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Metastable Phase Equilibria in the Aqueous Ternary Systems $KCl + MgCl_2 + H_2O$ and $KCl + RbCl + H_2O$ at 298.15 K

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ABSTRACT: The solubilities and physicochemical properties such as density and refractive index of the solution in the ternary systems $KCl + MgCl_2 + H_2O$ and $KCl + RbCl + H_2O$ were investigated at 298.15 K using an isothermal evaporation method. The crystalloid forms of the solid phase were determined using chemical analysis and an X-ray diffraction method. On the basis of experimental data, the metastable equilibrium phase diagrams and the physicochemical properties vs composition in the ternary systems at 298.15 K were constructed. In the metastable phase diagram of the ternary system $KCl + MgCl_2 + H_2O$ at 298.15 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 double salt carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). 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), rubidium chloride (RbCl), and a solid solution of potassium and rubidium chloride [(K, Rb)Cl]. Comparisons between the metastable phase diagrams at 298.15 K and at 323.15 K show that the crystallization forms have not changed, while the crystallization zones have slight changes. The calculated densities and refractive indices using an empirical equation have the maximum relative error < 0.016.

INTRODUCTION

Salt lakes and underground brine are widely distributed in the west of China. Sodium, potassium, lithium, borate, magnesium, and the rare alkali elements rubidium and cesium are the major ions in the brine, especially the Pingluoba underground brine.[1] The Pingluoba underground brine is of the chloride type, which belongs to the marine sedimentary deep brine, and the main components of the brine are sodium, potassium, lithium, rubidium, cesium, chlorine, bromine, iodine, borate, etc.[1] After the brine is exploited, sodium chloride is supersaturated and can be precipitated easily; bromine, iodine, and borate can be separated using the acid method and extraction method; although the magnesium content in the original brine is not high, in the exploiting process, magnesium continues to be enriched in the brine. At this point, 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 form various hydrated salts and the solid solution can be easily formed between potassium and rubidium in chloride solution, which increases the complexity of the investigation on the phase equilibrium.

It is well-known that metastable phase equilibrium and phase diagram are the guidance of separation techniques of salts. To the best of our knowledge, the research is almost all concentrated on the metastable equilibrium of the salt lakes and the seawater system,[2−4] including our earlier works;[5−8] research aiming at the component characteristics of underground brine have scarcely been reported in the literature yet. To economically exploit the Pingluoba underground brines, the relevant metastable phase diagrams at different temperatures are required.

The ternary system $KCl + MgCl_2 + H_2O$ and $KCl + RbCl + H_2O$ are two important subsystems of the above-mentioned quinary system. The metastable phase equilibria of these two ternary systems at 323.15 K have been studied in our previous research;[9] the stable phase equilibrium of the ternary system $KCl + RbCl + H_2O$ at 298.15 K has also been reported.[10,11] In this paper, the metastable phase equilibria of the ternary systems $KCl + MgCl_2 + H_2O$ and $KCl + RbCl + H_2O$ at 298.15 K are presented. Comparisons between the metastable phase diagrams at 298.15 K and at 323.15 K have been made.

EXPERIMENTAL SECTION

Apparatus and Reagents. All chemicals used were of analytical grade purity and were obtained from either the Chengdu Kelong Chemical Reagent Plant or the Jiangxi Dongpeng New Materials Co. Ltd. They are potassium chloride (KCl; 99.5 % (w/w)), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$; 98.0 % (w/w)), and rubidium chloride (RbCl; 99.5 % (w/w)). Deionized water, with electrical conductivity less than $1 \cdot 10^{-4}\ S \cdot m^{-1}$ and pH = 6.60, was used in the experiments.

A SHH-250 type thermostatic evaporator, made by the Chongqing Inborn Instrument Corp., China, was used for the metastable phase equilibrium experiments. The 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. Experimental Values of Solubilities, Refractive Indices, and Densities of the Ternary System $KCl + MgCl_2 + H_2O$ at 298.15 K[a]

