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Phase Equilibria for the Reciprocal Aqueous Quaternary System Li^+, Rb^+//Cl^-, Borate–H_2O at 323.2 K

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Abstract

The isothermal dissolution equilibrium method was applied for the solid–liquid equilibria experiments of the reciprocal aqueous quaternary system Li^+, Rb^+//Cl^-, borate–H_2O at 323.2 K, and the relevant diagrams (phase diagram, water content diagram, density/refractive index against composition diagram) were plotted. It was found that there are two commensurate type quaternary invariant points with three-salt cosaturated, five univariant curves, and four crystallization fields corresponding to four single salts, rubidium chloride (RbCl), lithium chloride monohydrate ($LiCl·H_2O$), lithium tetraborate trihydrate ($Li_2B_4O_7·3H_2O$), and rubidium pentaborate tetrahydrate ($RbB_5O_8·4H_2O$), respectively. $LiCl·H_2O$ has a salting out effect on other coexisting salts and the size of the $LiCl·H_2O$ crystallization field is the smallest. $Li_2B_4O_7·3H_2O$ has the largest crystallization field, which demonstrates that $Li_2B_4O_7·3H_2O$ can be more easily separated from the solutions.

Keywords Solid–liquid equilibria · Quaternary system · Lithium · Borate · Solubility

1 Introduction

Salt lakes and underground brines contain valuable resources. Comprehensive resource assessment and utilization have been performed for salt lakes in the US, Chile, Bolivia, China, Israel and Jordan among others. Salt lake mineral resources are of two types, solid and liquid deposits. Resources in the liquid phase mainly include Na, K, Mg, Li, Rb, Cs, Cl^-, Br^-, I^-, SO_4^{2-}, CO_3^{2-}(HCO_3^-), and borates [1–3]. According to the chemical composition of the brine, the brine can be divided into five types, i.e. chloride type, sulfate type (sodium sulfate sub-type and magnesium sulfate sub-type), carbonate type, nitrate type, and borate type [4]. The statistics showed the amount of boron resource (calculated as H_3BO_3) in Pingluo underground brine is nearly 2.987×10^7 tons [3]; there

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are 113 borate deposits in the salt lakes in Qinghai-Tibet Plateau and about 50% of total reserves of China [5]. The utilization of boron resources in brines can meet the increasing demand for boron.

Phase diagrams are widely applied to describe the dissolution and crystallization of salts and for the purpose of separation and purification of salts in chemical industry. Therefore, research on the phase equilibria aimed on borate type brine is necessary for the comprehensive utilization of the borate type brine resources. As for the borate containing system Li–Na–K–Ca–Mg–Rb–Cl^-–CO_3^{2-}–SO_4^{2-}–borate–H_2O, a series of solubility data for the related subsystems can be found in the open literature as seen in Table 1. Based on the analysis of the above literature, it can be found that boron appears in many polymeric forms, including BO_2^-, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$, and the crystalline form of boron is related to the coexisting ions and temperature. As for the quaternary system Li^+, Rb^+//Cl^-, borate–H_2O, the phase equilibria of three ternary subsystems Li^+, Rb^+//borate–H_2O [12], Rb^+//Cl^-, borate–H_2O [13], Li^+//Cl^-, borate–H_2O [19] were investigated at 323.2 K, research results show that all three ternary subsystems belong to the simple type, without double salt or solid solution formation. Nevertheless, there is almost no literature about the phase equilibria for the quaternary system Li^+, Rb^+//Cl^-, borate–H_2O system at 323.2 K; whether there is a new salt crystalline form or crystalline law in the quaternary system depends on phase equilibrium research. In view of this, the phase equilibrium of the quaternary Li^+, Rb^+//Cl^-, borate–H_2O system at 323.2 K is presented here in detail, including the solubilities, densities and refractive indices of this quaternary system.

