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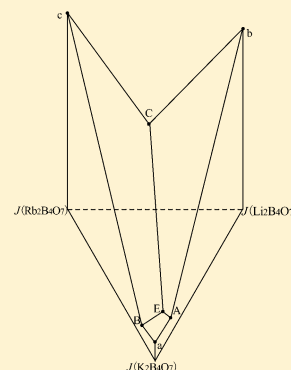
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ABSTRACT: The solubility values and physicochemical properties (pH values, refractive indices, and densities) of electrolyte mixtures in quaternary system containing lithium, potassium, rubidium, and borate were investigated at 348 K by isothermal dissolution method. The space phase diagram, the planar projection diagram, the water content diagram, and the diagrams of physicochemical properties depending on the composition were obtained using the measured data. The phase diagram of this quaternary system contains one invariant point, three univariant curves, and three single salts corresponding to lithium tetraborate trihydrate ($\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$), potassium tetraborate tetrahydrate ($\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$), and rubidium pentaborate tetrahydrate ($\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$). This quaternary system is of a simple cosaturation type, no double salt or solid solution formed. The scope of areas of crystallization of salts is such that $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O} > \text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O} > \text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, which demonstrates the salt $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ can be more easily separated from the solution than the other coexisting salts at 348 K. The physicochemical properties of the solutions at equilibrium on the univariant curve CE increase obviously with increasing Jänecke index, $J(\text{K}_2\text{B}_4\text{O}_7)$; whereas on the univariant curve AE or BE, the physicochemical properties change slightly along with the changes of $J(\text{K}_2\text{B}_4\text{O}_7)$.



INTRODUCTION

The alkali metal elements combine with boron oxyanions to form a number of inorganic salts called borates in nature. More than three-quarters of the world's supply is sold into the following four end uses: glass industry, agricultural fertilizer, detergents, and ceramic. The borates were extracted primarily by mining and to a lesser extent in brine.^{1,2} China possesses more than 100 borate deposits in 14 provinces, while the boron resources are of low quality, averaging about 8.4%³ Conversely, the content of boron in Pingluoba underground brine is up to 4.99 g/L, which is about 32 times that of the industrial grade for comprehensive utilization. Incomplete statistics show that the amount of boron resource (calculated as H_3BO_3) in Pingluoba underground brine is up to $2.987 \cdot 10^7$ t.^{4–6} Thus, the Pingluoba brine has a great potential for extraction borates.

It is well-known that the solubility data of inorganic salts along with the phase diagram provide a very important basis for the comprehensive utilization of brine. In the solution with borate, the solubility behavior is complex because boron appears in many forms such as B_3O_8^- , $\text{B}_{10}\text{O}_{17}^{4-}$, $\text{B}_4\text{O}_7^{2-}$, and BO_2^- et al. With an aim to understand the thermodynamics behavior of the borate in aqueous solution, some phase equilibria have been performed. Teeple⁷ studied the seven component system $\text{Na}^+//\text{Cl}^-$, CO_3^{2-} , PO_4^{3-} , $\text{B}_4\text{O}_7^{2-}$, HCO_3^- , HPO_4^{2-} , $\text{B}_2\text{O}_4^{2-}$ – H_2O at 293 K, and the results were used to comprehensive utilize Searles salt lake; the double salt named Teepleite $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$ had been found in the system $\text{Na}^+//\text{Cl}^-$, CO_3^{2-} , HCO_3^- , $\text{B}_4\text{O}_7^{2-}$, $\text{B}_2\text{O}_4^{2-}$ – H_2O at 308 K by

Gale;⁸ Churiko⁹ studied the ternary systems $\text{Na}^+//\text{BO}_2^-$, OH^- – H_2O , and $\text{K}^+//\text{BO}_2^-$, OH^- – H_2O at 263 K.

