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Solid−Liquid Isothermal Evaporation Metastable Phase Equilibria in the Aqueous Quaternary System LiCl + KCl + RbCl + H₂O at 298.15 K

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ABSTRACT: The metastable phase equilibria in the aqueous quaternary system LiCl + KCl + RbCl + H₂O were investigated at 298.15 K using an isothermal evaporation method. The solubilities and physicochemical properties such as the density and refractive index of the equilibrated solution were determined. On the basis of the experimental results, the stereo phase diagram, the projected phase diagram, the water content diagram, and the physicochemical properties versus composition diagrams were constructed. The projected phase diagram consists of two invariant points, five isothermal univariant curves, and four crystallization fields corresponding to single salts potassium chloride (KCl), rubidium chloride (RbCl), lithium chloride monohydrate (LiCl·H₂O), and a solid solution of potassium and rubidium chloride [(K, Rb)Cl]. The two invariant points are cosaturated with three salts, which are LiCl·H₂O + RbCl + (K, Rb)Cl and LiCl·H₂O + KCl + (K, Rb)Cl, respectively. No double salt was formed. The crystallization region of the solid solution [(K, Rb)Cl] almost occupies the entire phase region, which shows that it is difficult to separate potassium from rubidium in chloride solution by only using evaporation and crystallization methods at 298.15 K. The calculated densities and refractive indices using empirical equations have a maximum relative error of <0.016.

■ INTRODUCTION

Lithium and rubidium are rare and scattered in nature; their applications are widely in the fields of lithium battery, nuclear energy, and space technologies.[1,2] Potassium is widely used in agriculture. In chloride solution, rubidium and potassium are easily formed into solid solution because of their similar ion radius: potassium, $1.33 \cdot 10^{-10}$ m, and rubidium, $1.49 \cdot 10^{-10}$ m. Compared with the traditional process of extracting rubidium and lithium from solid ore, it is more economical to extract them from brine.

Brine, an important liquid mineral resource abundant with sodium, potassium, lithium, and rubidium, is widely distributed in west China: not only salt lake brine, but also underground brine. The salt lakes are widely distributed in the Qinghai-Xizang (Tibet) Plateau, such as Zabuye Salt Lake, Chaidamu Saline Lake, Caerhan Lake, Dongtai Lake, and Xitai Lake.[2] Huge amounts of underground brine were also discovered in the Sichuan Basin, especially Pingluoba underground brine. The hydro-chemistry of Pingluoba underground brine is a chloride type, with the main components sodium, potassium, lithium, borate, and rubidium.[3]

To exploit brine resources, mineral equilibrium studies on the different types of brine are necessary. So far, a lot of work has been done on metastable and stable phase equilibrium aimed at different types of salt lakes, including our earlier works focused on the component characteristics of Zabuye Salt Lake.[4−6] The investigation of the thermodynamics and phase diagram of the solid−liquid system is of theoretical and practical importance. For example, the stable and metastable phase diagrams of Na⁺, K⁺//Cl⁻, CO₃²⁻, SO₄²⁻, and B₄O₇²⁻−H₂O at 293.15 K have

been used to comprehensively utilize Searles Salt Lake,[7] and the metastable phase diagram of Na⁺, K⁺, Mg²⁺//Cl⁻, and SO₄²⁻−H₂O at 288.15 K, 298.15 K, and 308.15 K have been used to extract MgSO₄·K₂SO₄·6H₂O or K₂SO₄ from Chaidamu Saline Lake.[8−10] However, previous research mainly focused on salt lake brine; research about the underground brine is reported less in literature.

Pingluoba underground brine largely consists of the complex six-component system Li⁺ + K⁺ + Rb⁺ + Mg²⁺ + Cl⁻ + borate + H₂O. To economically exploit Pingluoba underground brine, relevant metastable phase diagrams at different temperatures are required.

The quaternary system LiCl + KCl + RbCl + H₂O is a subsystem of the complex six-component system mentioned above. The phase equilibria of the three ternary subsystems of this quaternary system have been investigated at 298.15 K or 323.15 K in our previous research.[11−14] Research results show that the ternary systems LiCl + KCl + H₂O and LiCl + RbCl + H₂O at 298.15 K are a simple type, and no double salt or solid solution was found in these two ternary systems. Whereas the ternary system KCl + RbCl + H₂O is a complex type, the solid solution [(K, Rb)Cl] was formed at 298.15 K and 323.15 K.

