Study on the Metastable Equilibria of the Salt Lake Brine System Li_2SO_4 + Na_2SO_4 + K_2SO_4 + $Li_2B_4O_7$ + $Na_2B_4O_7$ + $K_2B_4O_7$ + H_2O at 288 K

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An experimental study on phase equilibria at 288 K in the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ was performed using the isothermal evaporation method. Equilibrium solubility and density of the solution were measured. The equilibrium phase diagram for the solution saturated with the salt $Li_2B_2O_4 \cdot 16H_2O$ was constructed. The phase diagram of this system consists of 7 invariant points, 14 univariant curves, and 8 crystallization fields corresponding to potassium tetraborate pentahydrate ($K_2B_4O_7 \cdot 5H_2O$), borax ($Na_2B_4O_7 \cdot 10H_2O$), potassium sulfate, lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), sodium sulfate, lithium−potassium sulfate double salt ($Li_2SO_4 \cdot K_2SO_4$), lithium−sodium sulfate double salt ($Li_2SO_4 \cdot Na_2SO_4$), and potassium−sodium sulfate double salt ($3K_2SO_4 \cdot Na_2SO_4$). There are three kinds of double salts formed in the system. The crystallization forms of lithium and potassium borate were $K_2B_4O_7 \cdot 5H_2O$ and $Li_2B_2O_4 \cdot 16H_2O$, respectively, which are different from the usual forms of $K_2B_4O_7 \cdot 4H_2O$ and $Li_2B_4O_7 \cdot 3H_2O$ that occur at stable equilibrium.

Introduction

Alkaline lakes are widely distributed in the area of the Qinghai-Tibet Plateau, People's Republic of China. More than 210 salt lakes, which cover an area greater than 1 km,[2] have been found in Tibet.[1] Most of the salt lakes are famous for their high concentration of lithium, potassium, and boron, such as the Zabuye Salt Lake, which contains 38.56 $g \cdot L^{-1}$ potassium, 1.72 $g \cdot L^{-1}$ lithium, and 11.57 $g \cdot L^{-1}$ B_2O_3.[2] The brines mostly belong to the complex eight-component system of $Li^+ + K^+ + Na^+ + Cl^- + CO_3^{2-} + HCO_3^- + SO_4^{2-}$ + borate ($B_4O_7^{2-}$) + H_2O. This system is different from the classic seawater system, and we usually call it the "Salt Lake Brine System".

It is well-known that the technologies of solar ponds and the comprehensive utilization of brines are strongly dependent on the phase equilibria in the brine systems. In the process of evaporating, the phase equilibria among the salts are always assumed to be metastable. Compared with stable equilibria, the investigation of metastable equilibria is more important for salts exploited from liquid resources.

Recently, metastable equilibrium studies of subsystems of the complex eight-component system have been reported, such as $Na^+ + K^+ + Cl^- + SO_4^{2-} + CO_3^{2-} + H_2O$[3] at 298 K; $Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288 K;[4] and $Na^+ + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$ at 288, 298, and 308 K.[5−7] To date, the metastable equilibrium of the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ has not been reported.

In this paper, the metastable equilibrium of the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ was studied. Because the average temperature of Tibet in summer is about 288 K, the solubilities of the five-component system were measured at this temperature.

Experimental Section

Reagents. The chemicals used were of analytical grade purity and were obtained from either the Beijing Xinghua Chemical Reagent Plant or the Chengdu Chemical Reagent Manufactory. They are lithium borate ($Li_2B_4O_7$, 99.0 mass %), potassium borate ($K_2B_4O_7 \cdot 5H_2O$, 99.0 mass %), sodium borate ($Na_2B_4O_7 \cdot 10H_2O$, 99.5 mass %), lithium sulfate ($Li_2SO_4 \cdot H_2O$, 99.0 %), potassium sulfate (K_2SO_4, 99.0 mass %), and sodium sulfate (Na_2SO_4, 99.0 mass %). Doubly deionized water (electrical conductivity less than 1×10^{-4} $S \cdot m^{-1}$, pH 6.6) was used to prepare the solutions.

Instruments. A SHH-250 type thermostatic evaporator was used for the phase equilibrium measurements. A thermostatic evaporator made by the Chongqing INBORN Instrument Corporation, China, was used to control the temperature to ± 0.1 K.

