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Stable Phase Equilibrium of Aqueous Quaternary System Li^+, K^+, Mg^{2+}//Borate−H_2O at 348 K

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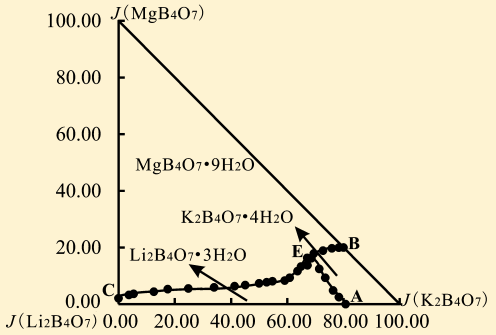
ABSTRACT: The solubility values and physicochemical properties such as densities, refractive indices, and pH values of the equilibrium solution in the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K were measured by isothermal dissolution method. The phase diagram, water content diagram, and the diagrams of the physicochemical properties versus composition were constructed using the measured data. Results show that this quaternary system at 348 K is of a simple type, no double salt or solid solution formed. The stable phase diagram of this quaternary system consists of one invariant point, three univariant curves, and three crystalline phase areas. The invariant point saturated with three salts corresponding to lithium tetraborate trihydrate ($Li_2B_4O_7{\cdot}3H_2O$), potassium tetraborate tetrahydrate ($K_2B_4O_7{\cdot}4H_2O$), and hungchaoite ($MgB_4O_7{\cdot}9H_2O$). The crystallization field of $MgB_4O_7{\cdot}9H_2O$ is the maximum, meaning that the salt magnesium borate has the smallest solubility among the coexisting salts. Comparisons between the stable phase diagrams at 288 K and 348 K show that the crystallization zones of $MgB_4O_7{\cdot}9H_2O$ decreased at 348 K, while the crystallization zones of $K_2B_4O_7{\cdot}4H_2O$ and $Li_2B_4O_7{\cdot}3H_2O$ both enlarged at 348 K. On the univariant curve CE, the water contents decrease with the increase of $J(K_2B_4O_7)$; the densities and refractive indices both increase with the increase of $J(K_2B_4O_7)$ and reach the maximum at invariant point *E*.



INTRODUCTION

Brine, including salt lake brine and underground brine, is an important mineral resource. Pingluo underground brine, located in the west of Sichuan Basin, is well-known for being rich in potassium, lithium, and borate.[1] The content of potassium is as high as 53.27 $g{\cdot}L^{-1}$, which is much higher than other famous salt lake brines such as Qarhan Salt Lake brine (15 $g{\cdot}L^{-1}$)[2] and Atacama Salt Lake brine (23.6 $g{\cdot}L^{-1}$).[3] The content of boron in the brine is up to 4.99 $g{\cdot}L^{-1}$, nearly 32 times of the industrial grade for comprehensive utilization. The content of lithium is also much higher than the industry mined grade.[4] Thus, there is vast developing prospective for the Pingluo underground brine.

The thermodynamic investigation of the phase diagrams of the solid−liquid system plays an important role in exploiting brine resources and also in describing the geochemistry evolution of brine minerals. Pingluo underground brine is a complex water−salt coexisting system; the main components of the brine are sodium, potassium, magnesium, lithium, rubidium and chloride, and borate, etc.[5] When the sodium chloride is separated by crystallization in the process of evaporation, the main composition of Pingluo underground brine can be simplified as a six-component system Li^+, K^+, Rb^+, Mg^{2+}//Cl^-, borate−H_2O.[6] The Pingluo underground brine is deeply buried in the ground (over 4500 m), and the temperature of the brine is up to 393 K.[4] In the mining process, the temperature of the brine decreased gradually. Therefore, the thermodynamics stable phase equilibria research focus on different temperature is necessary. So far, a series of phase equilibria studies focused on the subsystem of Pingluo underground brine at different temperatures has been done by our group, such as the ternary system K^+, Mg^{2+}//Cl^-−H_2O and K^+, Rb^+//Cl^-−H_2O at 298 K,[7] 323 K,[8] and 348 K;[9] the quaternary system Li^+, K^+, Rb^+//Cl^-−H_2O at 298 K,[10] 323 K,[11] and 348 K;[12] and the quaternary system Li^+, K^+, Mg^{2+}//Cl^-−H_2O at 323 K.[13] The aqueous quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O is one of the most important subsystems of the complex multiple systems mentioned previously. The stable phase equilibrium of this quaternary system at 288 K has been studied by Xiao et al.;[14] results show that the stable phase diagram of this quaternary system at 288 K consists of three single salt crystallization fields corresponding to $Li_2B_4O_7{\cdot}3H_2O$, $K_2B_4O_7{\cdot}4H_2O$, and $MgB_4O_7{\cdot}9H_2O$. In order to figure out the effect of temperature on this quaternary system and provide basic data for the development of underground brine, research focused on the stable phase equilibrium of the system Li^+, K^+, Mg^{2+}//borate−H_2O at different temperature is necessary.