Furthermore, some salt–water systems focused on borate containing systems have been done by our research group, such as ternary systems Li^+ , $\text{K}^+//\text{borate}$ – H_2O ,¹⁰ Rb^+ , $\text{Mg}^{2+}//\text{borate}$ – H_2O ¹¹ and Rb^+ , $\text{Cl}^-//\text{borate}$ – H_2O ¹² at 348 K; quaternary systems $\text{Li}^+//\text{Cl}^-$, SO_4^{2-} , borate– H_2O ¹³ at 273 K and Li^+ , Na^+ , $\text{K}^+//\text{borate}$ – H_2O ¹⁴ at 288 K; quinary systems Li^+ , Na^+ , $\text{K}^+//\text{SO}_4^{2-}$, borate– H_2O ¹⁵ at 288 K and $\text{Li}^+//\text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , borate– H_2O ¹⁶ at 298 K. Results show that: the crystalloid form of rubidium borate is $\text{RbB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ at 348 K; the equilibrium solid phases of lithium borate correspond to $\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$ at 273 K,¹³ 288 K^{14,15} and $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$ at 298 K,¹⁶ 348 K;^{10,11} the crystalloid form of potassium borate is $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ at 288 K and 348 K.^{10,14,15}

To date, the stable phase equilibrium of the quaternary system containing the borates of lithium, rubidium, and potassium in aqueous solution at 348 K has not been reported. Consequently, the solubilities and physicochemical properties (densities, refractive indices, and pH values) of the quaternary system are presented here in detail.

EXPERIMENTAL SECTION

Reagents and Apparatus. The chemicals, referred to in our study, $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{K}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, were supplied by the

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Table 1. Experimental Values of Solubility and Physicochemical Properties Value of the Equilibrated Solution in the Quaternary System Li^+ , K^+ , Rb^+ //Borate– H_2O at 348 K and Perssure $p = 0.1 \text{ MPa}^a$

no.	density/ ($\text{g}\cdot\text{cm}^{-3}$)	refractive index	pH	composition of solution, $w(\text{B})\cdot 10^2$				Jänecke index of dry salt $J(\text{Li}_2\text{B}_4\text{O}_7) + J(\text{K}_2\text{B}_4\text{O}_7) + J(\text{Rb}_2\text{B}_4\text{O}_7) = 100$				equilibrated solid phase
				$w(\text{Li}_2\text{B}_4\text{O}_7)$	$w(\text{K}_2\text{B}_4\text{O}_7)$	$w(\text{Rb}_2\text{B}_4\text{O}_7)$	$w(\text{H}_2\text{O})$	$J(\text{Li}_2\text{B}_4\text{O}_7)$	$J(\text{K}_2\text{B}_4\text{O}_7)$	$J(\text{Rb}_2\text{B}_4\text{O}_7)$	$J(\text{H}_2\text{O})$	
1,A	1.5628	1.3982	9.84	6.33	36.71	0.00	56.96	19.23	80.77	0.00	1624	LiB + KB
2	1.5645	1.4044	9.28	5.75	35.3	1.28	57.67	17.98	79.95	2.07	1692	LiB + KB
3	1.5664	1.4095	9.20	5.31	34.32	2.63	57.74	16.84	78.84	4.32	1718	LiB + KB
4	1.5704	1.4111	9.12	4.93	33.5	3.83	57.74	15.81	77.82	6.37	1738	LiB + KB
5,E	1.5821	1.4154	8.96	4.63	32.35	5.16	57.86	15.06	76.24	8.70	1766	LiB + KB + RB
6,B	1.5989	1.4080	9.81	0.00	36.47	7.53	56	0.00	87.13	12.87	1733	KB + RB
7	1.5891	1.4083	9.37	1.52	33.93	5.52	59.03	5.25	84.87	9.88	1913	KB + RB
8	1.5865	1.4085	9.24	2.28	33.8	5.50	58.42	7.70	82.67	9.63	1851	KB + RB
9	1.5850	1.4091	9.12	2.74	33.61	5.28	58.37	9.19	81.64	9.18	1837	KB + RB
10	1.5830	1.4110	9.03	3.56	32.44	5.27	58.73	11.95	78.88	9.17	1850	KB + RB
11,E	1.5821	1.4154	8.96	4.63	32.35	5.16	57.86	15.06	76.24	8.70	1766	LiB + KB + RB
12,C	1.2079	1.3480	7.25	3.79	0.00	8.03	88.18	47.65	0.00	52.35	10405	LiB + RB
13	1.2100	1.3500	7.27	3.79	0.61	7.95	87.65	45.37	5.29	49.34	9847	LiB + RB
14	1.2120	1.3532	7.31	3.8	1.24	7.92	87.04	43.16	10.20	46.64	9278	LiB + RB
15	1.2198	1.3534	7.33	3.84	2.04	7.15	86.97	42.55	16.38	41.08	9044	LiB + RB
16	1.2290	1.3541	7.36	3.87	2.93	6.46	86.74	41.43	22.72	35.85	8714	LiB + RB
17	1.2425	1.3580	7.40	3.88	3.98	6.26	85.88	38.76	28.81	32.43	8053	LiB + RB
18	1.2523	1.3581	7.58	3.92	5.04	6.06	84.98	36.59	34.08	29.33	7444	LiB + RB
19	1.2893	1.3640	7.60	3.95	6.91	5.95	83.19	32.80	41.58	25.62	6484	LiB + RB
20	1.3344	1.3707	7.72	4.01	9.44	5.9	80.65	28.83	49.17	21.99	5442	LiB + RB
21	1.3742	1.3754	7.87	4.06	14.82	5.81	75.31	22.80	60.29	16.92	3969	LiB + RB
22	1.3928	1.3790	7.98	4.15	17.27	5.65	72.93	21.18	63.86	14.95	3494	LiB + RB
23	1.4343	1.3890	8.53	4.17	22.48	5.53	67.82	17.88	69.83	12.29	2729	LiB + RB
24	1.5019	1.4023	8.74	4.23	26.66	5.27	63.84	16.10	73.50	10.40	2280	LiB + RB
25	1.5468	1.4147	8.80	4.26	27.83	5.13	62.78	15.73	74.45	9.82	2176	LiB + RB
26,E	1.5821	1.4154	8.96	4.63	32.35	5.16	57.86	15.06	76.24	8.70	1766	LiB + KB + RB