The present paper is a continuation of a previously undertaken project. To date, the metastable equilibrium of the quaternary system LiCl + KCl + RbCl + H₂O has not been reported.

Table 1. Solubilities of the Quaternary System LiCl + KCl + RbCl + H$_2$O at 298.15 K^a

no.	composition of solution, $w(B) \cdot 10^2$				Jänecke index of dry salt $J(KCl) + J(LiCl) + J(RbCl) = 100$				equilibrated solid phase
	w(KCl)	w(LiCl)	w(RbCl)	w(H$_2$O)	J(KCl)	J(LiCl)	J(RbCl)	J(H$_2$O)	
1,A	25.63	0.00	0.74	73.63	98.25	0.00	1.75	1169	KCl + (K, Rb)Cl
2	23.51	1.35	0.80	74.34	89.14	9.00	1.86	1167	KCl + (K, Rb)Cl
3	23.23	1.58	0.90	74.29	87.43	10.47	2.10	1158	KCl + (K, Rb)Cl
4	23.07	1.77	0.95	74.21	86.20	11.61	2.19	1149	KCl + (K, Rb)Cl
5	21.99	2.36	1.20	74.45	81.79	15.45	2.76	1147	KCl + (K, Rb)Cl
6	21.15	2.99	1.42	74.44	77.51	19.28	3.21	1130	KCl + (K, Rb)Cl
7	18.91	4.61	1.97	74.51	66.96	28.74	4.30	1093	KCl + (K, Rb)Cl
8	18.27	5.39	3.76	72.58	60.76	31.52	7.72	1000	KCl + (K, Rb)Cl
9	17.18	6.12	3.57	73.13	57.01	35.70	7.29	1005	KCl + (K, Rb)Cl
10	15.56	7.80	3.93	72.71	49.08	43.27	7.65	949.8	KCl + (K, Rb)Cl
11	12.43	10.56	4.72	72.29	36.65	54.78	8.57	882.8	KCl + (K, Rb)Cl
12	8.05	16.43	6.43	69.09	19.67	70.64	9.69	699.6	KCl + (K, Rb)Cl
13	9.35	22.46	7.35	60.84	17.53	73.99	8.48	472.1	KCl + (K, Rb)Cl
14	7.86	26.25	8.50	57.39	13.27	77.90	8.83	401.1	KCl + (K, Rb)Cl
15,E$_1$	5.06	29.39	9.88	55.67	8.06	82.25	9.69	366.9	LiI + KCl + (K, Rb)Cl
16,B	0.95	0.00	47.49	51.56	3.15	0.00	96.85	706.6	RbCl + (K, Rb)Cl
17	1.04	1.40	44.24	53.32	3.39	7.98	88.63	717.9	RbCl + (K, Rb)Cl
18	1.05	1.53	44.03	53.39	3.39	8.70	87.91	716.3	RbCl + (K, Rb)Cl
19	0.95	2.15	43.21	53.69	3.03	12.04	84.93	709.0	RbCl + (K, Rb)Cl
20	0.99	2.55	42.64	53.82	3.13	14.12	82.75	701.7	RbCl + (K, Rb)Cl
21	0.95	3.40	40.92	54.73	2.96	18.61	78.43	704.9	RbCl + (K, Rb)Cl
22	0.87	5.04	38.54	55.55	2.61	26.46	70.93	687.1	RbCl + (K, Rb)Cl
23	0.73	7.87	35.00	56.40	2.03	38.30	59.67	646.1	RbCl + (K, Rb)Cl
24	0.47	14.48	26.10	58.95	1.11	60.61	38.28	581.0	RbCl + (K, Rb)Cl
25	0.49	18.87	21.03	59.61	1.06	71.14	27.80	529.3	RbCl + (K, Rb)Cl
26	0.42	20.94	21.15	57.49	0.84	73.24	25.92	473.5	RbCl + (K, Rb)Cl
27,E$_2$	0.34	26.06	18.15	55.45	0.59	79.91	19.50	400.5	LiI + RbCl + (K, Rb)Cl
28,C	3.23	42.20	0.00	54.57	4.16	95.84	0.00	291.8	LiI + KCl
29	4.57	39.02	5.48	50.93	5.97	89.62	4.41	275.5	LiI + KCl
30,E$_1$	5.06	29.39	9.88	55.67	8.06	82.25	9.69	366.9	LiI + KCl + (K, Rb)Cl
31,D	0.00	29.74	23.22	47.04	0.00	78.52	21.48	292.5	LiI + RbCl
32,E$_2$	0.34	26.06	18.15	55.45	0.59	79.91	19.50	400.5	LiI + RbCl + (K, Rb)Cl