Table 1 Phase equilibria of the borate containing system in the references

System	Temperature/(K)	Refs.
Li^+, Na^+(K^+/Ca^{2+})//BO_2^-–H_2O	298.2	[6, 7]
K^+//Cl^- (SO_4^{2-}), $B_5O_8^-$–H_2O	298.2	[8]
Li^+(Na^+), K^+//$B_5O_8^-$–H_2O	298.2	[9]
K^+(Mg^{2+})//Cl^-, $B_4O_7^{2-}$–H_2O	273.2	[10]
Li^+(K^+)//SO_4^{2-} ($B_4O_7^{2-}$)–H_2O	273.2	[11]
Li^+, K^+(Rb^+)//borate–H_2O	323.2	[12]
Rb^+(Mg^{2+}) //Cl^-, borate–H_2O	323.2	[13]
Rb^+, K^+(Mg^{2+})//borate–H_2O	323.2	[14]
Na^+, Ca^{2+}//Cl^-, borate–H_2O	288.2	[15]
Na^+, Mg^{2+}//Cl^-, borate–H_2O	273.2	[16]
Li^+, K^+, Rb^+//borate–H_2O	323.2, 348.2	[17, 18]
Li^+, Mg^{2+}//Cl^-, borate–H_2O	323.2	[19]
Rb^+, Mg^{2+}//Cl^-, borate–H_2O	323.2, 348.2	[20, 21]
Li^+, K^+, Rb^+, Mg^{2+}//borate–H_2O	323.2, 348.2	[22, 23]
Li^+, Na^+, K^+//CO_3^{2-}, $B_4O_7^{2-}$–H_2O	298.2	[24]
Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O	298.2	[25]

2 Experimental

2.1 Reagents

Double-deionized water with $\kappa \le 5.5\times10^{-6}$ S·m^{-1} was used in the phase equilibria experiments. The chemicals LiCl (CAS No. 7447-41-8) and $Li_2B_4O_7$ (CAS No. 12007-60-2) with a purity over 99.0% were purchased from the Chengdu Chron Chemicals Co., Ltd; RbCl (CAS No. 7791-11-9) and Rb_2CO_3 (CAS No. 584-09-8) with a purity over 99.5% were obtained from JiangXi Dongpeng New Materials Co., Ltd; H_3BO_3 (CAS No. 10043-35-3) with a purity over 99.8% was from Sinopharm Chmical Reagent Co., Ltd; $RbB_5O_8\cdot4H_2O$ used in this experiment was synthesized in our laboratory from an aqueous solution of Rb_2CO_3 and H_3BO_3 [26]. All chemicals mentioned above were dried at 383.2 K about 5–8 h before they were used for experiments.

2.2 Apparatus and Procedure

An isothermal dissolution method was used to carry out the phase equilibria experiments for the quaternary system Li^+, Rb^+//Cl^-, borate–H_2O at 323.2 K. First, an initial solution containing two salts and water was prepared according to the compositions of the invariant points of the four corresponding ternary subsystems at 323.2 K, using a BSA124S type analytical balance (the precision is ±0.0001 g). Then, a third salt was added gradually to the ternary saturated solution at 323.2 K. All samples were shaken by using an oscillation and placed in the thermostatic bath (the precision is ±0.2 K) at 323.2 K, the system can be considered to reach equilibrium when the analytical relative deviation between two adjacent samplings was less than 0.3%. Experimental results show that the time for reached equilibria is about 5 weeks with stirring. After equilibration, the clarified liquid phases of the samples was taken out to analyze the composition for each component. Also, the density (ρ) was measured using a specific gravity bottle (the uncertainty is $\pm2.0\times10^{-4}$ g·cm^{-3}) and the refractive index (n_D) was measured by an WYA type Abbe refractometer (the precision is $\pm1.0\times10^{-4}$). The wet residue was filtered from the equilibrium solution and dried at 323.2 K, a DX-2700 type X-ray powder diffraction with Cu Kα radiation, operating conditions 40 kV and 30 mA, and scanning angle 10–70° was used to analyze the crystalline form of solid phases at the quinary invariant points.