^aNote: Standard uncertainties u are $u(T) = 0.50 \text{ K}$; $u_r(p) = 0.05$; $u_r(\rho) = 2.0\cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$; $u_r(n) = 1.0\cdot 10^{-4}$; $u_r(\text{pH}) = 0.02$; $u_r(\text{Li}_2\text{B}_4\text{O}_7) = 0.0030$; $u_r(\text{K}_2\text{B}_4\text{O}_7) = 0.0050$; $u_r(\text{Rb}_2\text{B}_4\text{O}_7) = 0.0050$; $\text{LiB-Li}_2\text{B}_4\text{O}_7\cdot 3\text{H}_2\text{O}$, $\text{RB-RbB}_5\text{O}_6(\text{OH})_4\cdot 2\text{H}_2\text{O}$, $\text{KB-K}_2\text{B}_4\text{O}_5(\text{OH})_4\cdot 2\text{H}_2\text{O}$.

Sinopharm Chemical Reagent Co., Ltd. with purities higher than 99.0 %. $\text{RbB}_5\text{O}_8\cdot 4\text{H}_2\text{O}$ was obtained from an aqueous solution of Rb_2CO_3 and H_3BO_3 in stoichiometric proportions with purities higher than 99.0 %.¹⁷ In addition, doubly deionized water, with electrical conductivity $\kappa \leq 1.0\cdot 10^{-4} \text{ S}\cdot\text{m}^{-1}$ and $\text{pH} \approx 6.60$, was required in the preparation of artificial solutions and analytical operations.

The following instrumentation was used: An THZ-82 type thermostatic water bath oscillator with the temperature range ($RT - 373 \text{ K}$) and temperature controlling precision $\pm 0.5 \text{ K}$ was employed in the solubility experiments. An AL104 type analytical balance of a resolution of 0.0002 g was applied to determine the weight of solution samples. All pH values were measured with PHS-25 type pH meter and the data displayed were of an uncertainty of 0.02 . WYA type Abbe refractometer was used for measuring the refractive index of equilibrated solution with a precision of 0.0001 . A DX-2700 X-ray diffractometer with $\text{Cu K}\alpha$ radiation was used to analyze the crystalloid form of solid phases. The operating conditions of X-ray diffractometer were 40 kV and 30 mA . The 5300 V type inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the lithium and rubidium concentration in solution.