^{a} Note: $w(B)$ = mass fraction of B; LiI = LiCl·H$_2$O.

Accordingly, the metastable equilibrium of the quaternary system at 298.15 K is presented in detail.

■ 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)), lithium chloride (LiCl; 99.0 % (w/w)), and rubidium chloride (RbCl; 99.5 % (w/w)). The deionized water, with an electrical conductivity less than $1 \cdot 10^{-4}$ S·m^{-1} and pH = 6.60, was used in the experiments.

An SHH-250 type thermostatic evaporator, made by the Chongqing Inborn Instrument Corp., China, was used for metastable phase equilibrium experiments. The range of the temperature is (258.15 to 373.15) K, and the temperature precision is ± 0.1 K.

An inductively coupled plasma optical emission spectrometer (type 5300 V, PerkinElmer Instrument Corp. of America) was employed for the determination of the lithium and rubidium ion concentrations 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 employed in this study. The required amounts of reagent, calculated according to the solubility of the salt at 298.15 K and

Table 2. Comparison of the Calculated and Experimental Values of Densities and Refractive Indices in the Quaternary System LiCl + KCl + RbCl + H$_2$O at 298.15 K

no.	density/ g·cm^{-3}			refractive index		
	exptl	calcd	relative error	exptl	calcd	relative error
1,A	1.1769	1.1796	−0.0023	1.3688	1.3698	−0.0007
2	1.1762	1.1732	0.0025	1.3692	1.3698	−0.0004
3	1.1791	1.1737	0.0046	1.3694	1.3700	−0.0005
4	1.1823	1.1742	0.0069	1.3698	1.3703	−0.0004
5	1.1824	1.1725	0.0084	1.3700	1.3703	−0.0002
6	1.1792	1.1726	0.0056	1.3704	1.3708	−0.0003
7	1.1775	1.1720	0.0047	1.3714	1.3718	−0.0003
8	1.1810	1.1902	−0.0078	1.3724	1.3747	−0.0017
9	1.1811	1.1850	−0.0033	1.3724	1.3746	−0.0016
10	1.1834	1.1875	−0.0034	1.3740	1.3764	−0.0017
11	1.1861	1.1902	−0.0034	1.3764	1.3790	−0.0019
12	1.2057	1.2135	−0.0064	1.3858	1.3878	−0.0015
13	1.2490	1.2750	−0.0204	1.4010	1.4046	−0.0025
14	1.2817	1.3025	−0.0160	1.4118	1.4124	−0.0004
15,E$_1$	1.2982	1.3175	−0.0146	1.4155	1.4172	−0.0012
16,B	1.4967	1.4990	−0.0015	1.3889	1.3886	0.0002
17	1.4815	1.4705	0.0075	1.3895	1.3881	0.0010
18	1.4823	1.4691	0.0090	1.3902	1.3881	0.0015
19	1.4723	1.4630	0.0063	1.3902	1.3884	0.0013
20	1.4654	1.4597	0.0039	1.3899	1.3887	0.0008
21	1.4636	1.4450	0.0129	1.3896	1.3886	0.0007
22	1.4368	1.4283	0.0059	1.3902	1.3894	0.0006
23	1.4111	1.4070	0.0029	1.3930	1.3914	0.0011
24	1.3682	1.3514	0.0124	1.3979	1.3955	0.0017
25	1.3400	1.3269	0.0099	1.4024	1.3996	0.0020
26	1.3397	1.3429	−0.0024	1.4060	1.4043	0.0012
27,E$_2$	1.3583	1.3463	0.0089	1.4150	1.4124	0.0019
28,C	1.2967	1.2862	0.0082	1.4340	1.4322	0.0012
29	1.3237	1.3348	−0.0083	1.4334	1.4335	−0.0001
30,E$_1$	1.2982	1.3175	−0.0146	1.4155	1.4172	−0.0012
31,D	1.4171	1.4312	−0.0099	1.4324	1.4265	0.0042
32,E$_2$	1.3583	1.3463	0.0089	1.4150	1.4124	0.0019