The analytical methods [27, 28] of Li^+, Rb^+, Cl^- and borate are listed as below:

Cl^-: $AgNO_3$ gravimetric method, standard uncertainty $u_r(w(Cl^-)) = 0.0027$;
Rb^+: sodium tetraphenylborate–cetyltrimethylammonium bromide titration using titan yellow as an indicator, standard uncertainty $u_r(w(Rb^+)) = 0.0050$;
Li^+: ICP-OES, PerkinElmer, 5300 V-type, standard uncertainty $u_r(w(Li^+)) = 0.0050$;
borate: neutralization titration in the presence of mannitol, standard uncertainty $u_r(w(B_4O_7^{2-})) = 0.0030$.

Table 2 The mass fraction (w), refractive index (n_D) and density (ρ) for the quaternary system Li^+, Rb^+// Cl^-, borate–H_2O at 323.2 K and 94.77 kPa[a]

No	Density/($g \cdot cm^{-3}$)	Refractive index/(n_D)	Equilibrium solutions composition, $w(B) \times 10^2$				
			$w(Li^+)$	$w(Rb^+)$	$w(Cl^-)$	$w(B_4O_7^{2-})$	$w(H_2O)$
1, A	1.3618	1.4334	7.43	0.00	37.84	0.39	54.34
2	1.3992	1.4344	7.00	4.71	37.64	0.14	50.51
3	1.4521	1.4358	6.63	8.24	37.20	0.14	47.79
4	1.4915	1.4379	6.58	9.66	37.58	0.13	46.05
5	1.5001	1.4385	5.77	15.10	35.66	0.14	43.33
6	1.5493	1.4404	5.73	16.37	36.00	0.14	41.76
7, E_1	1.5801	1.4422	5.33	20.26	35.58	0.13	38.70
8, B	1.4095	1.4322	4.62	18.43	31.27	0.00	45.68
9, E_1	1.5801	1.4422	5.33	20.26	35.58	0.13	38.70
10, C	1.1415	1.3472	0.30	2.34	0.00	5.43	91.93
11	1.1486	1.3477	0.27	2.82	0.28	4.92	91.71
12	1.1586	1.3482	0.26	3.31	0.56	4.67	91.20
13	1.1635	1.3489	0.26	4.08	0.93	4.54	90.19
14	1.1705	1.3504	0.25	5.24	1.50	4.28	88.73
15	1.1958	1.3524	0.22	7.83	2.61	3.86	85.48
16	1.2609	1.3576	0.09	12.95	4.60	2.69	79.67
17	1.3560	1.3694	0.11	20.34	7.84	2.50	69.21
18	1.3957	1.3680	0.08	21.66	8.41	2.11	67.74
19	1.4499	1.3729	0.07	24.46	9.77	1.64	64.06
20, E_2	1.6998	1.3976	0.16	34.83	14.58	1.45	48.98
21, D	1.6451	1.3965	0.00	36.67	14.82	0.78	47.73
22	1.6513	1.3974	0.06	34.53	14.13	1.06	50.22
23, E_2	1.6998	1.3976	0.16	34.83	14.58	1.45	48.98
24	1.6157	1.3955	0.86	30.42	16.29	1.55	50.88
25	1.5947	1.4020	1.17	22.16	14.61	1.17	60.89

No	Jänecke index of dry salt					Equilibrium solid phase
	$J(Li_2^{2+}) + J(Rb_2^{2+}) = J(Cl_2^{2-}) + J(B_4O_7^{2-}) = 100$					
	$J(Li_2^{2+})$	$J(Rb_2^{2+})$	$J(Cl_2^{2-})$	$J(B_4O_7)^-)$	$J(H_2O)$	
1, A	100.0	0.00	99.53	0.47	563.2	LiX + LiB
2	94.82	5.18	99.83	0.17	527.7	LiX + LiB
3	90.83	9.17	99.83	0.17	505.2	LiX + LiB
4	89.35	10.65	99.84	0.16	481.9	LiX + LiB
5	82.47	17.53	99.82	0.18	477.8	LiX + LiB
6	81.17	18.83	99.82	0.18	456.1	LiX + LiB
7,E_1	76.41	23.59	99.83	0.17	427.8	LiX + LiB + RX
8,B	75.53	24.47	100.0	0.00	575.5	LiX + RX
9, E_1	76.41	23.59	99.83	0.17	427.8	LiX + LiB + RX
10, C	61.22	38.78	0.00	100.0	14,601	RB + LiB
11	54.11	45.89	11.08	88.92	14,295	RB + LiB
12	49.17	50.83	20.79	79.21	13,340	RB + LiB
13	43.97	56.03	30.96	69.04	11,828	RB + LiB