Experimental Procedure. The solubility determinations were performed by means of an isothermal dissolution method. The component of the invariant points of the ternary subsystems (saturated with two salts) was taken as the composition of initial samples. The desired samples were

compounded by adding the different quantities of the third salt to the initial samples. The ratio of the third salt was dependent the solubility of the salts at 348 K . All of the samples were transferred into waterproof and tightly sealed bottles and then placed in the THZ-82 type thermostatic water bath oscillator with the temperature of $(348 \pm 0.5) \text{ K}$ and a constant oscillation frequency (120 rpm) to accelerate equilibration. When the composition of the solution remained constant, the system was assumed to be at equilibrium.

After equilibration, stirring was stopped, the solids were allowed to settle for at least 24 h , and the solution became clear. Then, the physicochemical properties (densities, refractive indices, and pH values) of the solution were measured by the previous-mentioned apparatus. The compositions of the liquid phase were determined by chemical or instrument analysis. The solid phase was separated by suction filtration, dried at 348 K , and identified by the powder X-ray diffraction method.

Analytical Methods. The concentration of the borate ion was determined by neutralization titration in the presence of mannitol (precision: $\pm 0.3 \%$).¹⁸ The total amount of potassium and rubidium was analyzed by sodium tetraphenylborate (STPB)–hexadecyl trimethyl ammonium bromide (CTAB) back-titration (precision: $\pm 0.5 \%$). The concentration of lithium and rubidium were analyzed by ICP-OES method (precision: $\pm 0.5 \%$), then the composition of K^+ can be calculated by subtracting the content of rubidium from the total amount of potassium and rubidium.

Table 2. Experimental Solubility Values Corresponding to the Invariant Points of the Binary and Ternary Subsystems in the Quaternary System Li^+ , K^+ , Rb^+ //Borate– H_2O at 348 K^b

no.	system	composition of solution, $w(\text{B}) \cdot 10^2$				Jänecke index of dry salt $J(\text{Li}_2\text{B}_4\text{O}_7) + J(\text{K}_2\text{B}_4\text{O}_7) + J(\text{Rb}_2\text{B}_4\text{O}_7) = 100$				equilibrated solid phase
		$w(\text{Li}_2\text{B}_4\text{O}_7)$	$w(\text{K}_2\text{B}_4\text{O}_7)$	$w(\text{Rb}_2\text{B}_4\text{O}_7)$	$w(\text{H}_2\text{O})$	$J(\text{Li}_2\text{B}_4\text{O}_7)$	$J(\text{K}_2\text{B}_4\text{O}_7)$	$J(\text{Rb}_2\text{B}_4\text{O}_7)$	$J(\text{H}_2\text{O})$	
a	$\text{K}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$	0.00	37.86	0.00	62.14	0.00	100.0	0.00	2129	KB
b	$\text{Li}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$	4.14	0.00	0.00	95.86	100.0	0.00	0.00	21755	LiB
c	$\text{Rb}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$	0.00	0.00	7.02	92.98	0.00	0.00	100.0	24001	RB
A	Li^+ , K^+ //borate– H_2O	6.33	36.71	0.00	56.96	19.23	80.77	0.00	1625	LiB + KB
B	K^+ , Rb^+ //borate– H_2O	0.00	36.47	7.53	56.00	0.00	87.13	12.87	1735	KB + RB
C	Li^+ , Rb^+ //borate– H_2O	3.79	0.00	8.03	88.18	47.65	0.00	52.35	10417	LiB + RB
E	Li^+ , K^+ , Rb^+ //borate– H_2O	4.63	32.35	5.16	57.86	15.06	76.24	8.70	1768	LiB + KB + RB

^bNote: Standard uncertainties u are $u(T) = 0.50$ K; $u_r(p) = 0.05$; $u_r(\text{Li}_2\text{B}_4\text{O}_7) = 0.0030$; $u_r(\text{K}_2\text{B}_4\text{O}_7) = 0.0050$; $u_r(\text{Rb}_2\text{B}_4\text{O}_7) = 0.0050$; $\text{LiB--Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$, $\text{RB--Rb}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, $\text{KB--K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$.