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Table 1. Solubility and Analytical Experimental Reagents

chemical name	source	mass fraction purity
potassium tetraborate ($K_2B_4O_7{\cdot}5H_2O$)	Chengdu Kelong Chemical Reagent Plant	0.995
lithium tetraborate ($Li_2B_4O_7$)	Chengdu Kelong Chemical Reagent Plant	0.995
Hungchaoite ($MgB_4O_5(OH)_4{\cdot}7H_2O$)	synthesized in laboratory[17]	0.990
sodium tetraphenylboron (STPB)	Chengdu Kelong Chemical Reagent Plant	0.990
cetyltrimethylammonium bromide (CTAB)	Chengdu Kelong Chemical Reagent Plant	0.990
ethylenediamine tetraacetic acid disodium salt (EDTA)	Chengdu Kelong Chemical Reagent Plant	0.990

Table 2. Experimental Values of Densities, Refractive Indices, pH Value and Solubility of the Equilibrium Solution in the Quaternary System Li^+, K^+, Mg^{2+}//Borate−H_2O at 348 K and Pressure p = 0.1 MPa[a]

	density			w(B) × 100				Jänecke index of dry salt $J(MgB_4O_7)$ + $J(Li_2B_4O_7)$ + $J(K_2B_4O_7)$ = 100				
no.	($g{\cdot}cm^{-3}$)	refractive index	pH value	$w(MgB_4O_7)$	$w(Li_2B_4O_7)$	$w(K_2B_4O_7)$	$w(H_2O)$	$J(MgB_4O_7)$	$J(Li_2B_4O_7)$	$J(K_2B_4O_7)$	$J(H_2O)$	solid phase
1A	1.5628	1.3892	9.84	0.00	6.33	36.71	56.96	0.00	19.23	80.77	1624	LB + KB
2	1.5466	1.4035	9.82	0.91	6.58	37.25	55.26	2.49	19.11	78.40	1507	LB + KB
3	1.5635	1.4055	9.67	1.87	6.87	38.43	52.83	4.83	18.84	76.33	1359	LB + KB
4	1.5709	1.4110	9.57	4.09	7.10	41.97	46.84	9.31	17.17	73.52	1063	LB + KB
5	1.5962	1.4195	9.46	5.59	6.84	41.64	45.93	12.46	16.18	71.36	1020	LB + KB
6E	1.6077	1.4230	9.30	7.31	6.44	40.19	46.06	16.22	15.17	68.60	1019	LB + MB + KB
7B	1.5634	1.4128	8.99	8.11	0.00	42.28	49.61	19.96	0.00	80.04	1217	MB + KB
8	1.5689	1.4130	9.04	7.54	0.63	38.56	53.27	19.91	1.77	78.32	1402	MB + KB
9	1.5700	1.4135	9.13	7.69	1.62	38.49	52.20	19.71	4.41	75.88	1333	MB + KB
10	1.5748	1.4192	9.20	7.66	3.21	38.45	50.68	18.85	8.39	72.77	1242	MB + KB
11	1.5883	1.4225	9.22	7.60	5.06	38.43	48.91	17.87	12.63	69.50	1146	MB + KB
12E	1.6077	1.4230	9.30	7.31	6.44	40.19	46.06	16.22	15.17	68.60	1019	LB + MB + KB
13C	1.1248	1.3381	7.82	0.12	5.26	0.00	94.62	2.10	97.90	0.00	16527	LB + MB
14	1.1251	1.3400	7.84	0.20	5.39	0.29	94.12	3.25	93.12	3.63	15260	LB + MB
15	1.1262	1.3405	7.87	0.29	6.84	0.56	92.31	3.63	90.97	5.40	11522	LB + MB
16	1.1361	1.3405	7.92	0.39	7.01	1.46	91.14	4.35	83.11	12.54	10141	LB + MB