the solubility data of the invariant point in the ternary subsystems, were dissolved into 1000 mL of deionized water and loaded into a clean opened polyethylene container (24 cm long, 14 cm wide, and 7 cm high). Then, the container was placed in a thermostatic evaporator (SHH-250 type) for isothermal evaporation. The experimental conditions were a relative humidity of (20 to 30) % and evaporation rate of (4.0 to 5.5) mm·d^{-1}. The temperature was controlled to [(298.15 ± 0.1) K] measured by a thermal resistance.

The measuring point depended on the changes of solid phase in the process of evaporation. When enough new solid appeared in the evaporating containers, the solids were separated from the solutions. The composition of solution was determined by methods of chemical and instrumental analysis. Corresponding physicochemical properties were determined by the above listed instruments. 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 solution were also measured with a gravity bottle method with a precision of ± 0.0002 g and used for mass fraction calculations of liquid components. The specific gravity bottle method with a correction of air buoyancy was used.[15]

Analytical Methods. The composition of chloride ion in liquids and their corresponding wet solid phases was determined by AgNO$_3$ titration with a precision of 0.3 %. The amount of 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 Li$^+$ concentration was determined by inductively coupled plasma optical emission spectrometry (precision: less than 0.06 mass %, type ICP-OES 5300 V).[16] Each analysis was repeated three times with triplicate samples prepared for each data point, and the average value of three measurements was considered as the final value of the analysis.

■ RESULTS AND DISCUSSION

The experimental results of solubilities of the quaternary system at 298.15 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) (with J(KCl) + J(RbCl) + J(LiCl) = 100). The experimental and calculated values of densities and refractive indices of the quaternary system at 298.15 K are presented in Table 2. The solubility data corresponding to the invariant points in the binary and ternary subsystems of this quaternary system are tabulated in Table 3. The Jänecke index values can be calculated according to the following correlations,

$$w(\text{Li}^+) = \frac{42.39\left[\dfrac{w(\text{Cl}^-)}{35.45} - \dfrac{w(\text{K}^+)}{39.09} - \dfrac{w(\text{Rb}^+)}{85.47}\right] \text{g}}{100 \text{ g(solution)}}$$

$$w(\text{H}_2\text{O}) = 1 - w(\text{LiCl}) - w(\text{KCl}) - w(\text{RbCl})$$

$$\text{letting } [\text{B}] = \frac{w(\text{LiCl})}{42.39} + \frac{w(\text{KCl})}{74.55} + \frac{w(\text{RbCl})}{120.95}$$

$$J(\text{LiCl}) = \frac{w(\text{LiCl})}{42.39[\text{B}]}\cdot 100$$

$$J(\text{H}_2\text{O}) = \frac{w(\text{H}_2\text{O})}{18.02[\text{B}]}\cdot 100$$

With the data of Jänecke index J(B) in Table 3, the stereophase diagram of the system at 298.15 K was constructed in Figure 1. Figure 2 is the shapes of the crystallization regions of the quaternary system. Figure 3 is the projected phase diagram of Figure 1.

There are three binary and three ternary subsystems of the quaternary system LiCl + KCl + RbCl + H$_2$O. The binary subsystems are LiCl + H$_2$O, KCl + H$_2$O, and RbCl + H$_2$O; the three ternary subsystems are LiCl + KCl + H$_2$O, LiCl + RbCl + H$_2$O,