			composition of equilibrated solution, $w(B) \cdot 10^2$		composition of wet solid phase, $w(B) \cdot 10^2$		
no.	density/$g \cdot cm^{-3}$	refractive index/n_D	$w(KCl)$	$w(MgCl_2)$	$w(KCl)$	$w(MgCl_2)$	equilibrium solid phase
1,A	1.1798	1.3704	26.65	0.00			KCl
2	1.1746	1.3722	21.91	3.10	70.55	1.21	KCl
3	1.1698	1.3726	21.77	3.40	64.24	1.59	KCl
4	1.1730	1.3732	20.81	3.99	76.04	1.33	KCl
5	1.1703	1.3738	20.35	4.57	73.78	1.59	KCl
6	1.1724	1.3747	19.75	5.08	69.87	1.98	KCl
7	1.1741	1.3747	18.96	5.56	58.82	2.91	KCl
8	1.1735	1.3762	16.82	7.53	59.23	3.65	KCl
9	1.1929	1.3855	10.26	14.35	64.63	5.62	KCl
10	1.2206	1.3951	5.96	19.79	40.29	12.85	KCl
11	1.2344	1.3996	4.61	22.90	38.62	14.55	KCl
12,E_1	1.2429	1.4038	3.11	24.72	40.97	15.26	KCl + Car
13	1.2657	1.4126	1.76	29.25	16.71	31.55	Car
14	1.2994	1.4239	0.66	33.54	10.64	34.61	Car
15,E_2	1.3344	1.4326	0.11	35.64	0.10	37.50	Bis + Car
16,B	1.3194	1.4314	0.00	36.31			Bis

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

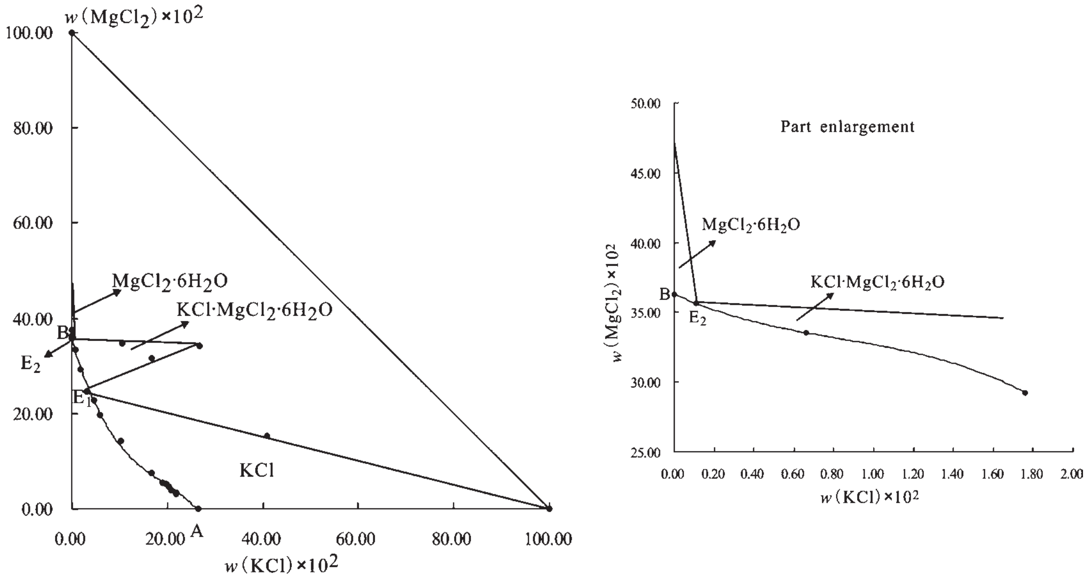


Figure 1. Metastable phase diagram of the ternary system $KCl + MgCl_2 + H_2O$ at 298.15 K.

A Siemens D500 X-ray diffractometer was used to identify the solid phase minerals. The operating conditions of XRD are 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.

A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL 104, supplied by Mettler Toledo Instruments Co., Ltd.) was employed for the determination of the density of solution.

Experimental Method. The isothermal evaporation method was used in this study.[9] According to the phase equilibrium composition, the appropriate quantity salts and deionized water were mixed together and loaded into a clean opened polyethylene containers (24 cm long, 14 cm wide, and 7 cm high). Then, the containers were placed in a thermostatic evaporator (SHH-250 type) for isothermal evaporation. The experimental conditions were a relative humidity of (20 to 30) %, evaporation rate of (4.0 to 5.5) $mm \cdot d^{-1}$. The temperature was controlled to