RESULTS AND DISCUSSION

The solubility data and physicochemical properties values obtained were listed in Table 1. The solubility of the invariant points in the binary and ternary subsystem of quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O were tabulated in Table 2. In Tables 1 and 2, the mass fraction of B was expressed by $w(\text{B})$ and the Jänecke index of it was expressed by $J(\text{B})$; B can be $\text{Li}_2\text{B}_4\text{O}_7$, $\text{K}_2\text{B}_4\text{O}_7$, $\text{Rb}_2\text{B}_4\text{O}_7$, or H_2O . The data of mass fraction and Jänecke index ought to comply with the formulas listed below.

$$w(\text{Li}_2\text{B}_4\text{O}_7) + w(\text{K}_2\text{B}_4\text{O}_7) + w(\text{Rb}_2\text{B}_4\text{O}_7) + w(\text{H}_2\text{O}) = 1$$

Letting

$$[\text{M}] = \frac{w(\text{Li}_2\text{B}_4\text{O}_7)}{169.12} + \frac{w(\text{K}_2\text{B}_4\text{O}_7)}{233.43} + \frac{w(\text{Rb}_2\text{B}_4\text{O}_7)}{326.17}$$

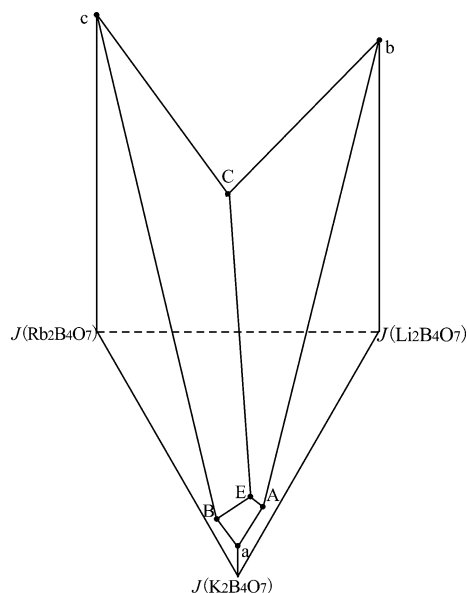
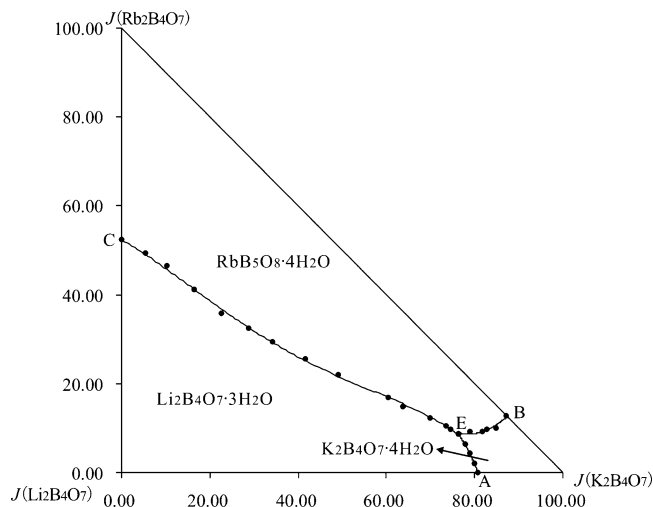
$$J(\text{Li}_2\text{B}_4\text{O}_7) = \frac{w(\text{Li}_2\text{B}_4\text{O}_7)}{169.12[\text{M}]} 100$$

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

$$J(\text{Li}_2\text{B}_4\text{O}_7) + J(\text{K}_2\text{B}_4\text{O}_7) + J(\text{Rb}_2\text{B}_4\text{O}_7) = 100$$

The space phase diagram, dependent on the Jänecke index displayed in Tables 1 and 2, was plotted in Figure 1. The planar projection diagram (Figure 2) was presented as a right triangle, each vertex corresponded to pure components, the points on the sides corresponded to the components of ternary systems, and the points inside the triangle characterized the composition of the quaternary system.

