+ + Mg^{2+} + Cl^- + H_2O$. In this quinary system, the salt magnesium chloride can be formed as various hydrated salts and the solid solution or the double salt can be easily formed between the coexisting ions, which increases the complexity of the investigation on the phase equilibrium.

It is well-known that phase diagrams are the basis and guidance of utilization of liquid mineral resources and separation techniques of salts. A lot of work on the phase equilibria has been done, including our research group work.[2–4] However, most of the effort has focused on the salt lake brine systems; research aimed at the component characteristics of underground brine has not been reported in the literature yet.

The ternary systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O are two important subsystems of the above-mentioned complex system. No report has been found to describe the metastable phase equilibria of these two systems at 323.15 K. In this paper, the metastable phase equilibria of the ternary systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O are presented. The solubilities, densities, and refractive indices of the equilibrated solution in the systems were measured at 323.15 K.

Experiments

Reagents. All chemicals used were of analytical grade purity and were obtained from either the Chengdu Kelong Chemical Reagent Plant or the Sichuan State Lithium Materials Co. Ltd. They are potassium chloride (KCl; 99.5 %), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$; 98.0 %), and rubidium chloride (RbCl; 99.5 %). The electrical conductivity of doubly deionized water was less than 1×10^{-4} $S \cdot m^{-1}$ and the pH was 6.60.

Instruments. An SHH-250 type thermostatic evaporator made by the Chongqing Inborn Instrument Corp., China, was used for the metastable phase equilibrium experiments. The equipment has a temperature-controlling apparatus with a blower accessory to control the temperature and the evaporation quantity of the evaporating system. The evaporation rate is (4.0 to 5.5) $mm \cdot d^{-1}$, the operating range of the temperature is (258.15 to 373.15) K, and the temperature precision is ± 0.1 K.

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Table 1. Solubilities, Refractive Indices, and Densities of Equilibrated Solutions in the Ternary System KCl + $MgCl_2$ + H_2O at 323.15 K[a]

	density		composition of equilibrated solution, 100 w(B)		composition of wet solid phase, 100 w(B)		
no.	$g \cdot cm^{-3}$	refractive index, n_D	B = KCl	B = $MgCl_2$	B = KCl	B = $MgCl_2$	equilibrium solid phase
1A	1.2020	1.3696	28.99	0.00			KCl
2	1.2912	1.3727	24.60	3.52	71.51	1.36	KCl
3	1.2947	1.3778	23.63	4.05	63.16	1.98	KCl
4	1.2932	1.3778	23.48	4.39	71.71	1.76	KCl
5	1.3016	1.3788	23.22	4.69	65.61	2.23	KCl
6	1.3156	1.3779	22.73	5.06	70.75	2.11	KCl
7	1.3098	1.3791	21.38	6.04	73.25	2.04	KCl
8	1.3171	1.3805	20.59	7.09	63.30	3.38	KCl
9	1.3243	1.3810	19.17	8.05	56.00	4.63	KCl
10	1.3348	1.3854	16.63	10.44	73.23	3.84	KCl
11	1.3320	1.3884	12.76	14.30	42.62	9.56	KCl
12	1.3590	1.3994	10.39	17.35	37.59	12.70	KCl
13E_1	1.3767	1.4090	4.60	25.68	34.36	18.14	KCl + Car
14	1.4080	1.4172	2.14	29.47	12.98	30.21	Car
15	1.4220	1.4251	1.61	32.92	13.23	33.96	Car
16E_2	1.4883	1.4336	0.20	37.11	0.17	41.91	Bis + Car
17B	1.4486	1.4324	0.00	37.35			Bis

[a] Definitions: w(B), mass fraction of B; Bis, $MgCl_2 \cdot 6H_2O$; Car, $KCl \cdot MgCl_2 \cdot 6H_2O$.

A Siemens D500 X-ray diffractometer with Ni-filtered Cu Kα radiation and a Hitachi S-530 scanning electron microscope were used to analyze the crystalloid form of the solid phases. The operating conditions of the X-ray diffractometer were 35 kV and 25 mA.

An inductively coupled plasma optical emission spectrometer (type 5300 V, PerkinElmer Instrument Corp. of America) was employed for the determination of the rubidium ion concentration in solution.

A 2WAJ Abbe refractometer was used for measuring the refractive index of the equilibrated solution with a precision of 0.0001.