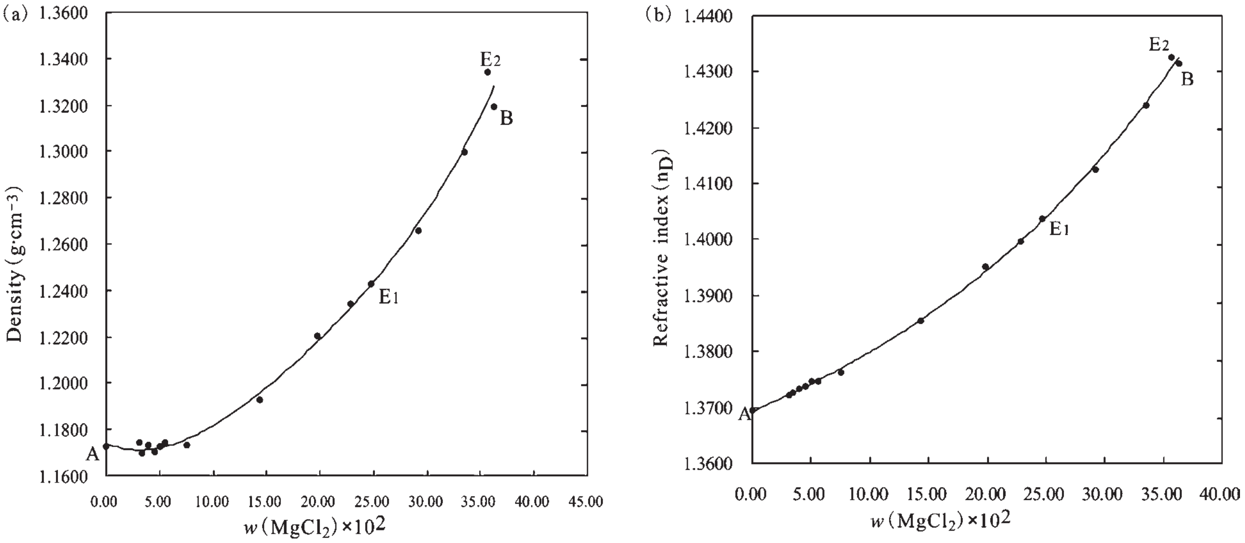


Figure 2. Physicochemical properties vs composition diagrams for the ternary system KCl + $MgCl_2$ + H_2O at 298.15 K: (a) density vs composition and (b) refractive index vs composition.

Table 2. Experimental Values of Solubilities, Refractive Indices, and Densities of the Ternary System KCl + RbCl + H_2O at 298.15 K

			composition of equilibrated solution, $w(B) \times 10^2$		composition of wet solid phase, $w(B) \times 10^2$		
no.	density/g·cm^{-3}	refractive index/n_D	w(KCl)	w(RbCl)	w(KCl)	w(RbCl)	equilibrium solid phase
1,A	1.1798	1.3704	26.65	0.00			KCl
2	1.1800	1.3694	26.07	0.71	81.36	0.21	KCl
3,F_1	1.1769	1.3688	25.63	0.74	67.68	0.48	KCl + (K,Rb)Cl
4	1.2012	1.3704	25.62	2.27	64.17	1.48	(K,Rb)Cl
5	1.1893	1.3701	24.35	2.73	78.68	2.02	(K,Rb)Cl
6	1.2042	1.3709	23.20	5.08	81.03	3.33	(K,Rb)Cl
7	1.2122	1.3714	22.14	6.75	80.59	4.59	(K,Rb)Cl
8	1.2326	1.3730	20.05	11.29	73.57	7.37	(K,Rb)Cl
9	1.2715	1.3752	18.24	15.40	77.30	11.32	(K,Rb)Cl
10	1.2933	1.3771	16.52	18.86	76.01	13.33	(K,Rb)Cl
11	1.3136	1.3786	15.58	20.76	61.90	17.19	(K,Rb)Cl
12	1.3653	1.3824	12.52	27.94	67.93	24.27	(K,Rb)Cl
13	1.3967	1.3842	9.20	34.02	30.64	40.82	(K,Rb)Cl
14	1.4193	1.3856	6.74	38.98	33.48	59.04	(K,Rb)Cl
15	1.4448	1.3873	3.52	43.92	17.56	73.58	(K,Rb)Cl
16	1.4584	1.3875	2.40	45.39	12.15	80.75	(K,Rb)Cl
17	1.4657	1.3879	1.50	46.41	7.34	86.42	(K,Rb)Cl
18,F_2	1.4967	1.3889	0.95	47.48	0.91	79.19	RbCl + (K,Rb)Cl
19	1.4913	1.3880	0.76	47.44	0.10	82.72	RbCl
20,B	1.4942	1.3876	0.00	47.82			RbCl

[(298.15 ± 0.1) K] measured by a thermal resistance. When enough new solid appeared in the evaporating containers, the solids were separated from the solutions. The obtained wet salts were determined using a chemical analysis method. 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 for the analysis of the compositions of the liquid phase. The relevant physicochemical properties were measured. 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 were measured with the gravity bottle method with a precision of ± 0.0002 g and used for the mass fraction calculation of liquid components. The specific gravity bottle method with correction of the air floating force was used.[12]