There are three binary and three ternary subsystems of the quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O , that are binary systems $\text{Li}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$, $\text{K}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$, $\text{Rb}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$, and ternary systems Li^+ , K^+ //borate– H_2O , Li^+ , Rb^+ //borate– H_2O , K^+ , Rb^+ //borate– H_2O . In Figure 1, points a–c are invariant points of the binary systems, and points A–C are invariant points of the ternary systems. All of these three ternary systems belong to a simple type, without double salt or solid solution formed. As shown in Figure 2, the planar projection diagram consists of three crystallization fields, three univariant curves, and one invariant point. The three crystallization fields correspond to three single salts, $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, and $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The crystallization field of salt $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ is the smallest,

**Figure 1.** Space diagram of the quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O at 348 K.**Figure 2.** The planar projection diagram of quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O at 348 K.

whereas the crystallization field of salt $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ is the largest, which shows that $\text{K}_2\text{B}_4\text{O}_7$ has the largest solubility

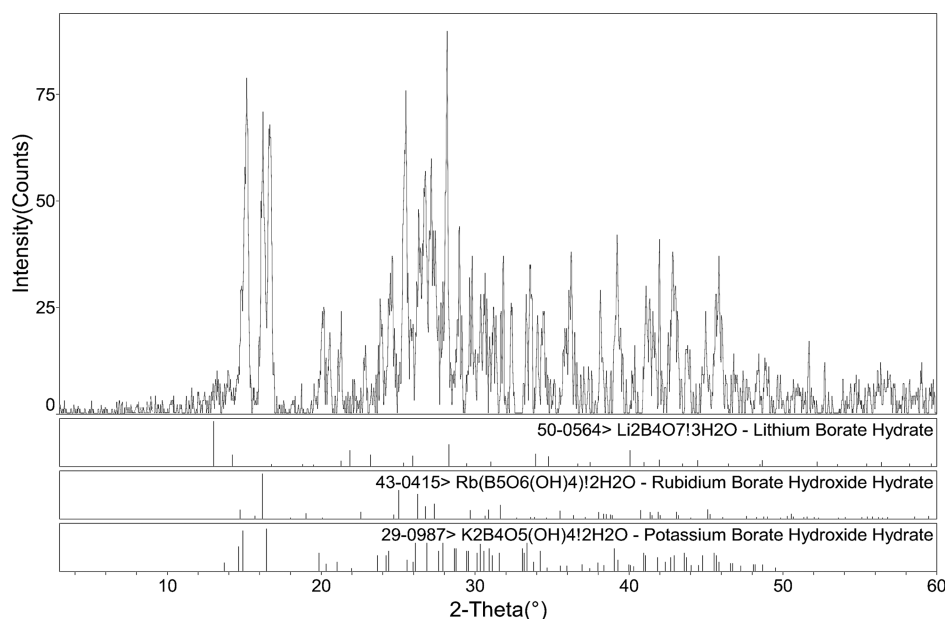


Figure 3. X-ray diffraction pattern of invariant point E ($\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$).

in water than other two salts, and $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ can be easier to separate from solution in this system at research temperature. The three univariant curves, namely, curves AE, BE, and CE, coexist with two salts and an equilibrated solution, respectively.