Experimental Methods. The metastable phase equilibria of the ternary system were studied at 323.15 K using an isothermal evaporation method. According to the phase equilibrium composition, the appropriate quantities of salts and deionized water were mixed together as a series of artificial synthesized brines and loaded into clean opened polyethylene containers (24 cm long, 14 cm wide, and 7 cm high). The containers were placed in a thermostatic evaporator (SHH-250 type) for isothermal evaporation. The temperature was controlled to (323.15 ± 0.1) K measured by thermal resistance. When enough new solid appeared in the evaporating containers, the solids were separated from the solutions. The obtained wet salts were analyzed by a chemical method named the Schreinemakers method to determine the composition of the salts.[5] 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. The observations and photography of the solid phases were determined by scanning electron microscopy (SEM). Meanwhile, a 5.0 mL sample of the clarified solution was taken from the liquid phase through a pipet and then diluted to a 50 mL final volume in a volumetric flask filled with deionized water to analyze the liquid-phase compositions. Some other filtrates were used to measure the relative physicochemical properties individually. The remainder of the solution continued to be evaporated to reach the next measuring point. The same procedure was repeated until the solution was fully evaporated.

The densities of the equilibrated solution were measured with a gravity bottle method with a precision of ± 0.0002 g and used for mass fraction calculation of liquid components. The specific gravity bottle method with correction of the air floating force was used. The correction equation for density, ρ ($g \cdot cm^{-3}$), is

$$\rho = \frac{m_1 + A}{m_2 + A} \cdot \rho_0 \tag{1}$$

where $\rho_0 = 0.9982\ g \cdot cm^{-3}$, the density of distilled water at 293.15 K, m_1 is the mass of the gravity bottle filled with sample, m_2 is the mass of the gravity bottle filled with distilled water, and A is the correction value of the air floating force

$$A = \rho_a \cdot \frac{m_2}{0.9970} \tag{2}$$

where $\rho_a = 0.0012\ g \cdot cm^{-3}$, the density of dry air at 293.15 K and normal atmospheric pressure.[6]

The sample was obtained at 323.15 K and measured at 293.15 K. The excursion caused by the temperature difference was calibrated by using a multipoint temperature revision method.[7]

Analytical Methods. The amount of the composition of K^+ and Rb^+ in the liquids and their corresponding wet solid phases was measured by a sodium tetraphenylborate−cetyltrimethylammonium bromide titration (precision ± 0.5 %).[8] The composition of Rb^+ in the liquids and their corresponding wet solid phases was measured by inductively coupled plasma optical emission spectrometry (ICP-OES; precision less than 0.06 %, type ICP-OES 5300 V), and then the composition of K^+ was calculated by a subtraction method. The Mg^{2+} concentration was determined by ethylenediaminetetraacetic acid titration (precision less than 0.5 %).[8] The Cl^- concentration was determined by $AgNO_3$ titration with a precision of 0.3 %.[9] Each analysis was repeated three times, and the average value of the three measurements was considered as the final value of the analysis.

Results and Discussion

KCl + $MgCl_2$ + H_2O System. The experimental results of the solubilities and properties of the ternary system KCl + $MgCl_2$ + H_2O at 323.15 K are shown in Table 1. In Table 1, the ion concentration values of the metastable equilibrated solution and the wet salts are both expressed in mass fraction w(B). w(B) expresses the B salt in grams per 100 g of solution or wet solid phase, that is, g/(100 g of solution) or g/(100 g of wet solid solution). On the basis of the experimental data, the metastable equilibrium phase diagram is plotted in Figure 1. In Figure 1, the black points present the experimental points, and

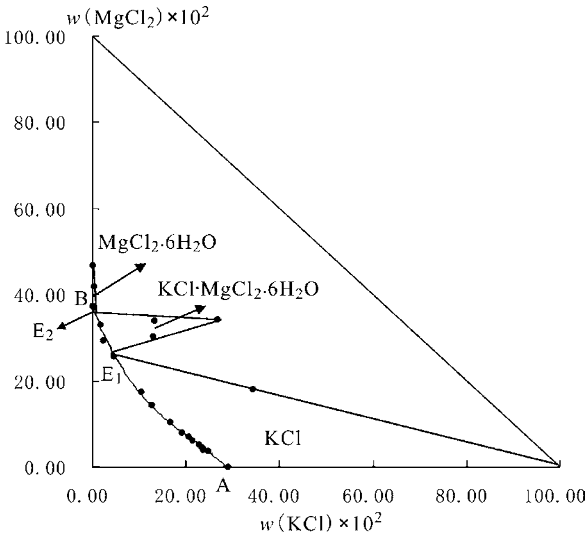


Figure 1. Metastable phase diagram of the ternary system KCl + $MgCl_2$ + H_2O at 323.15 K: ●, metastable experimental points; —, metastable isothermal curve.