Analytical Methods. The composition of chloride ion in liquids and their corresponding wet solid phases were determined by $AgNO_3$ titration with a precision of 0.3 %. The amount of the composition of K^+ and Rb^+ was measured by a sodium tetraphenylborate—cetyltrimethylammonium bromide titration (precision, ± 0.5 %). The composition of Rb^+ was measured by inductively coupled plasma optical emission spectrometry (precision, less than 0.06 mass %, type ICP-OES 5300 V), and then the composition of K^+ was calculated by the subtraction method. The Mg^{2+} concentration was determined by ethylenediaminetetraacetic acid titration (precision, less than 0.5 %).[13] Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis.

RESULTS AND DISCUSSION

$KCl + MgCl_2 + H_2O$ System. The solubilities and relevant physicochemical property values of the ternary system at 298.15 K were determined and listed in Table 1. The ion concentration values of the metastable equilibrated solution and the wet salts were both expressed in mass fraction *w* (B). *w* (B) expresses the Bth salt in grams per 100 g of solution or wet solid phase, that is grams/(100 g of solution) or grams/(100 g of wet solid solution). On the basis of the experimental data in Table 1, the metastable equilibrium phase diagram was constructed in Figure 1.

Figure 1 shows that the phase diagram of this ternary system consists of three crystallization fields, two invariants (labeled as points E_1 and E_2), and three univariant curves. Point E_2 is of a commensurate invariant point, whereas point E_1 is of incommensurate invariant point. Point E_1 coexists with $KCl + KCl \cdot MgCl_2 \cdot 6H_2O$, and the compositions of the corresponding liquid phase is *w* (KCl) = 3.11 %, *w* ($MgCl_2$) = 24.72 %. Point E_2 coexists with $MgCl_2 \cdot 6H_2O + KCl \cdot MgCl_2 \cdot 6H_2O$, and the compositions of the corresponding liquid phase is *w* (KCl) = 0.11 %, *w* ($MgCl_2$) = 35.64 %. The three univariant curves AE_1, E_1E_2, and BE_2 correspond to the solubility isotherms where the solution was saturated with KCl, $KCl \cdot MgCl_2 \cdot 6H_2O$, and

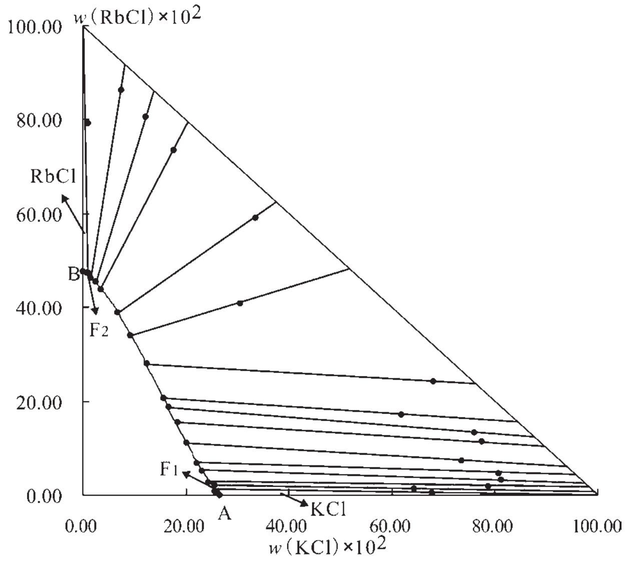
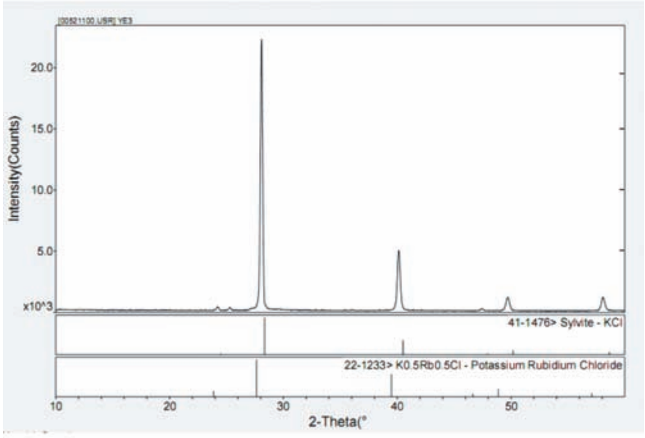


Figure 3. Metastable phase diagram of the ternary system $KCl + RbCl + H_2O$ at 298.15 K.