17	1.1422	1.3415	8.01	0.52	7.21	2.26	90.01	5.25	77.22	17.54	9047	LB + MB
18	1.1541	1.3426	8.09	0.65	7.37	3.64	88.34	5.77	69.40	24.83	7807	LB + MB
19	1.1601	1.3435	8.17	0.79	7.48	5.84	85.89	5.97	60.06	33.97	6472	LB + MB
20	1.2086	1.3467	8.26	0.96	7.42	8.07	83.55	6.38	52.36	41.26	5533	LB + MB
21	1.2671	1.3478	8.31	1.06	7.13	9.20	82.61	6.75	48.20	45.05	5241	LB + MB
22	1.2804	1.3497	8.37	1.31	7.14	11.56	79.99	7.37	42.63	50.00	4482	LB + MB
23	1.3041	1.3538	8.49	1.47	7.08	13.02	78.43	7.74	39.56	52.70	4113	LB + MB
24	1.3553	1.3596	8.59	1.59	6.88	13.97	77.56	8.10	37.19	54.71	3935	LB + MB
25	1.3896	1.3621	8.66	1.82	6.72	16.88	74.58	8.30	32.52	59.18	3387	LB + MB
26	1.4566	1.3785	8.72	2.15	6.48	18.27	73.10	9.31	29.81	60.88	3156	LB + MB
27	1.4859	1.3830	8.87	3.17	6.41	22.47	67.95	11.63	24.97	63.40	2484	LB + MB
28	1.5202	1.3917	8.91	4.14	6.43	26.37	63.06	13.25	21.85	64.91	2011	LB + MB
29	1.5533	1.4019	9.14	4.93	6.48	31.44	57.15	13.70	19.11	67.19	1582	LB + MB
30	1.5901	1.4206	9.21	6.60	6.34	35.37	51.69	16.28	16.61	67.11	1271	LB + MB
31E	1.6077	1.4230	9.30	7.31	6.44	40.19	46.06	16.22	15.17	68.60	1019	LB + MB + KB

[a]Standard uncertainties u are as follows: $u(T)$ = 0.50 K; $u_r(p)$ = 0.05; $u_r(\rho) = 2.0 \times 10^{-4}$; $u_r(n) = 1.0 \times 10^{-4}$; u_r(pH) = 0.02; $u_r(Li_2B_4O_7)$ = 0.0050; $u_r(K_2B_4O_7)$ = 0.0050; $u_r(MgB_4O_7)$ = 0.0050; w(B), mass fraction of B; J(B), the Jänecke index values of B; LB, $Li_2B_4O_7{\cdot}3H_2O$; MB, $MgB_4O_7{\cdot}9H_2O$; KB, $K_2B_4O_7{\cdot}4H_2O$.

The quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O consists of three ternary subsystems. In our previous research, the phase equilibria of its ternary subsystems Li^+, K^+//borate−H_2O[15] and K^+, Mg^{2+}//borate−H_2O[16] at 348 K have been studied. Results show that these two ternary systems at 348 K are all of simple type, no double salt or solid solution formed. This work is a continuation of our previous research. Up to now, no report has been found about the stable phase equilibrium of the aqueous quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K. Therefore, the solubility values and physicochemical properties such as densities, refractive indices, and pH values of the equilibrium solution are presented in this work. Meanwhile, the comparisons between the stable phase diagrams at 288 and 348 K are made in this work.