Table 3. Experimental Solubility Values Corresponding to the Invariant Points of the Binary and Ternary Subsystems in the Quaternary System LiCl + KCl + RbCl + H$_2$O at 298.15 K^a

| no. | system | composition of solution, $w(B) \cdot 10^2$ | | | | Jänecke index of dry salt $J(KCl) + J(LiCl) + J(RbCl) = 100$ | | | | equilibrated solid phase |
		$w(KCl)$	$w(LiCl)$	$w(RbCl)$	$w(H_2O)$	$J(KCl)$	$J(LiCl)$	$J(RbCl)$	$J(H_2O)$	
a	LiCl–H$_2$O	0.00	45.37	0.00	54.63	0.00	100.0	0.00	283.6	LiCl·H$_2$O
b	KCl–H$_2$O	26.60	0.00	0.00	73.40	100.0	0.00	0.00	1143	KCl
c	RbCl–H$_2$O	0.00	0.00	47.82	52.18	0.00	0.00	100.0	733.2	RbCl
A	KRbCl	25.63	0.00	0.74	73.63	98.25	0.00	1.75	1169	KCl + (K,Rb)Cl
B	KRbCl	0.95	0.00	47.49	51.56	3.15	0.00	96.85	706.6	RbCl + (K,Rb)Cl
C	LiKCl	3.23	42.20	0.00	54.57	4.16	95.84	0.00	291.8	LiCl·H$_2$O + KCl
D	LiRbCl	0.00	29.74	23.22	47.04	0.00	78.52	21.48	292.5	LiCl·H$_2$O + RbCl
E$_1$	LiKRbCl	5.06	29.39	9.88	55.67	8.06	82.25	9.69	366.9	LiCl·H$_2$O + KCl + (K,Rb)Cl
E$_2$	LiKRbCl	0.34	26.06	18.15	55.45	0.59	79.91	19.50	400.5	LiCl·H$_2$O + RbCl + (K,Rb)Cl

^{a} Note: KRbCl—KCl + RbCl + H$_2$O; LiKCl—KCl + LiCl + H$_2$O; LiRbCl—RbCl + LiCl + H$_2$O; LiKRbCl—LiCl + KCl + RbCl + H$_2$O.
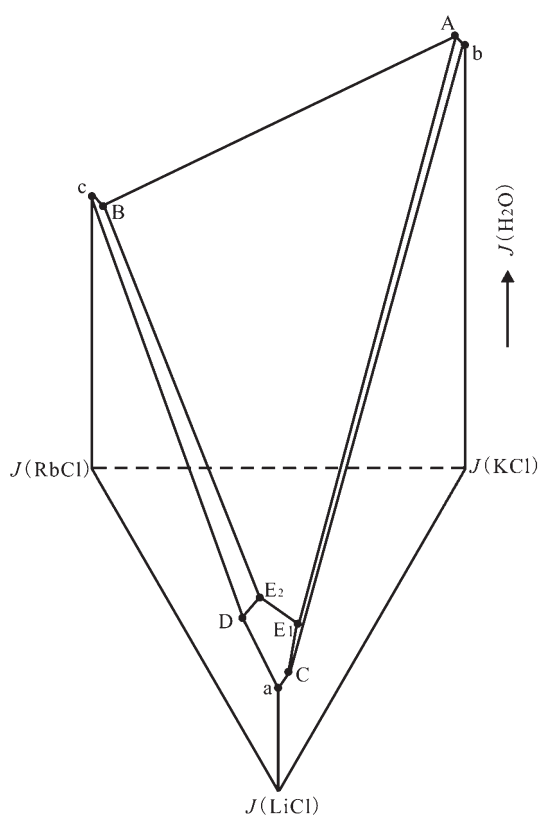
Figure 1. Stereodiagram of the quaternary system LiCl + KCl + RbCl + H$_2$O at 298.15 K.

Figure 2. Shapes of crystallization regions of the quaternary system LiCl + KCl + RbCl + H$_2$O at 298.15 K.
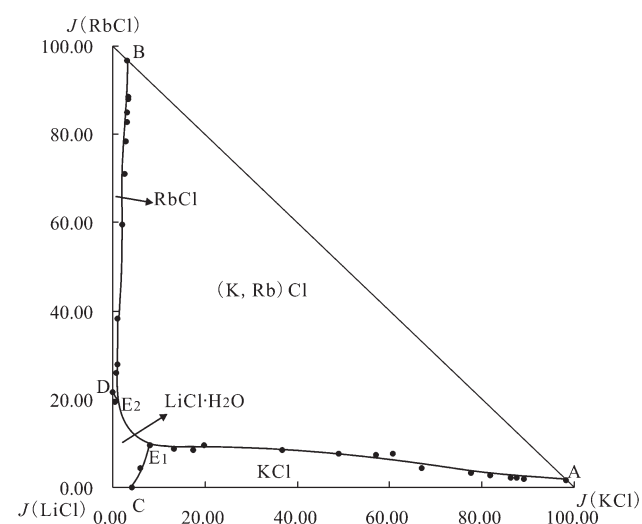
Figure 3. Projected phase diagram of the quaternary system LiCl + KCl + RbCl + H$_2$O at 298.15 K.

and KCl + RbCl + H$_2$O. In Figure 1, points a, b, and c are invariant points of the three binary systems. Points A, B, C, and D are invariant points of the three ternary systems. Points E$_1$ and E$_2$ are invariant points of the quaternary system.