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

Figure 5. X-ray diffraction pattern of the invariant point F_1 (KCl + (K, Rb)Cl).

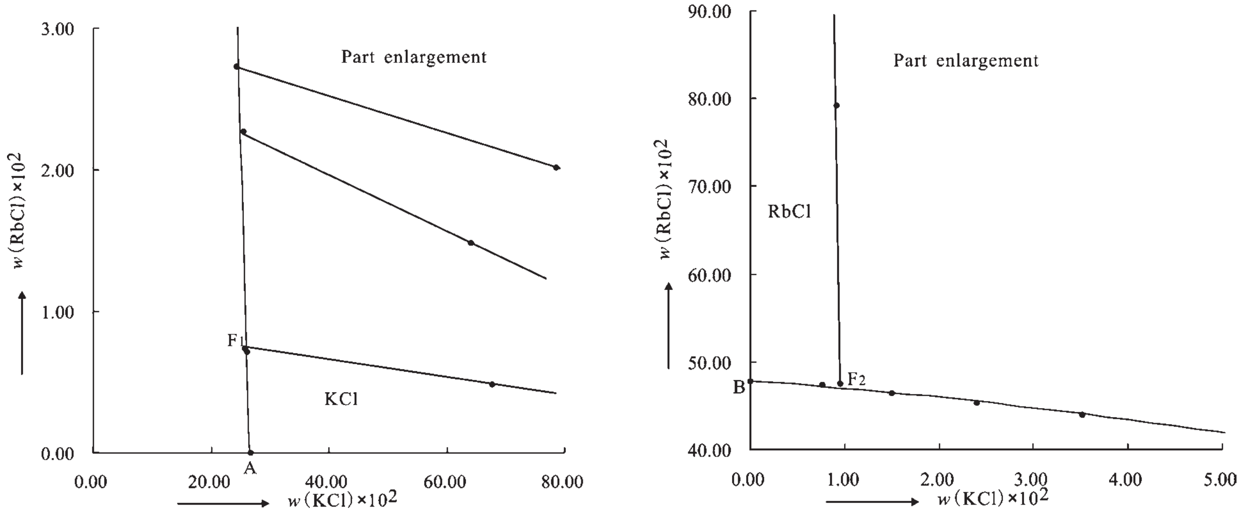
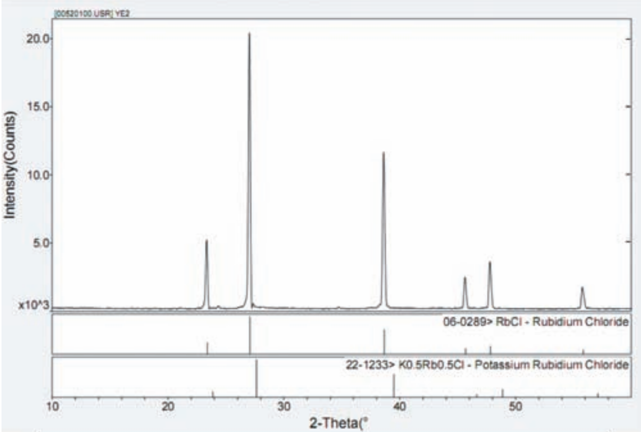


Figure 4. Partial enlarged diagrams of Figure 3.

$MgCl_2 \cdot 6H_2O$, respectively. The three crystallization zones correspond to the single salts KCl, $MgCl_2 \cdot 6H_2O$, and the double salt $KCl \cdot MgCl_2 \cdot 6H_2O$. No solid solution was formed in the system. The crystal region of KCl is the largest, which indicates that KCl is of low solubility, and the areas of the crystallization zones decrease in the order of $KCl \cdot MgCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$. These results show that KCl is easy to saturate and crystallize from solution and that $MgCl_2 \cdot 6H_2O$ has a high solubility during isothermal evaporation.

The salt magnesium chloride can be formed into various hydrated salts, such as $MgCl_2 \cdot 12H_2O$, $MgCl_2 \cdot 8H_2O$, $MgCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 4H_2O$, and $MgCl_2 \cdot 2H_2O$. Results of previous study show that the $MgCl_2$ crystallization form is $MgCl_2 \cdot 6H_2O$ at 269.75 to 389.85 K. When the temperature is lower than 269.75 K, there is a reaction between the $MgCl_2 \cdot 6H_2O$ and H_2O, that is $MgCl_2 \cdot 6H_2O + 2H_2O \Leftrightarrow MgCl_2 \cdot 8H_2O$; thus, the number of the crystal water is eight. When the temperature is higher than 389.85 K, the $MgCl_2$ crystallization form is $MgCl_2 \cdot 4H_2O$.[14] It is consistent with our experimental conclusion.