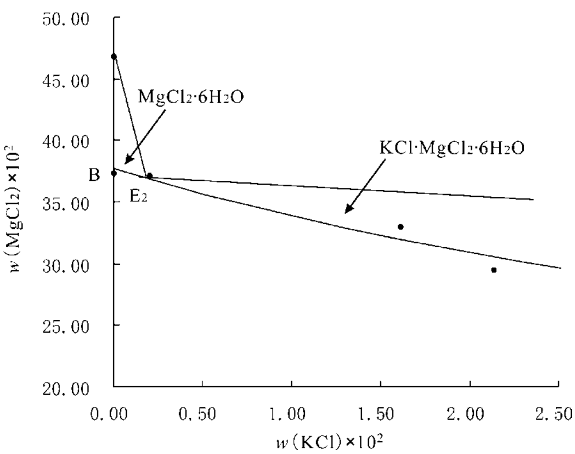


Figure 2. Partial enlarged diagram of Figure 1.

the solid lines through the points express the isothermal evaporation curves. Figure 2 is a partial enlarged diagram of Figure 1.

The phase diagram of the ternary system consists of two invariant points, three univariant curves, and three crystallization fields. The three crystallization fields correspond to the single salts KCl and $MgCl_2 \cdot 6H_2O$ and double salt $KCl \cdot MgCl_2 \cdot 6H_2O$. The salt $MgCl_2 \cdot 6H_2O$ causes a salting out effect on the salt KCl. The crystallization field of the salt $MgCl_2 \cdot 6H_2O$ is the smallest, while the crystallization field of the salt KCl is the largest. These results indicate that KCl is more easily saturated and crystallized from the solution containing potassium and magnesium chloride.

The three univariant curves saturated with one salt in the system correspond to curves AE_1, E_1E_2, and BE_2.

Two invariant points in this system are noted as E_1 and E_2. Point E_2 is a commensurate invariant point, whereas point E_1 is an incommensurate invariant point. Point E_1 is saturated with salts KCl and $KCl \cdot MgCl_2 \cdot 6H_2O$. The mass fraction composition of the corresponding liquid phase is 100 w(KCl) = 4.60, 100 $w(MgCl_2)$ = 25.68. Point E_2 is saturated with salts $MgCl_2 \cdot 6H_2O$ and $KCl \cdot MgCl_2 \cdot 6H_2O$. The mass fraction composition of the corresponding liquid phase is 100 w(KCl) = 0.20, 100 $w(MgCl_2)$ = 37.11.

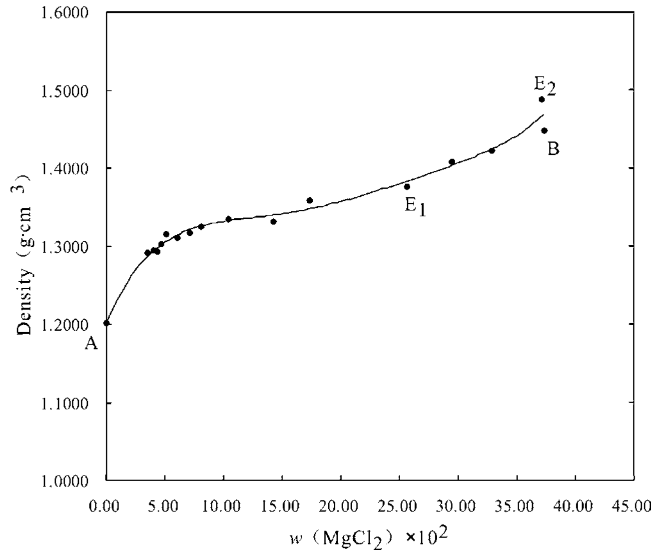


Figure 3. Density vs composition diagram of the ternary system KCl + $MgCl_2$ + H_2O at 323.15 K: ●, experimental value; —, experimental relationship diagram.