EXPERIMENTAL SECTION

Reagents and Apparatus. The inorganic chemicals used in this study were all analytical purity grade and tabulated in Table 1. Deionized water, used in the experiments, has an electrical conductivity less than 1×10^{-4} $s{\cdot}m^{-1}$ and pH ≈ 6.60.

A THZ-82 type digital display constant temperature water bath kettle (Jintan Guosheng Experimental Instrument Manufactory, China) was used for the stable phase equilibrium experiments. The temperature precision was ± 0.5 K. A

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standard analytical balance of 110 g capacity and 0.0001 g resolution (type AL104, Mettler Toledo Instruments Co., Ltd.) was employed to determine the weight of samples. A WYA type Abbe refractometer, conducted in a thermostat at (348 ± 0.5) K, was used for measuring the refractive index of the equilibrated solution with a precision of 0.0001. All pH values were measured with pHS-25 type pH meter at (348 ± 0.5) K. An inductively coupled plasma optical emission spectrometer (type 5300 V, PerkinElmer Instrument Corp. of America) was employed to determine the lithium ion concentrations in solution. An X-ray diffraction analyzer (DX-2700 with Cu Kα radiation) was used to analyze the phase composition of solid salt.

Analytical Methods. The Li^+ composition was analyzed by inductively coupled plasma optical emission spectrometry (precision, less than 0.5 mass %, type ICP-OES 5300 V). The amount of K^+ was analyzed by sodium tetraphenylborate−hexadecyl trimethylammonium bromide (STPB−CTAB) back-titration with a precision of ± 0.5 %; The Mg^{2+} concentration was determined by titration with ethylenediamine tetraacetic acid (EDTA) stand solution in the presence of indicator of K−B with a precision of ± 0.5 %. The composition of borate was measured by alkalimetry in the presence of mannitol (precision, ± 0.5 %).[18] Every sample was analyzed 3 times in parallel; the precision was calculated as the following equation.

$$\text{precision}/\% = \frac{V_{exp} - V_{av}}{V_{av}} \times 100 \quad (1)$$

where, V_{exp} is the experimental data; V_{av} is the average data of the parallel samples. 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.

Experimental Method. The stable phase equilibrium of the quaternary system was investigated at 348 K using an isothermal dissolution method.[19] The third component was added gradually from the invariant point of the ternary system at the same temperature to obtain the system points. For instance, from the invariant point of system K^+, Mg^{2+}//borate−H_2O at 348 K, $Li_2B_4O_7$ was added gradually for obtaining the system points. All of the artificial brine samples were put into the tightly sealed glass bottles, and these bottles were placed in the constant temperature water bath kettle with the temperature ((348 ± 0.5) K) and a constant oscillation frequency (120 rpm) to achieve a balance. During the equilibrium process, the supernatant phase was taken for chemical analysis periodically, when the composition of the supernatant phase remained constant, the dissolution equilibrium was reached. Experimental results show that in order to accelerate equilibration, the artificial brine samples need a constant oscillation frequency (120 rpm) for more than 4 weeks at (348 ± 0.5) K. After reaching equilibrium, the liquid and solid phases were separated by suction filtration at (348 ± 0.5) K. The composition of solution were measured by chemical analysis; the densities of the liquid samples were measured with the specific gravity bottle method with a precision of ± 0.0002 g·cm^{-3}; the refractive indices of equilibrated liquid phase were determined by Abbe refractometer, which was conducted in a thermostat at (348 ± 0.5) K. The equilibrium solid samples were dried at 348 K and identified by the powder X-ray diffraction method.