A SIEMENS D500 X-ray diffraction analyzer with Ni-filtered Cu Kα radiation was used for the analysis of solid phases. The operating condition is 35 kV and 25 mA. A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, supplied by Mettler Toledo Instruments (Shanghai) Co., Ltd.) was employed for the determination of the solution density. An atomic absorption spectrometry (type WYD-YΠ) was employed for the determination of the lithium ion and sodium ion concentration in solution.

Experimental Methods. The isothermal evaporation method was used.[4] The experiments were done at (288.15 ± 0.1) K, and a thermostatic evaporator was used for evaporation.

The measuring point depended on the changes of solid phase in the process of evaporation. When enough new solid phases appeared in the complex, the liquid and solid phases were separated by filtration. A 5.0 mL sample of the clarified solution was then taken from the liquid phase and diluted to a 50 mL final volume in a volumetric flask filled with deionized water to analyze the concentration of the liquid-phase components. The remainder of the solution was then evaporated further until it reached another measured point. A part of the wet crystals

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Table 1. Experimental Solubility Values of the Quinary System $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288.15$ K (saturated with $Li_2B_2O_4 \cdot 16H_2O$)[a]

	composition of liquid phase, (w(B) × 10^2)						Janëcke index, n(B)				ρ
no.	$w(Li^+)$	$w(Na^+)$	$w(K^+)$	$w(SO_4^{2-})$	$w(B_4O_7^{2-})$	$w(H_2O)$	$n(Na_2^{2+})$	$n(K_2^{2+})$	$n(SO_4^{2-})$	equilibrium solid phase	$g \cdot cm^{-3}$
1, A	0.009	0.49	2.70	0.00	7.12	89.68	23.79	76.21	0.00	KB + NaB + LiB	1.0788
2	0.074	0.71	2.65	0.86	7.09	88.62	22.65	64.14	13.21	KB + NaB + LiB	1.1032
4	0.105	0.75	3.07	1.89	6.74	87.44	21.68	52.16	26.16	KB + NaB + LiB	1.1050
5	0.166	0.95	3.68	2.80	5.97	86.43	21.38	48.55	30.07	KB + NaB + LiB	1.1099
6, K_1	0.181	1.22	3.94	3.37	5.80	86.87	23.64	45.01	31.35	KB + NaB + LiB + LiKS	1.1174
7	0.094	1.01	4.19	3.78	6.67	84.26	19.11	46.64	34.25	LiB + KB + KS	1.1196
8	0.074	0.88	4.31	4.19	5.58	84.97	16.23	46.76	37.01	LiB + KB + KS	1.1198
9	0.073	0.85	4.93	5.06	5.29	83.80	13.77	46.98	39.25	LiB + KB + KS	1.1201
10	0.069	0.68	5.35	4.89	5.78	83.23	11.02	51.01	37.97	LiB + KB + KS	1.1227
11, B	0.060	0.00	5.38	3.67	5.43	85.46	0.00	64.30	35.70	LiB + KB + KS	1.1231
12, C	0.811	0.00	3.13	8.97	0.80	86.29	0.00	30.04	69.96	LiB + LiKS + KS	1.1466
13	0.864	0.71	2.82	10.23	1.14	84.24	9.82	22.83	67.35	LiB + LiKS + KS	1.1505
14	1.051	1.09	2.95	12.00	1.92	81.01	12.73	20.25	67.01	LiB + LiKS + KS	1.1536
15	1.258	2.42	3.17	16.78	3.41	72.96	19.64	15.12	65.24	LiB + LiKS + KS	1.1738
16	1.339	2.52	3.22	16.30	3.53	73.09	20.62	15.50	63.88	LiB + LiKS + KS	1.2249
17, K_3	1.449	2.59	3.14	16.80	4.03	71.99	20.75	14.80	64.45	LiB + LiKS + KS + NaKS	1.2251
18	1.638	2.80	2.88	17.93	4.52	70.23	21.43	12.95	65.62	LiB + LiKS + NaKS	1.2284
19	1.887	3.05	2.47	19.44	4.88	68.27	22.08	10.52	67.40	LiB + LiKS + NaKS	1.2460
20	2.097	3.20	1.89	20.36	5.09	67.36	22.74	7.91	69.35	LiB + LiKS + NaKS	1.2501
21	2.385	3.61	1.71	22.77	5.47	64.06	23.29	6.48	70.23	LiB + LiKS + NaKS	1.2631