According to the following empirical equation about the density calculation of the mixed solution, the density has a positively correlated relationship with the composition:[10]

$$\ln \frac{d}{d_0} = \sum A_i \cdot w_i$$

where d and d_0 refer to the density values of the solution and pure water at 323.15 K, respectively; the density d_0 for pure water at 323.15 K is 0.98807 g·cm^{-3}. A_i is the constant for the ith component in the solution and can be obtained from the densities of the two boundary values in the ternary system with the mass fraction at 323.15 K. The constants A_i of KCl and $MgCl_2$ for calculation of the density of the solution are 0.0079 and 0.0102, respectively.

In this system, the solubility of the salt $MgCl_2$ is greater than that of the salt KCl; therefore, the concentration of $MgCl_2$ is the main factor affecting the solution density. Figure 3 is the density vs composition diagram of this system. The density increases with an increase of the concentration of $MgCl_2$ and reaches a maximum value at the invariant point E_2.

Figure 4 is the refractive index vs composition diagram of this system. The refractive index also changes regularly with the mass fraction changes of $MgCl_2$ in the solution. At the invariant point E_2, the system has the largest refractive index.

During the evaporation process, the evaporation rate slows down with increasing concentration of magnesium chloride in solution. This may be caused by the salt magnesium chloride crystallizing with a large amount of water and with huge hygroscopicity and moisture retention.

KCl + RbCl + H_2O System. The experimental results of the solubilities and properties of the ternary system KCl + RbCl + H_2O at 323.15 K are shown in Table 2. In Table 2, the composition of the metastable equilibrated solution and the wet salts are both expressed in mass fraction w(B). The experimental solubility isothermal metastable phase diagram of the system at 323.15 K is plotted in Figure 5. Figures 6 and 7 are two partial enlarged phase diagrams of Figure 5.

The phase diagram of the ternary system consists of three crystallization fields, corresponding to the single salts KCl and RbCl and a solid solution, (K, Rb)Cl.

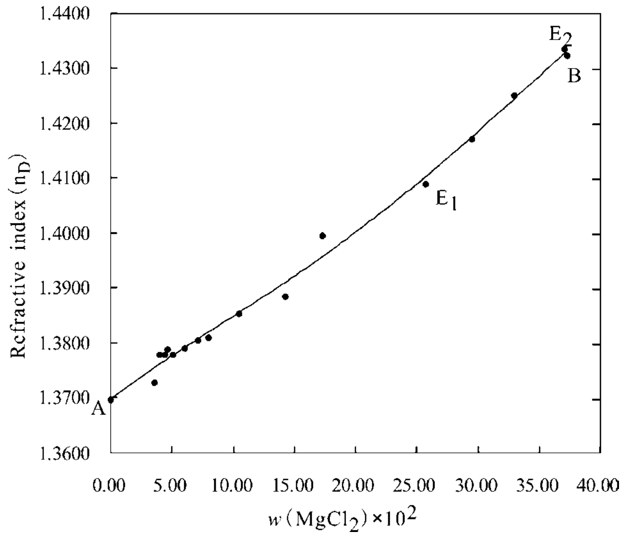


Figure 4. Refractive index vs composition diagram of the ternary system $KCl + MgCl_2 + H_2O$ at 323.15 K: ●, experimental value; —, experimental relationship diagram.

Two invariant points in this system are noted as E_1 and E_2. The equilibrated solid phases in the invariant points were confirmed with X-ray diffraction analysis. Figures 8 and 9 give the XRD photograph and the SEM photograph of the salts corresponding to the invariant point E_1, respectively. The results show that invariant point E_1 is cosaturated with salts KCl and (K, Rb)Cl. Figure 10 gives the XRD photograph of the invariant point E_2, which shows that invariant point E_2 is cosaturated with salts RbCl and (K, Rb)Cl. The mass fraction composition of the corresponding liquid phase of point E_1 is 100 w(KCl) = 27.51, 100 w(RbCl) = 1.50, while that of point E_2 is 100 w(KCl) = 1.17, 100 w(RbCl) = 48.15.