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

Figure 6. X-ray diffraction pattern of the invariant point F_2 (RbCl + (K, Rb)Cl).

Comparisons of the metastable equilibrium system KCl + $MgCl_2$ + H_2O at 298.15 K and the metastable equilibrium at 323.15 K[9] show that the crystallization forms of the salts are the same, whereas the crystallization zones have slight changes. The crystallization regions of the salts KCl, $KCl \cdot MgCl_2 \cdot 6H_2O$ are larger at 298.15 K than at 323.15 K, while the crystallization regions of the salt $MgCl_2 \cdot 6H_2O$ is smaller at 298.15 K than at 323.15 K.

The physicochemical properties vs composition diagram of this system are shown in Figure 2. In this system at 298.15 K, the solubility of the salt $MgCl_2$ is greater than salt KCl, and salt $MgCl_2$ has a salting-out effect on salt KCl; therefore, the concentration of $MgCl_2$ is the main factor affecting the density and refractive index in the solution. As shown in Figure 2a,b, the densities and refractive indices of the equilibrated aqueous solution are increasing with the increase of the concentration of $MgCl_2$ and reach the largest value at the invariant point E_2.

KCl + RbCl + H_2O System. The experimental results for solubilities, densities, refractive indices, and equilibrium solids of the ternary system KCl + RbCl + H_2O at 298.15 K were tabulated in Table 2. The ion concentration values of the metastable equilibrated solution and the wet salts were both expressed in mass fraction w (B). On the basis of the experimental data in Table 2, the isothermal evaporation diagram was plotted in Figure 3. Figure 4 is a partial enlarged diagram of Figure 3.

In Figure 3, the ordinate is the mass fraction of RbCl, and the abscissa is the mass fraction of KCl. Points A and B represent the solubility of the single-salts of potassium chloride and rubidium chloride, and the mass fraction of the corresponding liquid phase is $w(KCl) = 26.65$ %, $w(RbCl) = 47.82$ %. Points labeled as F_1 and F_2 are the invariant points of the ternary system. Figures 5 and 6 give the X-ray diffraction pattern of the salts corresponding to the invariant point F_1 and F_2. Point F_1 is cosaturated with salts KCl and (K,Rb)Cl, and the composition of corresponding liquid phase is $w(KCl) = 25.63$ %, $w(RbCl) = 0.74$ %. Point F_2 is

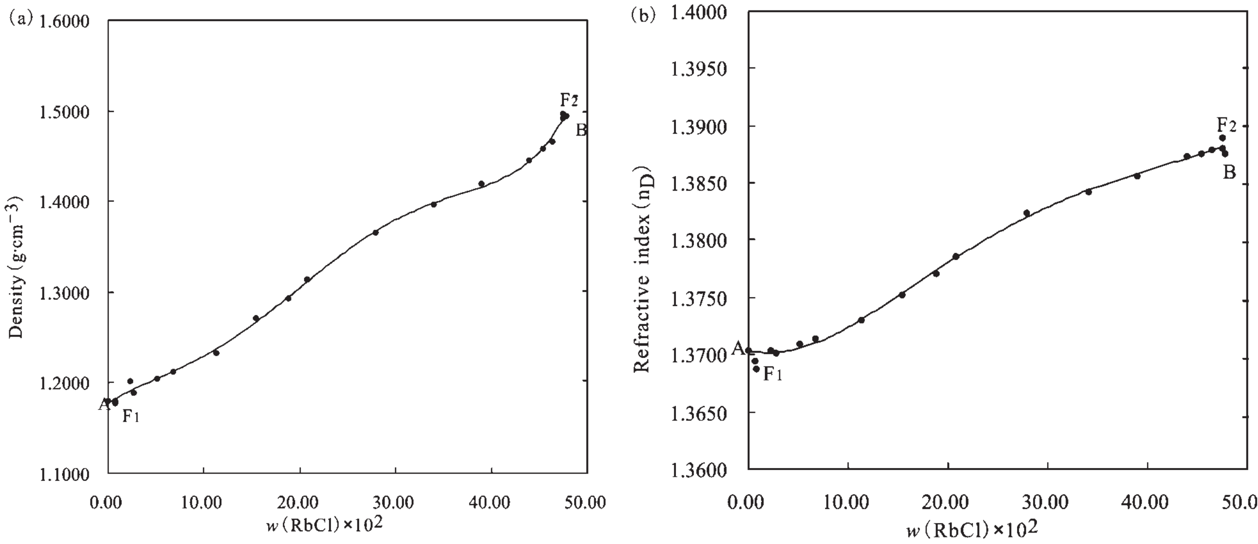


Figure 7. Physicochemical properties vs composition diagrams for the ternary system KCl + RbCl + H_2O at 298.15 K: (a) density vs composition and (b) refractive index vs composition.