22	2.608	4.16	1.11	24.52	5.80	61.80	25.14	3.94	70.92	LiB + LiKS + NaKS	1.2840
23, K_4	2.595	4.93	0.97	27.57	3.03	61.61	26.37	3.05	70.58	LiB + LiKS + NaKS + LiS	1.3009
24	2.081	3.07	0.99	20.46	2.54	67.92	22.83	4.33	72.84	LiB + LiKS + LiS	1.2872
25	2.004	2.31	1.03	18.48	2.38	71.62	19.63	5.15	75.22	LiB + LiKS + LiS	1.2454
26	1.959	2.13	1.03	18.62	1.03	71.96	18.26	5.20	76.54	LiB + LiKS + LiS	1.2356
27	1.565	1.17	1.09	14.05	0.91	77.95	13.70	7.51	78.79	LiB + LiKS + LiS	1.2277
28, D	1.686	0.00	1.12	12.70	0.53	83.95	0.00	9.75	90.25	LiB + LiKS + LiS	1.1610
29, E	1.830	4.57	0.00	21.55	0.98	71.07	46.97	0.00	53.03	LiB + LiS + LiNaS	1.1675
30	1.834	5.26	0.17	22.76	1.81	68.17	32.35	0.62	67.03	LiB + LiS + LiNaS	1.2374
31	1.899	5.28	0.19	23.10	2.09	67.44	32.08	0.68	67.24	LiB + LiS + LiNaS	1.2825
32, K_5	2.303	5.44	0.24	26.15	2.33	63.54	30.05	0.78	69.17	LiB + LiS + LiNaS + NaKS	1.3094
33, K_6	1.339	5.70	1.40	22.20	1.10	68.27	33.21	4.81	61.98	LiB + NaS + LiNaS + NaKS	1.2849
34	1.253	5.67	1.35	21.51	1.07	69.15	33.82	4.74	61.44	LiB + LiNaS + NaS	1.2687
35	1.238	5.62	1.07	20.96	1.07	70.04	34.52	3.86	61.62	LiB + LiNaS + NaS	1.2501
36	1.246	5.59	0.86	20.72	1.02	70.56	34.90	3.16	61.94	LiB + LiNaS + NaS	1.2251
37	1.215	5.55	0.58	17.24	0.98	74.43	39.20	2.39	58.31	LiB + LiNaS + NaS	1.2063
38, F	1.184	5.54	0.00	20.59	0.97	71.72	52.92	0.00	47.08	LiB + LiNaS + NaS	1.1893
39, G	1.080	5.74	0.00	18.78	1.11	73.29	56.08	0.00	43.92	LiB + NaS + NaB	1.1969
40	0.669	5.09	1.21	15.35	2.25	75.43	38.70	5.41	55.89	LiB + NaS + NaB	1.1984
41	0.549	4.78	1.79	14.56	2.29	76.03	37.33	8.22	54.45	LiB + NaS + NaB	1.1991
42	0.516	4.46	2.13	14.03	2.38	76.48	35.88	10.08	54.04	LiB + NaS + NaB	1.1999
43, K_7	0.428	4.35	2.88	13.40	3.53	75.41	34.92	13.59	51.49	LiB + NaS + NaKS + NaB	1.2004
44	0.594	4.11	2.95	13.90	3.91	74.54	32.88	13.88	53.24	LiB + NaS + NaB	1.2085
45	0.773	3.89	2.97	14.41	4.38	73.58	31.03	13.93	55.04	LiB + NaS + NaB	1.2167
46	0.958	3.59	3.13	15.07	4.69	72.56	28.38	14.56	57.06	LiB + NaS + NaB	1.2203
47, K_2	1.267	3.22	3.27	15.96	5.74	70.54	25.18	15.11	59.71	LiB + NaKS + NaB + KS	1.2265
48	1.286	3.16	3.21	16.20	5.24	70.90	24.68	14.74	60.58	LiB + NaKS + NaB	1.2257
49	1.336	2.81	3.17	16.30	4.38	72.00	22.51	14.95	62.54	LiB + NaKS + NaB	1.2260
50	2.513	5.01	0.83	27.10	2.87	61.68	27.11	2.65	70.24	LiB + LiKS + NaKS	1.3011
51	2.430	5.14	0.78	26.93	2.55	62.17	27.79	2.48	69.73	LiB + LiKS + NaKS	1.3025
52	2.426	5.19	0.58	26.82	2.46	62.52	28.25	1.86	69.89	LiB + LiKS + NaKS	1.3073
53	2.391	5.21	0.51	26.60	2.35	62.94	28.55	1.65	69.80	LiB + LiKS + NaKS	1.3082
54	2.045	5.58	0.89	25.62	2.06	63.80	30.37	2.85	66.78	LiB + LiNaS + NaKS	1.2953
55	1.634	5.67	1.13	23.37	1.89	66.31	32.35	3.80	63.85	LiB + LiNaS + NaKS	1.2932
56	1.317	5.38	1.83	21.60	1.61	68.27	32.02	6.41	61.57	LiB + NaKS + NaS	1.2688
57	0.821	5.18	2.47	18.20	2.15	71.18	33.75	9.47	56.78	LiB + NaKS + NaS	1.2631
58	0.910	4.80	2.65	17.80	2.87	70.97	32.25	10.48	57.27	LiB + NaKS + NaS	1.2453
59	0.776	4.39	2.70	15.90	3.16	73.07	32.30	11.69	56.01	LiB + NaKS + NaS	1.2087
60	2.535	5.15	0.70	27.59	2.52	61.50	27.43	2.19	70.38	LiB + LiS + NaKS	1.3078
61	2.513	5.32	0.53	27.62	2.48	61.54	28.21	1.66	70.13	LiB + LiS + NaKS	1.3085