RESULTS AND DISCUSSION

The experimental results, including the solubility values, densities, refractive indices, pH values, and the chemical composition of equilibrium solids for the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K are listed in Table 2. The ion concentration values of the stable equilibrium solutions are expressed in mass fraction w(B) (with $w(Li_2B_4O_7)$ + $w(K_2B_4O_7)$ + $w(MgB_4O_7)$ + $w(H_2O)$ = 1) and Jänecke index J(B) (with $J(Li_2B_4O_7)$ + $J(K_2B_4O_7)$ + $J(MgB_4O_7)$ = 100), where B represents MgB_4O_7, $Li_2B_4O_7$, $K_2B_4O_7$, or H_2O. The Jänecke index J(B) is a dry salt mole percentage and can be calculated with the following correlations.

$$[M] = \frac{w(Li_2B_4O_7)}{169.12} + \frac{w(K_2B_4O_7)}{233.44} + \frac{w(MgB_4O_7)}{179.55} \quad (2)$$

$$J(K_2B_4O_7) = \frac{w(K_2B_4O_7)}{233.44[M]} \times 100 \quad (3)$$

$$J(H_2O) = \frac{w(H_2O)}{18.02[M]} \times 100 \quad (4)$$

Based on the experimental data in Table 2, the phase diagram of the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K was constructed in Figure 1. In Figure 1, points *A*, *B*, and *C* are

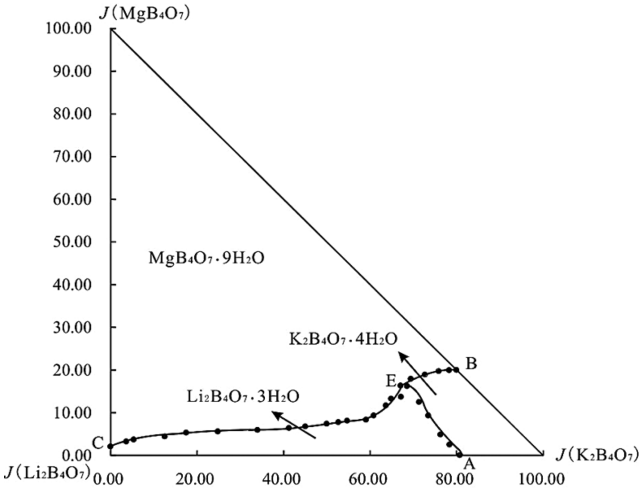

Figure 1. Phase diagram of the quaternary system Li^+, K^+, Mg^{2+}// borate−H_2O at 348 K.

the invariant points of three ternary subsystems and point *E* is the invariant point of the quaternary system. Figure 2 shows the comparison of the stable phase diagrams of this quaternary system at 288 K[14] and 348 K. The crystallization forms of the solid phase were confirmed with an X-ray diffraction analysis method and demonstrated in Figure 3.

As shown in Figure 3, the crystallographic form of borates of lithium, potassium, and magnesium at 348 K in the quaternary system are $Li_2B_4O_7{\cdot}3H_2O$, $K_2B_4O_5(OH)_4{\cdot}2H_2O$, and $MgB_4O_5(OH)_4{\cdot}7H_2O$, respectively; their corresponding molecular formulas can be abbreviated to $Li_2B_4O_7{\cdot}3H_2O$, $K_2B_4O_7{\cdot}4H_2O$, and $MgB_4O_7{\cdot}9H_2O$. The invariant point *E* are constructed with three salts, which are $Li_2B_4O_7{\cdot}3H_2O$ + $K_2B_4O_7{\cdot}4H_2O$ + $MgB_4O_7{\cdot}9H_2O$.

Table 2 and Figure 1 show that there is no double salt or solid solution formed in the quaternary system at 348 K. The phase diagram (Figure 1) is comprised of one invariant point,

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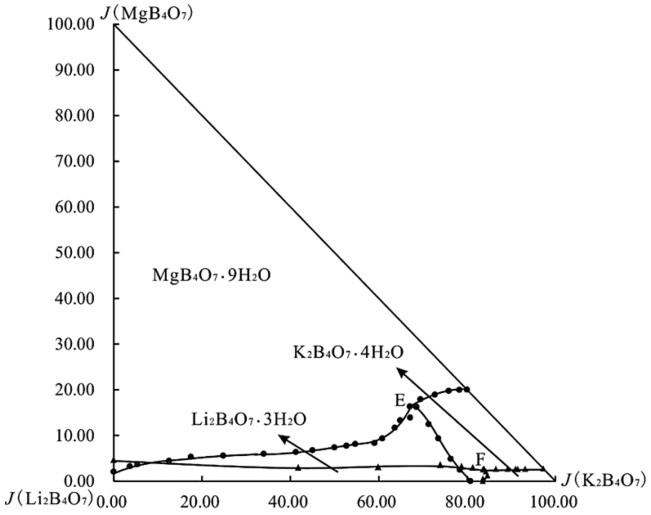