Commonly, $\text{B}_4\text{O}_7^{2-}$ is representative of all kinds of possible existing forms of boron ions in the solution. When the solid–liquid equilibrium is established between the solution and solid phase, the condensation or depolymerization reaction occurs, borates exist as the polyanions in solution, such as B_5O_8^- , $\text{B}_{10}\text{O}_{17}^{4-}$, $\text{B}_4\text{O}_7^{2-}$, BO_3^- , et al., and they can be crystallized in different solid forms.¹⁹ Point E is the invariant point of this quaternary system and corresponds with one equilibrium solution and three cosaturated salts. The component of the cosaturated salt was confirmed with an X-ray diffraction analysis method and demonstrated in Figure 3. As shown in Figure 3, crystallization forms for borates of potassium, rubidium, and lithium are, respectively, $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$. The mass fraction composition of the solution at equilibrium corresponding to invariant point E is $w(\text{Li}_2\text{B}_4\text{O}_7) = 4.63\%$, $w(\text{K}_2\text{B}_4\text{O}_7) = 32.35\%$, $w(\text{Rb}_2\text{B}_4\text{O}_7) = 5.16\%$, and $w(\text{H}_2\text{O}) = 57.86\%$.

Table 2 shows that the solubilities of potassium tetraborate is greater than those of lithium tetraborate and rubidium tetraborate; thus in solution the physicochemical properties are mainly affected by the potassium tetraborate content. Accordingly, the water content diagram (Figure 4) and the physicochemical properties versus composition diagrams (Figure 5–7) were plotted with the Jänecke index of potassium tetraborate as abscissa. Figure 4 shows that, on the univariant curve CE, the water content decreases obviously when the Jänecke index of potassium tetraborate increases; whereas on the univariant curve AE (with the coexistence of $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$) or BE (with the coexistence of $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$), the change of water content becomes slight along with the changes of the Jänecke index of potassium tetraborate. As shown in Figures 5 to Figure 7, on the univariant curve CE, the physicochemical properties values (density, refractive index,

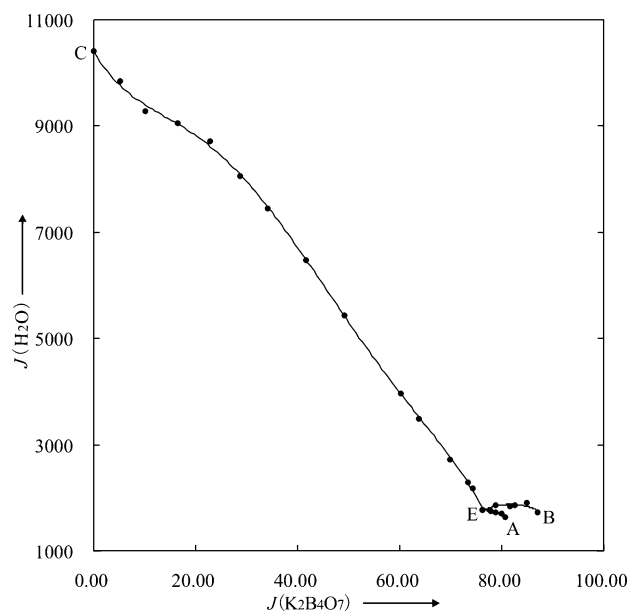


Figure 4. Water-content diagram of quaternary system Li^+ , K^+ , $\text{Rb}^+//\text{borate}-\text{H}_2\text{O}$ at 348 K.

pH value) increase obviously with the increase of potassium tetraborate content; whereas on the univariant curve AE or BE, the physicochemical properties change slightly along with the changes of Jänecke index, $J(\text{K}_2\text{B}_4\text{O}_7)$.

CONCLUSIONS

The results of the isothermal dissolution experiments of quaternary system Li^+ , K^+ , $\text{Rb}^+//\text{borate}-\text{H}_2\text{O}$ at 348 K belongs to a simple cosaturation type. The phase diagram consists of one invariant point, three univariant curves, and three crystallization fields. The crystalloid form of the borates on the invariant point E has been confirmed by the X-ray diffraction method. Point E coexisted with three borate salts: $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. In the view of crystallization fields, the crystallization