In this system, the solubility of RbCl is greater than that of KCl; therefore, the concentration of RbCl is the main factor affecting the solution density. Figure 11 is the density vs composition diagram of the equilibrated solution. The density is positively correlated with the concentration of RbCl. At the invariant point E_2, the system has the largest density.

Figure 12 is the refractive index vs composition diagram of this system. The refractive index increases with increasing concentration of RbCl and reaches a maximum value at the invariant point E_2.

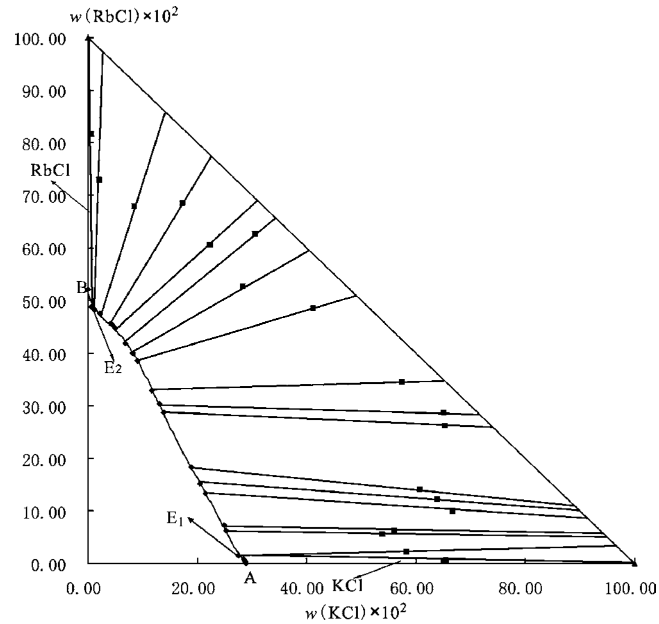


Figure 5. Metastable phase diagram of the ternary system $KCl + RbCl + H_2O$ at 323.15 K: ●, metastable experimental points; —, metastable isothermal curve.

Conclusions

The solubilities, densities, and refractive indices of the equilibrated solution of the systems $KCl + MgCl_2 + H_2O$ and $KCl + RbCl + H_2O$ were determined experimentally at 323.15 K. According to the measured data, the metastable equilibrium phase diagrams and the physicochemical properties vs composition were plotted.

The system $KCl + MgCl_2 + H_2O$ is of a complex type; there is a double salt formed at 323.15 K. The double salt of potassium and magnesium chloride was found with the form $KCl\cdot MgCl_2\cdot 6H_2O$. The crystalloid forms of the single salts are KCl and $MgCl_2\cdot 6H_2O$. $MgCl_2\cdot 6H_2O$ is the only crystalloid form of magnesium chloride at 323.15 K, and it has a high solubility. Potassium chloride has the largest crystallization field and can

Table 2. Solubilities, Refractive Indices, and Densities of Equilibrated Solutions in the Ternary System $KCl + RbCl + H_2O$ at 323.15 K

	density		composition of equilibrated solution, 100 w(B)		composition of wet solid phase, 100 w(B)		
no.	$g\cdot cm^{-3}$	refractive index, n_D	B = KCl	B = RbCl	B = KCl	B = RbCl	equilibrium solid phase
1A	1.2020	1.3696	28.99	0.00			KCl
2	1.1977	1.3704	28.66	0.51	65.15	0.41	KCl
3	1.2014	1.3696	28.54	0.86	65.39	0.66	KCl
$4E_1$	1.2266	1.3712	27.51	1.50	58.14	2.25	KCl + (K, Rb)Cl
5	1.2375	1.3720	25.21	6.26	53.79	5.58	(K, Rb)Cl
6	1.2452	1.3725	24.80	7.27	55.96	6.28	(K, Rb)Cl
7	1.2998	1.3744	21.45	13.34	66.60	9.99	(K, Rb)Cl
8	1.2870	1.3764	20.43	15.19	63.79	12.33	(K, Rb)Cl
9	1.2894	1.3780	18.82	18.28	60.71	14.16	(K, Rb)Cl
10	1.4427	1.3836	13.88	28.85	65.24	26.18	(K, Rb)Cl
11	1.4526	1.3854	13.04	30.36	65.11	28.83	(K, Rb)Cl
12	1.4544	1.3864	11.67	32.89	57.33	34.54	(K, Rb)Cl
13	1.4987	1.3890	9.04	38.59	41.18	48.51	(K, Rb)Cl
14	1.5949	1.3900	8.18	39.95	28.38	52.61	(K, Rb)Cl
15	1.5614	1.3918	6.87	41.79	30.60	62.77	(K, Rb)Cl
16	1.6294	1.3917	4.75	44.99	22.27	60.58	(K, Rb)Cl
17	1.6245	1.3915	4.18	45.58	17.31	68.64	(K, Rb)Cl
$18E_2$	1.6463	1.3921	1.17	48.15	2.01	72.91	RbCl + (K, Rb)Cl
19	1.6356	1.3887	0.70	48.84	0.64	81.71	RbCl
20B	1.5576	1.3889	0.00	52.09			RbCl