Figure 2. Phase diagram of the quaternary system Li^+, K^+, Mg^{2+}// borate−H_2O at 288 K[14] and 348 K: ●, experimental point at 348 K; ▲, experimental point at 288 K;[14] *E*, invariant point at 348 K; *F*, invariant point at 288 K.[14]

three univariant curves, and three crystallization fields. Point *E* is the invariant point of this quaternary system saturated with three salts. The composition of the equilibrium solution is $w(K_2B_4O_7)$ = 40.19%, $w(Li_2B_4O_7)$ = 6.44%, $w(MgB_4O_7)$ = 7.31%, and $w(H_2O)$ = 46.06%. The three crystallization fields correspond to three single salts, $K_2B_4O_7{\cdot}4H_2O$, $Li_2B_4O_7{\cdot}3H_2O$, and $MgB_4O_7{\cdot}9H_2O$. The size of the crystalline area is in the order $MgB_4O_7{\cdot}9H_2O$ > $Li_2B_4O_7{\cdot}3H_2O$ > $K_2B_4O_7{\cdot}4H_2O$, which shows that the solubility of $MgB_4O_7{\cdot}9H_2O$ is the lowest in the system; it means the salt $MgB_4O_7{\cdot}9H_2O$ can be more easily separated from the solution than the other coexisting salts at 348 K.

Figure 2 shows the comparisons between the stable phase diagrams at 288 K[14] and 348 K. The crystallization forms of the salts are not changed with the increase of temperature, whereas the crystallization zones of salts have changed. The crystallization zone of $MgB_4O_7{\cdot}9H_2O$ decreased at 348 K, while the crystallization zones of $K_2B_4O_7{\cdot}4H_2O$ and $Li_2B_4O_7{\cdot}3H_2O$ are both enlarged, meaning the solubility of $MgB_4O_7{\cdot}9H_2O$ increases evidently with the increase of temperature and the decrease of temperature is beneficial to the crystallization of magnesium borate. From Table 2 and Figure 1, it can be seen that the solubility of $K_2B_4O_7$ is the greatest among the coexisting salts at 348 K; thus, the physicochemical properties are mainly affected by the $K_2B_4O_7$ content in the equilibrium solution. On account of this, the water content diagram (Figure 4) and the physicochemical properties versus composition

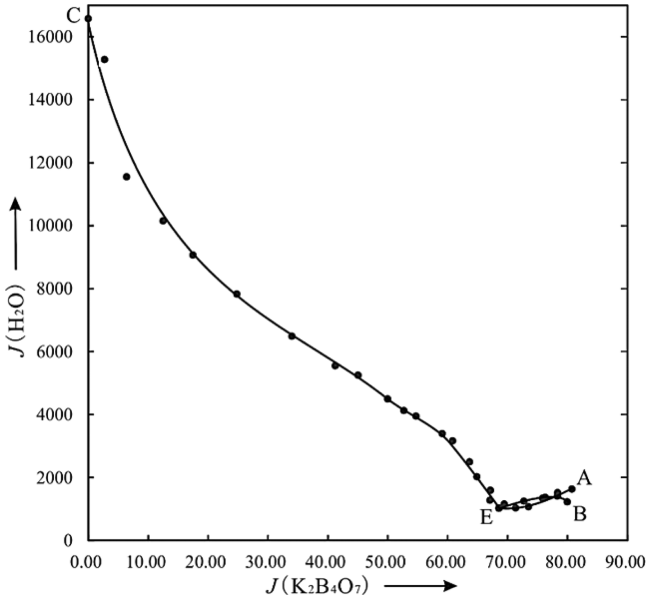

Figure 4. Water content diagram of the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K.