Table 3. Comparsion of the Calculated and Experimental Values of Densities and Refractive Indices in the Ternary System KCl + $MgCl_2$ + H_2O at 298.15 K

	density/g·cm^{-3}			refractive index		
no.	experimental	calculated	relative error	experimental	calculated	relative error
1,A	1.1798	1.1798	0.0000	1.3704	1.3704	0.0000
2	1.1746	1.1727	−0.0016	1.3722	1.3719	0.0002
3	1.1698	1.1744	0.0039	1.3726	1.3725	0.0000
4	1.1730	1.1726	−0.0003	1.3732	1.3728	0.0003
5	1.1703	1.1745	0.0035	1.3738	1.3737	0.0001
6	1.1724	1.1746	0.0019	1.3747	1.3742	0.0004
7	1.1741	1.1731	−0.0008	1.3747	1.3743	0.0003
8	1.1735	1.1751	0.0014	1.3762	1.3766	−0.0003
9	1.1929	1.1883	−0.0039	1.3855	1.3856	−0.0001
10	1.2206	1.2061	−0.0121	1.3951	1.3942	0.0006
11	1.2344	1.2249	−0.0078	1.3996	1.4008	−0.0009
12,E1	1.2429	1.2305	−0.0101	1.4038	1.4037	0.0001
13	1.2657	1.2634	−0.0018	1.4126	1.4142	−0.0012
14	1.2994	1.2969	−0.0019	1.4239	1.4246	−0.0005
15,E2	1.3344	1.3135	−0.0159	1.4326	1.4297	0.0020
16	1.3194	1.3194	0.0000	1.4314	1.4314	0.0000

Table 4. Comparsion of the Calculated and Experimental Values of Densities and Refractive Indices in the Ternary System KCl + RbCl + H_2O at 298.15 K

	density/g·cm^{-3}			refractive index		
no.	experimental	calculated	relative error	experimental	calculated	relative error
1,A	1.1798	1.1798	0.0000	1.3704	1.3704	0.0000
2	1.1800	1.1826	−0.0022	1.3694	1.3704	−0.0007
3,F_1	1.1769	1.1796	−0.0023	1.3688	1.3698	−0.0007
4	1.2012	1.1949	0.0053	1.3704	1.3715	−0.0008
5	1.1893	1.1899	−0.0005	1.3701	1.3702	−0.0001
6	1.2042	1.2051	−0.0007	1.3709	1.3713	−0.0003
7	1.2122	1.2140	−0.0015	1.3714	1.3717	−0.0002
8	1.2326	1.2450	−0.0100	1.3730	1.3740	−0.0007
9	1.2715	1.2744	−0.0023	1.3752	1.3762	−0.0007
10	1.2933	1.2981	−0.0037	1.3771	1.3777	−0.0004
11	1.3136	1.3113	0.0017	1.3786	1.3786	0.0000
12	1.3653	1.3668	−0.0011	1.3824	1.3825	−0.0001
13	1.3967	1.4091	−0.0088	1.3842	1.3848	−0.0004
14	1.4193	1.4468	−0.0190	1.3856	1.3870	−0.0010
15	1.4458	1.4683	−0.0154	1.3866	1.3875	−0.0007
16	1.4448	1.4782	−0.0226	1.3873	1.3882	−0.0006
17	1.4584	1.4861	−0.0187	1.3875	1.3882	−0.0005
18	1.4657	1.4905	−0.0166	1.3879	1.3881	−0.0002
19,F_2	1.4967	1.4988	−0.0014	1.3889	1.3886	0.0002
20	1.4913	1.4965	−0.0035	1.3880	1.3883	−0.0002
21,B	1.4942	1.4942	0.0000	1.3876	1.3876	0.0000

cosaturated with salts RbCl and (K,Rb)Cl, and the composition of the corresponding liquid phase is $w(\mathrm{KCl}) = 0.95\ \%$, $w(\mathrm{RbCl}) = 47.48\ \%$. There are three isotherm evaporation curves AF_1, F_1F_2, and BF_2. The three crystallization zones of the phase diagram correspond to salts KCl, RbCl, and a solid solution (K,Rb)Cl. No double salt was found in the system. As shown in Figure 3, the crystallization field of the solid solution (K,Rb)Cl almost occupies all the phase region and indicates that it is difficult to separate potassium from rubidium in chloride solution by only using evaporation and crystallization methods at 298.15 K.