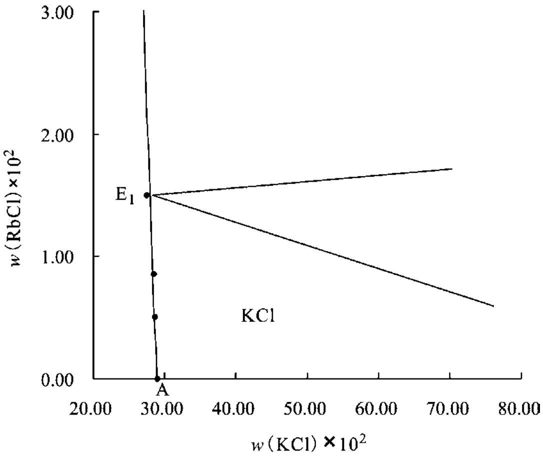


Figure 6. Partial enlarged diagram of Figure 5.

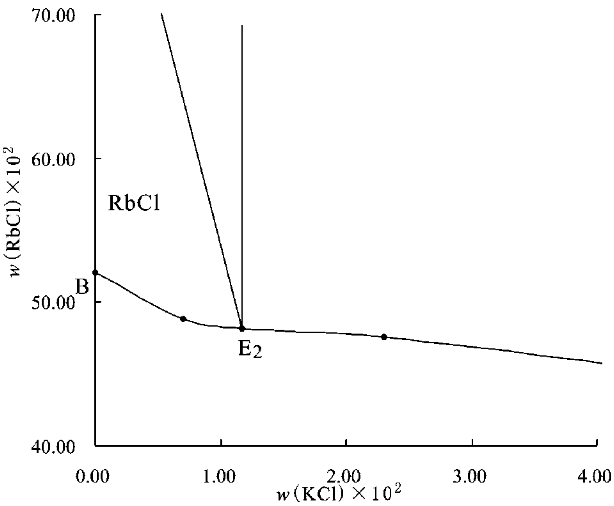
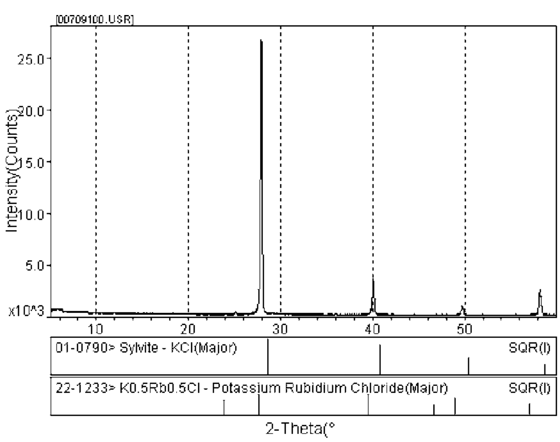


Figure 7. Partial enlarged diagram of Figure 5.



Chemical Formula	KCl	(K, Rb)Cl
D spacing	3.12	1.57
Score	28	59

Figure 8. X-ray diffraction photograph of the invariant point E_1 (KCl + (K, Rb)Cl).

be easily separated from the solution in this system at 323.15 K using a crystallization method.