diagrams (Figures 5−7) were plotted with $J(K_2B_4O_7)$ as abscissa. From Figure 4, it can be seen that the water content increases slightly with the increase of $J(K_2B_4O_7)$ on the univariant curves EB and EA, while the water contents of univariant curve CE decrease obviously from 16527 to 1019. Figures 5 to 7 respectively are the densities, refractive indices, and pH values versus composition diagrams of the system at

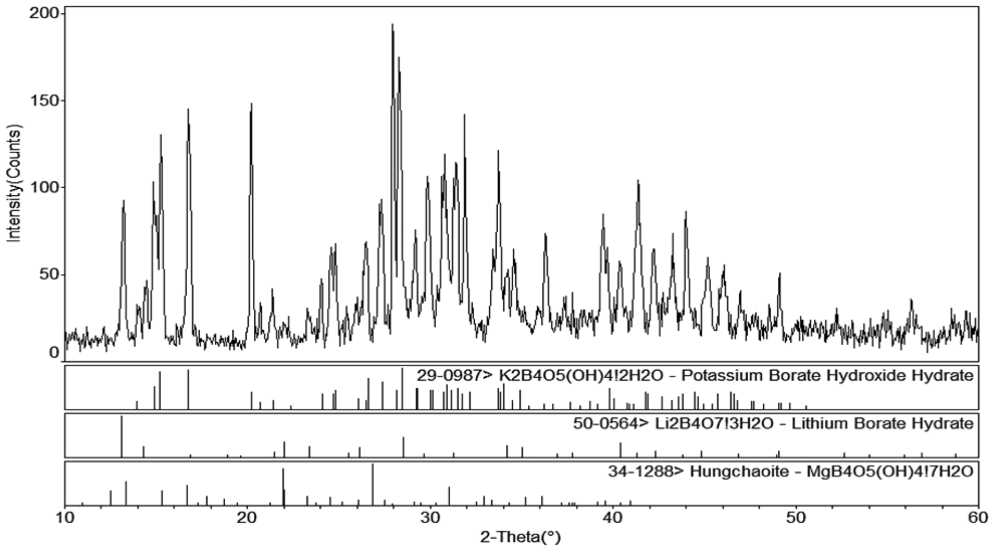

Figure 3. X-ray diffraction pattern of the invariant point *E* ($Li_2B_4O_7{\cdot}3H_2O$, $K_2B_4O_5(OH)_4{\cdot}2H_2O$, and $MgB_4O_5(OH)_4{\cdot}7H_2O$).

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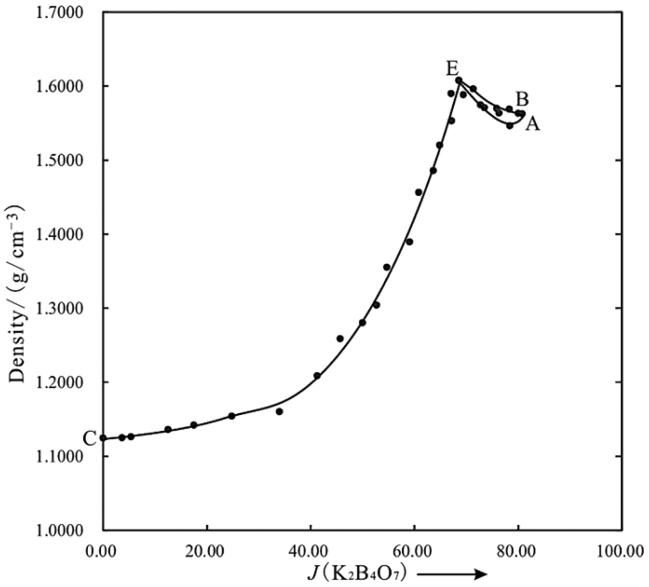

Figure 5. Densities vs composition diagram of the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K.