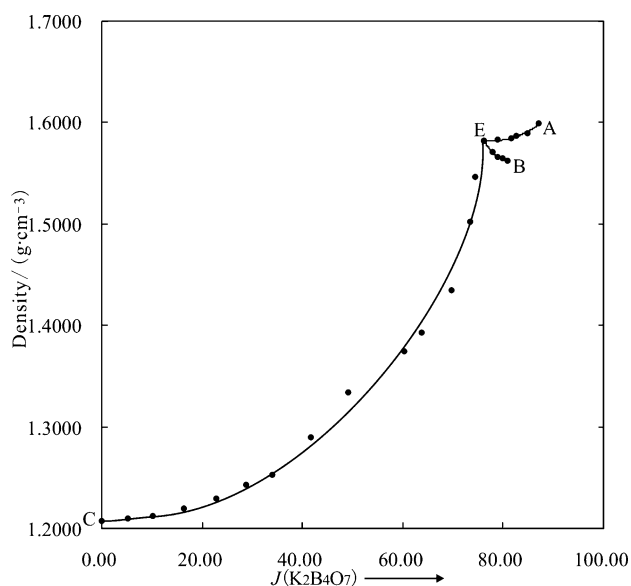


Figure 5. Densities vs composition diagram for quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O at 348 K.

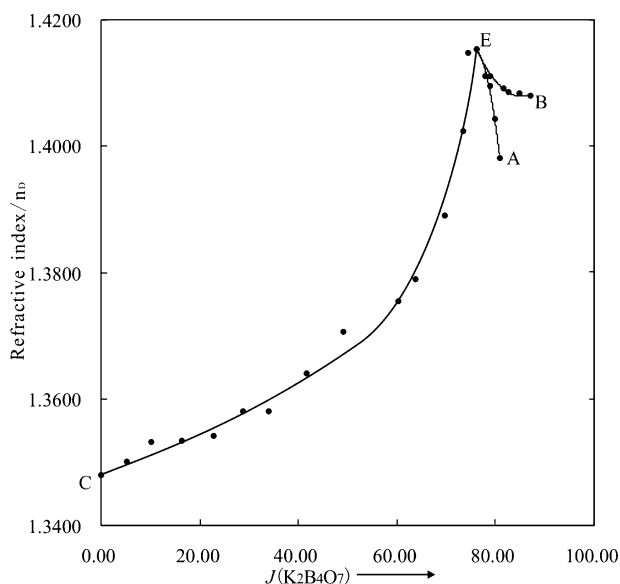


Figure 6. Refractive indices vs composition diagram for quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O at 348 K.

field of salt $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ occupies the smallest part, whereas salt $\text{RbB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ has the largest crystallization area. On account of 348 K and stable conditions, the crystalline form of lithium borate in the equilibrium solid phase is $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$; $\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$ is not found in the given system at 348 K. On the univariant curve CE, the water content decreases obviously and the physicochemical properties values increase obviously when the Jänecke index of potassium tetraborate increases; whereas on the univariant curve AE or BE, the change of water content and the physicochemical properties become slight along with the changes of Jänecke index, $J(\text{K}_2\text{B}_4\text{O}_7)$.

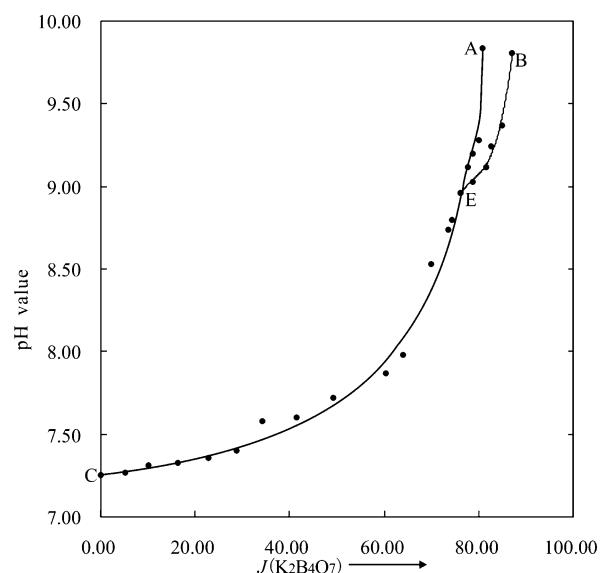


Figure 7. pH values vs composition diagram for quaternary system Li^+ , K^+ , Rb^+ //borate– H_2O at 348 K.

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Notes

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