The system KCl + RbCl + H_2O is also of a complex type. In this system at 323.15 K, the solid solution of a potassium and rubidium chloride was found with the form (K, Rb)Cl. The crystalloid forms of the single salts are KCl and RbCl. (K, Rb)Cl was a completely miscible solid solution, and the crystallization field of the solid solution (K, Rb)Cl almost occupies all the phase region; thus, it is difficult to separate potassium from

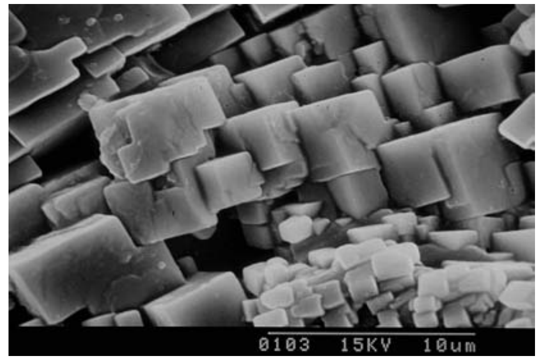
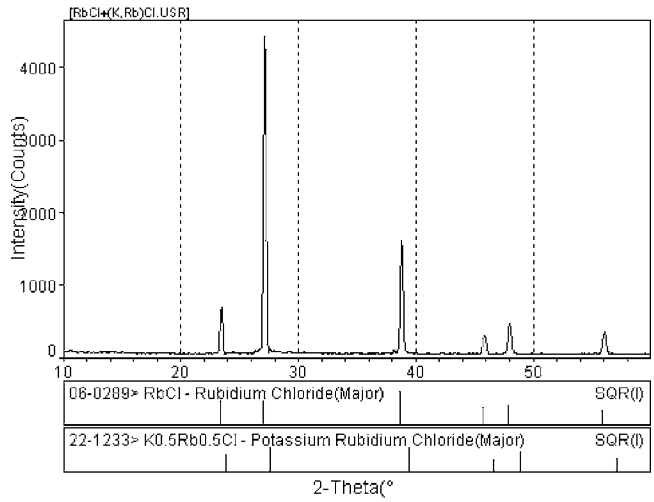


Figure 9. SEM photograph of the invariant point E_1 (KCl + (K, Rb)Cl).



Chemical Formula	RbCl	(K,Rb)Cl
D spacing	3.27	3.23
Score	26	27

Figure 10. X-ray diffraction photograph of the invariant point E_2 (RbCl + (K, Rb)Cl).

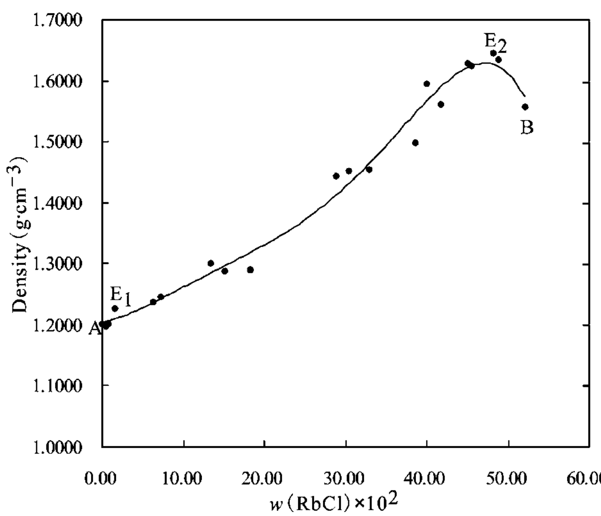


Figure 11. Density vs composition diagram of the ternary system KCl + RbCl + H_2O at 323.15 K: ●, experimental value; —, experimental relationship diagram.

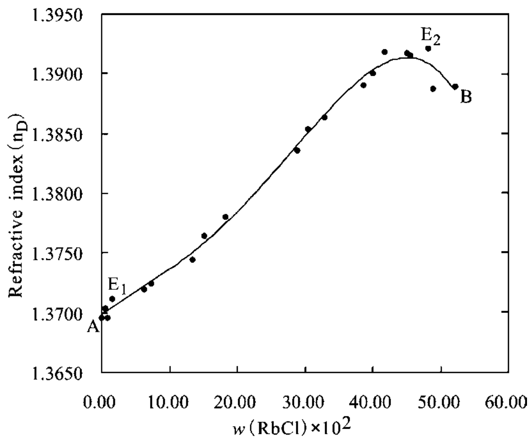


Figure 12. Refractive index vs composition diagram of the ternary system KCl + RbCl + H_2O at 323.15 K: ●, experimental value; —, experimental relationship diagram.

rubidium in chloride solution by only using evaporation and crystallization methods at 323.15 K.

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