Table 2 (continued)

No	Jänecke index of dry salt					Equilibrium solid phase
	$J(Li_2^{2+})+J(Rb_2^{2+})=J(Cl_2^{2-})+J(B_4O_7^{2-})=100$					
	$J(Li_2^{2+})$	$J(Rb_2^{2+})$	$J(Cl_2^{2-})$	$J(B_4O_7)^{-})$	$J(H_2O)$	
14	37.01	62.99	43.42	56.58	10,117	RB + LiB
15	25.70	74.30	59.68	40.32	7700	RB + LiB
16	7.88	92.12	78.92	21.08	5384	RB + LiB
17	6.24	93.76	87.29	12.71	3035	RB + LiB
18	4.35	95.65	89.72	10.28	2847	RB + LiB
19	3.40	96.60	92.88	7.12	2399	RB + LiB
20, E_2	5.35	94.65	95.65	4.35	1266	LiB + RB + RX
21, D	0.00	100.0	97.65	2.35	1239	RX + RB
22	2.09	97.91	96.69	3.31	1354	RX + RB
23, E_2	5.35	94.65	95.65	4.35	1266	LiB + RB + RX
24	25.82	74.18	95.83	4.17	1179	RX + LiB
25	39.40	60.60	96.47	3.53	1584	RX + LiB

Note standard uncertainties u are $u(T)=0.20$ K, $u(p)=0.50$ kPa, $u(n_D)=1.0\times10^{-4}$, $u(\rho)=2.0\times10^{-4}$ g·cm^{-3}, $u_r(w(Li^+))=0.0050$, $u_r(w(Rb^+))=0.0050$, $u_r(w(Cl^-))=0.0027$, $u_r(w(B_4O_7^{2-}))=0.0030$; LiB–$Li_2B_4O_7·3H_2O$, LiX–$LiCl·H_2O$, RB–$RbB_5O_8·4H_2O$, RX–RbCl

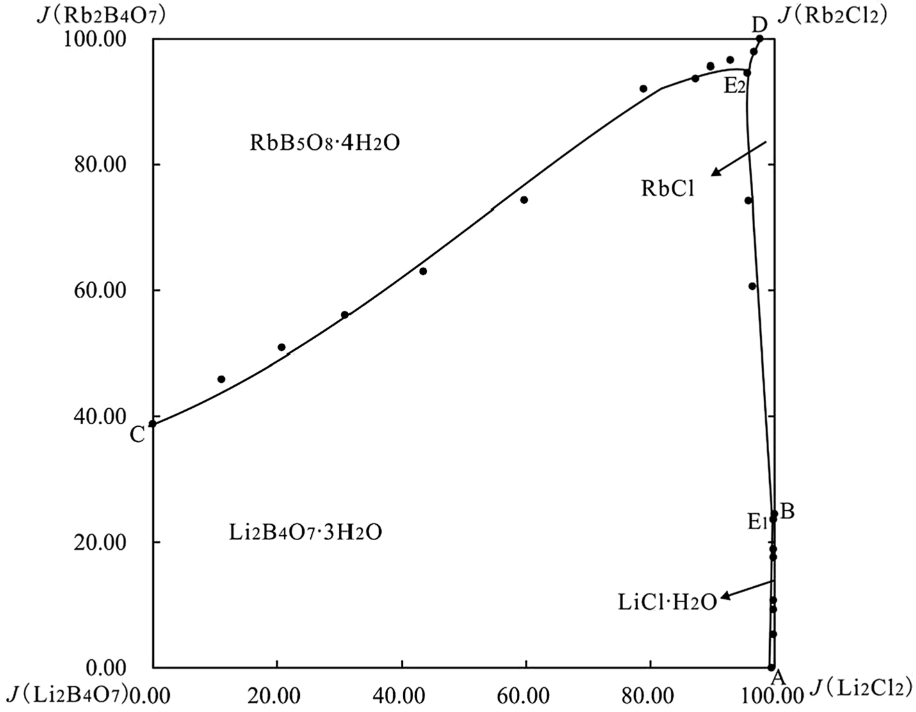

Fig. 1 The phase diagram of the quaternary system Li^+, Rb^+//Cl^- and borate–H_2O at 323.2 K