Comparisons between the metastable phase diagrams at 298.15 K and 323.15 K show that the crystallization regions of KCl and RbCl have decreased, while the crystallization regions of (K,Rb)Cl has enlarged at 298.15 K.

In the previous studies,[10,11] the researches consider just a completely miscible solid solution can be formed in the potassium and rubidium chloride solution, no purity KCl or RbCl is formed, and the system KCl-RbCl-H_2O belongs to Roozeboom's type I. However, in our studies on the metastable phase equilibria of this ternary system, besides the solid solution (K, Rb) Cl, the single salts KCl and RbCl are simultaneously formed at 298.15 K.

According to the experimental results in Table 2, the diagrams of the physicochemical properties (densities and refractive indices) vs the concentration of rubidium chloride were plotted in Figure 7. Figure 7 shows that the densities and refractive indices of the equilibrated aqueous solution change regularly with the changes of the content of rubidium chloride and reach the maximum value at the invariant point F_2.

CALCULATION SECTION

Calculation of Densities and Refractive Indices of the Equilibrium Solution. On the basis of the empirical eqs 1 and 2 for the density and refractive index of solutions developed in the previous study,[9,15] the density and refractive index of the equilibrated solutions were calculated:

$$\ln \frac{d}{d_0} = \sum A_i \cdot w_i \tag{1}$$

$$\ln \frac{n_D}{n_{D0}} = \sum B_i \cdot w_i \tag{2}$$

where d and d_0 refer to the density of the solution or the pure water at 298.15 K; n_D and n_{D0} refer to the refractive index of the solution or the pure water at 298.15 K. The d_0 and n_{D0} values of the pure water at 298.15 K are 0.99707 $g \cdot cm^{-3}$ and 1.33250, respectively. A_i and B_i are the constants of the ith component of the solution, and they can be obtained from the saturated solubility of the binary system. Values of the A_i constants of KCl, $MgCl_2$, and RbCl at 298.15 K are 0.006314, 0.007714, and 0.008459, respectively. Values of the B_i constants of KCl, $MgCl_2$, and RbCl at 298.15 K are 0.001052, 0.001972, and 0.0008473, respectively. In addition, the w_i is the mass fraction of the ith component of the solution. The calculated results are presented in Tables 3 and 4 and keep in line with experimental values. All of the calculated results have a maximum relative error < 0.016.

CONCLUSIONS

The metastable phase equilibria of the aqueous ternary systems KCl + $MgCl_2$ + H_2O and KCl + RbCl + H_2O at 298.15 K were studied using an isothermal evaporation method. The solubilities, densities, and refractive indices were determined experimentally. According to the measured data, the metastable equilibrium phase diagrams and the physicochemical properties vs composition were constructed.

The system KCl + $MgCl_2$ + H_2O is of a complex type; there is a double salt $KCl \cdot MgCl_2 \cdot 6H_2O$ formed at research temperatures. 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 298.15 K, and it has a high solubility. KCl has the largest crystallization field and can be easily separated from the solution in this system at 298.15 K using a crystallization method.

The system KCl + RbCl + H_2O is also of a complex type. In this system at 298.15 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 completely miscible solid solution, and the crystallization field of 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 298.15 K.

The comparison of the metastable equilibrium system KCl + RbCl + H_2O and KCl + $MgCl_2$ + H_2O at 298.15 K with the metastable equilibrium at 323.15 K shows that the crystallization forms of the salts are the same, whereas the crystallization zones have slight changes. The crystallization regions of the salts KCl, RbCl are smaller at 298.15 K than at 323.15 K, whereas the crystallization regions of the solid solution (K,Rb)Cl is larger at 298.15 K than at 323.15 K; the crystallization regions of the salts KCl and $KCl \cdot MgCl_2 \cdot 6H_2O$ are larger at 298.15 K than at 323.15 K, while the crystallization regions of the salt $MgCl_2 \cdot 6H_2O$ is smaller at 298.15 K than at 323.15 K.

The calculated densities and refractive indices using an empirical equation agree well with the experimental values. All of the calculated results have a maximum relative error < 0.016.

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