The phase diagram consists of four crystallization fields, five univariant curves, and two invariant points. The four crystallization fields correspond to single salts KCl, LiCl·H$_2$O, RbCl, and the solid solution (K,Rb)Cl. The salt's crystallization region decreases in the order of (K,Rb)Cl, KCl, LiCl·H$_2$O, and RbCl.
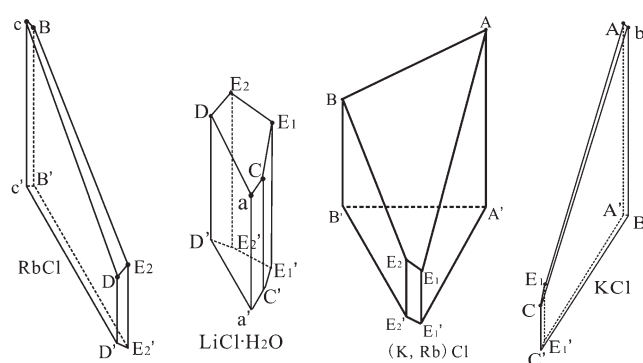
The crystallization zone of the solid solution (K,Rb)Cl almost occupies the entire phase region, which indicates that it is difficult

to separate potassium from rubidium in chloride solution by only using evaporation and crystallization methods at 298.15 K.

The five isothermal evaporation univariant curves, namely, curves AE_1, BE_2, CE_1, DE_2, and E_1E_2, are cosaturated with two salts and an equilibrated solution, respectively. The cosaturated salts for the five univariant curves are listed below.

(1) AE_1: saturated with KCl + (K, Rb)Cl
(2) BE_2: saturated with RbCl + (K, Rb)Cl
(3) CE_1: saturated with LiCl·H_2O + KCl
(4) DE_2: saturated with LiCl·H_2O + RbCl
(5) E_1E_2: saturated with LiCl·H_2O + (K, Rb)Cl

Two invariant points in this system are noted as E_1 and E_2.

Point E_1 is cosaturated with three salts LiCl·H_2O + KCl + (K, Rb)Cl and an equilibrated solution. The composition of the corresponding equilibrated solution is w (LiCl) = 29.39 %, w (KCl) = 5.06 %, w (RbCl) = 9.88 %, and $w(H_2O)$ = 55.67 %.

Point E_2 is cosaturated with three salts LiCl·H_2O + RbCl + (K, Rb)Cl and an equilibrated solution. The composition of corresponding equilibrated solution is w (LiCl) = 26.06 %, w (KCl) = 0.34 %, w (RbCl) = 18.15 %, and $w(H_2O)$ = 55.45 %.
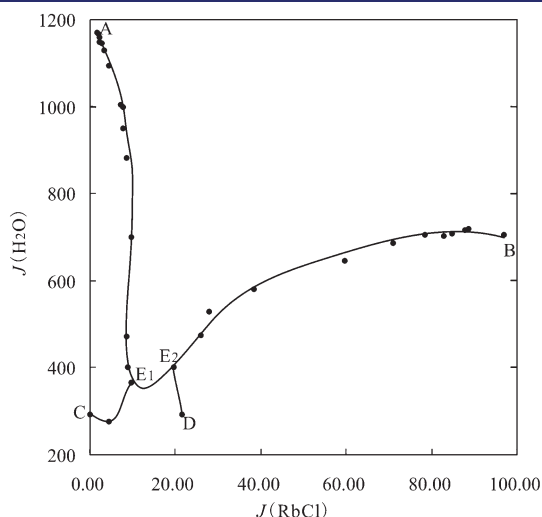

Figure 4. Water content diagram of the quaternary system LiCl + KCl + RbCl + H_2O at 298.15 K.