3 Results and Discussion

The values of solubilities, refractive indices, densities and composition of equilibrated solid phases in the quaternary system Li^+, $Rb^+//Cl^-$, borate–H_2O are presented in Table 2. To simplify the calculation, the traditional stoichiometric form $B_4O_7^{2-}$ was selected for description of the concentration of boron in solution. The mass fraction *w* and the Jänecke index *J* were used for the expression of the concentration of each solution component in Table 2. The Jänecke index, which is the mole percentage, can be calculated according to the following,

$$\text{Letting } [\mathrm{M}] = \frac{1}{2}\left\{\frac{w(\mathrm{Li}^+)}{6.94} + \frac{w(\mathrm{Rb}^+)}{85.47}\right\} = \frac{1}{2}\left\{\frac{w(\mathrm{Cl}^-)}{35.45} + \frac{w(\mathrm{B_4O_7^{2-}})}{155.237}\right\}$$

$$J(\mathrm{Li}_2^{2+}) = \frac{1}{2} \times \frac{w(\mathrm{Li}^+)}{6.94 \times [\mathrm{M}]} \times 100$$

$$J(\mathrm{Rb}_2^{2+}) = 100 - J(\mathrm{Li}_2^{2+})$$

$$J(\mathrm{Cl}_2^{2-}) = \frac{1}{2} \times \frac{w(\mathrm{Cl}^-)}{35.45 \times [\mathrm{M}]} \times 100$$

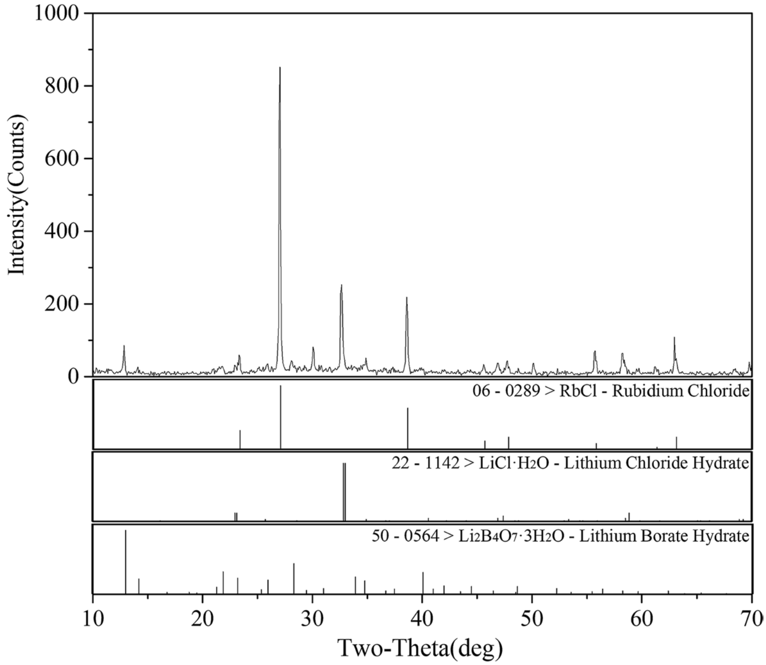

Fig. 2 X-ray diffraction pattern of the invariant point E_1 in the quaternary system Li^+, $Rb^+//Cl^-$, borate–H_2O at 323.2 K

$$J(B_4O_7^{2-}) = 100 - J(Cl_2^{2-})$$

$$J(H_2O) = \frac{w(H_2O)}{18.02 \times [M]} \times 100$$

With the Jänecke indices in Table 2, the planar projection diagram is presented in Fig. 1 as square coordinates; each vertex corresponds to a pure component, the points on the side correspond to the components of ternary systems, the points inside the square characterize the compositions of quaternary mixtures.