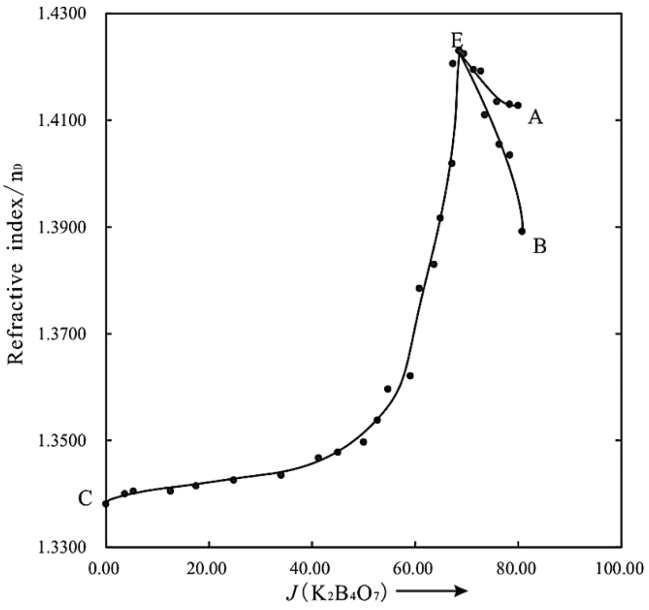

Figure 6. Refractive indices vs composition diagram of the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K.

348 K. With the increasing of $J(K_2B_4O_7)$, the densities and refractive indices both increase on the univariant curve CE, while decreasing on the univariant curve EB and EA and reaching the maximum at invariant point *E*. It can be observed from Figure 7 that on the univariant curves CE and EA, the pH values of the solution increase with the increasing of $J(K_2B_4O_7)$, while, on the univariant curve EB, the pH values have a different trend.

CONCLUSION

Stable phase equilibrium of the aqueous quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O was investigated at 348 K using an isothermal dissolution method. According to the experimental data, the phase diagram and corresponding physicochemical properties vs composition diagrams were plotted. Results show

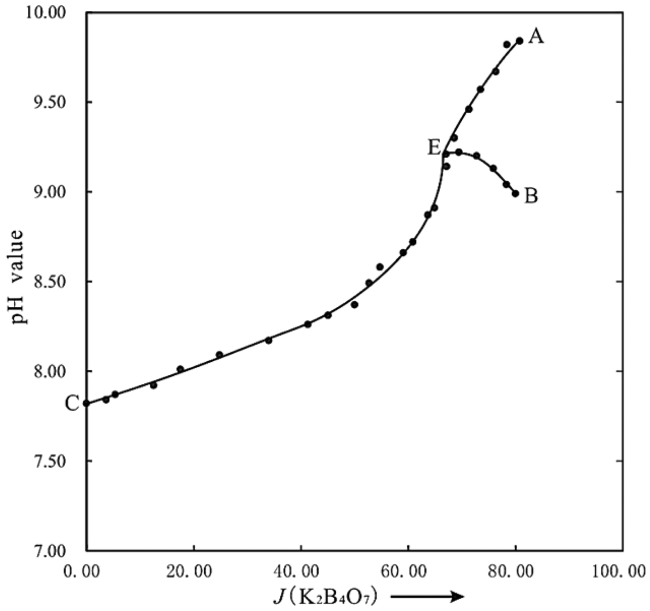

Figure 7. pH values vs composition diagram of the quaternary system Li^+, K^+, Mg^{2+}//borate−H_2O at 348 K.

that the quaternary system is of a simple type, neither solid solutions nor double salts formed at 348 K. The stable phase diagram of the quaternary system composed of one invariant point, three univariant curves, and three crystalline phase regions. Based on the comparisons between the stable phase diagrams at 288 K and 348 K, the crystallization form of the salts is not changed with the increase of temperature, whereas the scopes of the crystallization regions are obviously changed. With the increase of $J(K_2B_4O_7)$, the water contents decrease obviously from 16527 to 1019, and the physicochemical property values increase obviously on the univariant curve CE. While on the univariant curves EB and EA, the water content increases with the increase of $J(K_2B_4O_7)$, and the densities and refractive indices decrease slightly with the increase of $J(K_2B_4O_7)$.

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Notes

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