Figure 4 is the relevant water diagram of the system at 298.15 K. In Figure 4, the ordinate is the Jänecke index of water, and the abscissa is the Jänecke index of rubidium. Figure 4 shows that the water content changes regularly with the content change of rubidium chloride. The water decreased with the increase of J(RbCl) on the univariant curve AE_1, while the water increased with the decrease of J(RbCl) on the univariant curve E_2B.

According to the experimental results in Tables 1 and 2, the diagram of the physicochemical properties (densities and refractive indices) versus the composition of rubidium chloride in solution was constructed in Figure 5. Figure 5 shows that the densities and refractive indices of the equilibrated aqueous solution change regularly with the changes of the content of J(RbCl).

CALCULATION SECTION

Calculation of Densities and Refractive Indices of the Equilibrated Solution. Based on the empirical eqs 1 and 2 for the density and refractive index of solutions developed in the previous study,[1317] the densities and refractive indices 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 the density of the solution or the pure water at 298.15 K; n_D and n_{D0} refer the refractive index of the solution or the pure water at 298.15 K. The d_0 and n_{D0} value of the pure water at 298.15 K are 0.99707 g·cm^{-3} and 1.33250,[18] respectively. A_i and B_i are two constants of the ith salt in the solution, which can be obtained from the saturated solubility of the binary system. Values of the A_i constants of KCl, LiCl, and RbCl at 298.15 K are 0.006314, 0.005550, and 0.008459, respectively. Values of the B_i constants of KCl, LiCl, and RbCl at 298.15 K are 0.001052, 0.001630, and 0.0008473, respectively. In addition, w_i is the mass fraction of the ith salt in the solution. The calculated results are presented in Table 2 and identify well with the
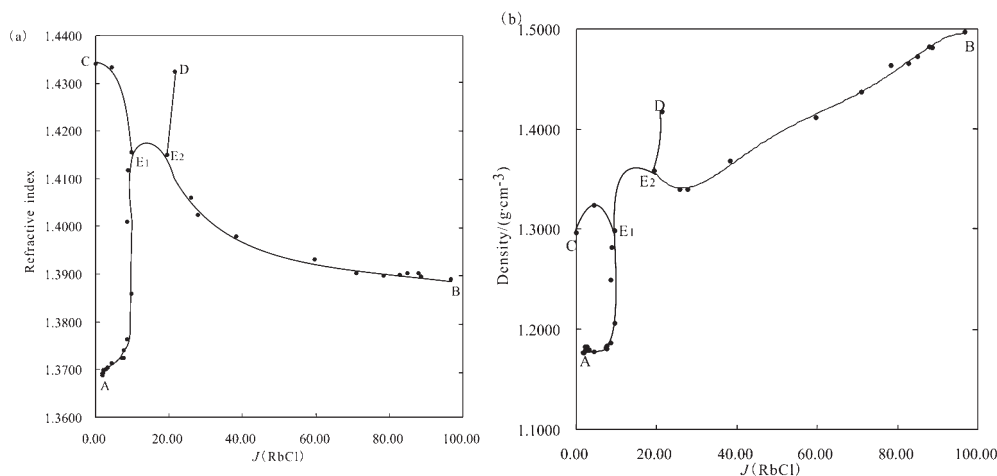

Figure 5. Physicochemical properties vs composition diagrams for the quaternary system LiCl + KCl + RbCl + H_2O at 298.15 K: (a) refractive index vs composition; (b) density vs composition.

experimental values. All of the calculated results have a maximum relative error less than 0.016.

CONCLUSIONS

The metastable phase equilibrium of the aqueous quaternary system LiCl + KCl + RbCl + H_2O at 298.15 K was studied using an isothermal evaporation method. The solubilities, densities, and refractive indices were determined experimentally. According to the measured data, the stereophase diagram, projected phase diagram, and the physicochemical properties versus composition were constructed.

The quaternary system LiCl + KCl + RbCl + H_2O is a complex type; there is a solid solution (K, Rb)Cl formed at 298.15 K. The crystalloid forms of the single salts are LiCl·H_2O, KCl, and RbCl. The solid solution (K,Rb)Cl is of a completely miscible solid solution, and its crystallization field occupies almost the whole phase region.

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

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