There are two quantrnary invariant points (E_1 and E_2), five isothermal dissolution curves, and four crystallization fields in the phase diagram as shown in Fig. 1. The invariant point of the quaternary system is cosaturated with three salts and an equilibrated solution. The results of X-ray diffraction analysis of point E_1 (Fig. 2) show that salts RbCl, $LiCl·H_2O$, and $Li_2B_4O_7·3H_2O$ coexist. The corresponding mass fraction composition of the equilibrated solution at the invariant point E_1 is $w(Li^+)=5.33\%$, $w(Rb^+)=20.26\%$, $w(Cl^-)=35.58\%$, $w({B_4O_7}^{2-})=0.13\%$, and $w(H_2O)=38.70\%$. The results of X-ray diffraction analysis of point E_2 (Fig. 3) show that salts $RbB_5O_8·4H_2O$, RbCl, and $Li_2B_4O_7·3H_2O$ coexist. The corresponding mass fraction composition of point E_2 is $w(Li^+)=0.16\%$, $w(Rb^+)=34.83\%$, $w(Cl^-)=14.58\%$, $w({B_4O_7}^{2-})=1.45\%$, and $w(H_2O)=48.98\%$.

For the invariant points in the reciprocal quaternary system, the quaternary invariant points can be divided into two types, incommensurate and commensurate, by the judgement of whether the invariant point lies in a triangle formed by corresponding

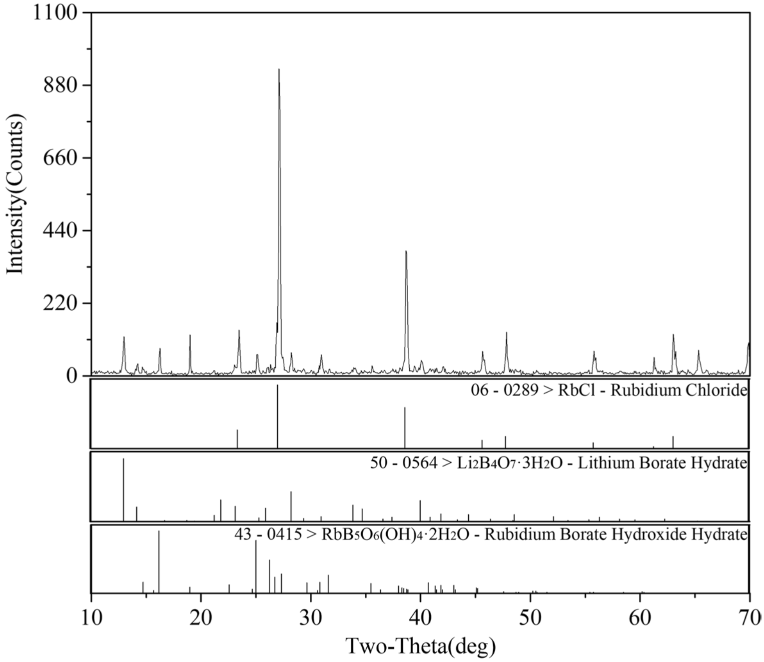

Fig. 3 X- ray diffraction pattern of the invariant point E_2 in the quaternary system Li^+, Rb^+//Cl^-, borate–H_2O at 323.2 K

cosaturated salts or not. The commensurate invariant point is located in the triangle, whereas the incommensurate invariant point lies out the triangle. In Fig. 2, point E_1 lies in the triangle formed by its cosaturated salts $LiCl{\cdot}H_2O$, RbCl, and $Li_2B_4O_7{\cdot}3H_2O$, point E_2 lies in the triangle formed by its cosaturated salts RbCl, $RbB_5O_8{\cdot}4H_2O$, and $Li_2B_4O_7{\cdot}3H_2O$, thus E_1 and E_2 are both commensurate invariant points.

The five isothermal dissolution curves, namely curves AE_1, BE_1, CE_2, DE_2 and E_1E_2, are cosaturated with two salts and an equilibrated solution. The cosaturated salts for each univariant curve are listed below.

AE_1: saturated with $LiCl{\cdot}H_2O + Li_2B_4O_7{\cdot}3H_2O$
BE_1: saturated with $RbCl + LiCl{\cdot}H_2O$
CE_2: saturated with $Li_2B_4O_7{\cdot}3H_2O + RbB_5O_8{\cdot}4H_2O$
DE_2: saturated with $RbCl + RbB_5O_8{\cdot}4H_2O$
E_1E_2: saturated with $RbCl + Li_2B_4O_7{\cdot}3H_2O$

The water content diagram is plotted in Fig. 4. The water content at curves AE_1, CE_2, and DE_2 decreases with $J\left(Rb_2^{2+}\right)$ increase, while at curves BE_1 and E_1E_2, the water content changes in the opposite way, with the increase of $J\left(Rb_2^{2+}\right)$, the water content increases. The relationships between density or refractive index and composition are presented in Figs. 5 and 6. Besides the curve E_1E_2, the values of density and refractive index of solution at equilibrium have the same change rule: with the increase of $J\left(Rb_2^{2+}\right)$

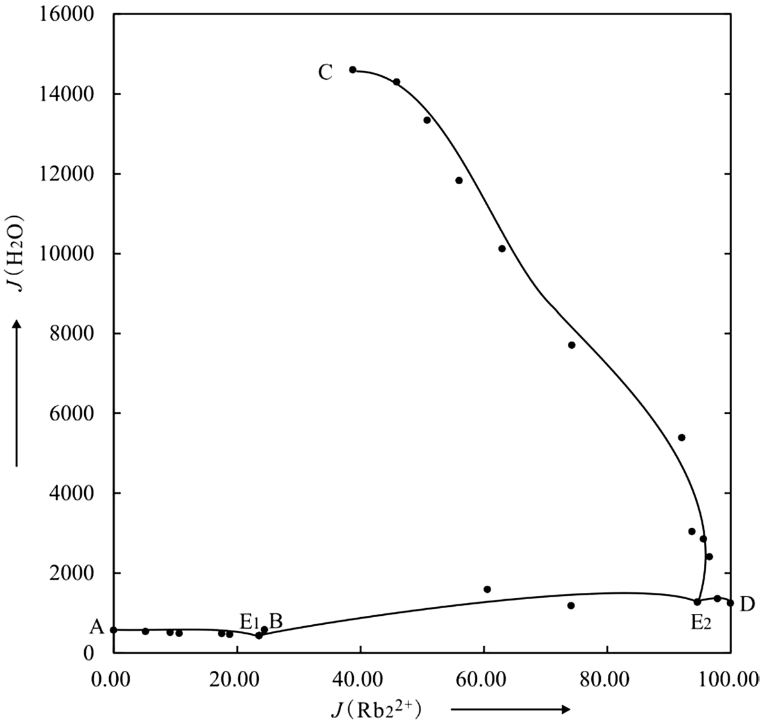

Fig. 4 The water content diagram of the quaternary system Li^+, Rb^+//Cl^- and borate–H_2O at 323.2 K

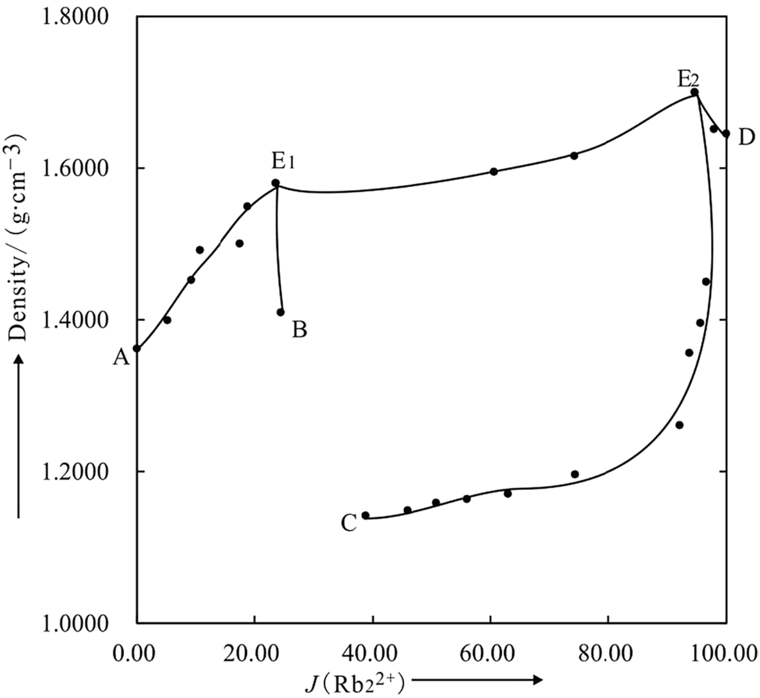

Fig. 5 The density vs composition diagam of the quaternary system Li^+, Rb^+//Cl^- and borate–H_2O at 323.2 K

at AE_1, BE_1, and CE_2, the values of density and refractive index increase; while at curve DE_2, with the $J\left(Rb_2^{2+}\right)$ increase, the values of density and refractive index decrease. The density of the system reaches its maximum value at point E_2, the refractive index value reaches the maximum at point E_1, and the water content of the system reaches the minimum value at point $E_{1.}$

4 Conclusions

(1) The solid–liquid equilibrium of reciprocal aqueous quaternary system Li^+, Rb^+//Cl^-, borate–H_2O at 323.2 K has been studied using the isothermal dissolution method. The system belongs to the simple cosaturation type, without double salt or solid solution formed.

(2) The stable phase diagram consists of two quaternary commensurate type invariant points, five isothermal dissolution curves, and four crystallization zones. The salt $Li_2B_4O_7{\cdot}3H_2O$ has the largest field of crystallization, and it is easily precipitated from the solution composed of lithium, rubidium, chloride, and borate at 323.2 K.

(3) The density of the system reaches its maximum value at point E_2, the refractive index value reaches its maximum at point E_1, and the water content of the system reaches its minimum value at point $E_{1.}$

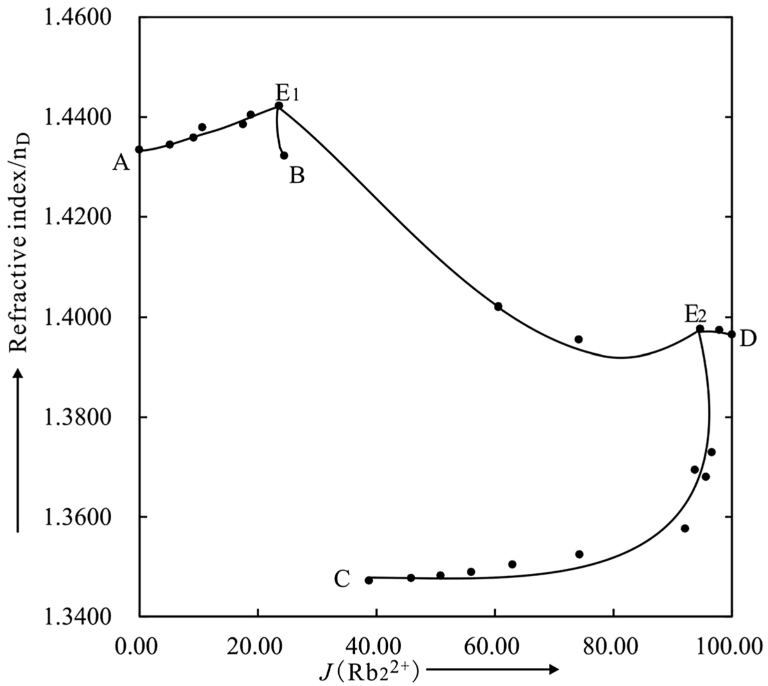

Fig. 6 The refractive index against composition diagram of the quaternary system Li^+, Rb^+//Cl^- and borate–H_2O at 323.2 K

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