[a] LiB, $Li_2B_2O_4 \cdot 16H_2O$; NaB, $Na_2B_4O_7 \cdot 10H_2O$; KB, $K_2B_4O_7 \cdot 5H_2O$; KS, K_2SO_4; LiKS, $LiKSO_4$; NaKS, $3K_2SO_4 \cdot Na_2SO_4$; NaS, Na_2SO_4; LiS, $Li_2SO_4 \cdot H_2O$; LiNaS, $LiNaSO_4$; w(B), mass fraction; $n(Na_2^{2+}) + n(K_2^{2+}) + n(SO_4^{2-}) = 100$ mol.

was analyzed directly after the equilibrium solution was filtered out. Subsequently, the other wet crystals in solid phase were separated from each other according to crystal shape as much as possible, dried at 288 K, pestled into a powder, and then analyzed by X-ray diffraction.

The densities of solution were also determined in this study and used for the mass fraction calculation of components.[4] The densities were determined by the specific gravity bottle method with correction for the floating force of air (precision: 0.0001 $g \cdot cm^{-3}$). The operation process was the same as pycnometric density; the pycnometer was simply substituted by the gravity bottle. The weighing bottles of 10 cm^3 volumes were dried beforehand by baking and flushing with dry nitrogen and then stored in a stoppered bottle. Then 5 mL of liquid was placed in the weighing bottle. The weighing bottle and the weighing bottle with liquid were weighted with a standard analytical balance. All the measurements were done at (288 ± 0.1) K.

Analytical Methods. The potassium ion concentration was measured by titration with a sodium tetraphenylborate−hexadecyl trimethyl ammonium bromide aqueous solution. First, a 1 % (w/v) kalignost (sodium tetraphenylborate) solution (a quantitative excess) was added to the potassium solution. Under

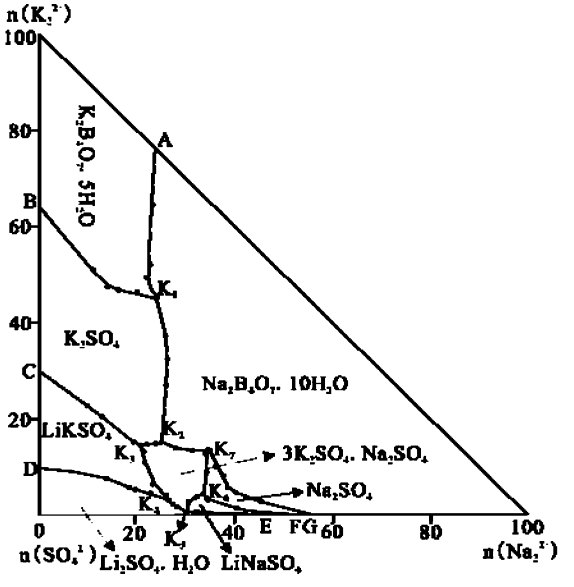

Figure 1. Metastable phase diagram of the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288 K (saturated with $Li_2B_2O_4 \cdot 16H_2O$).

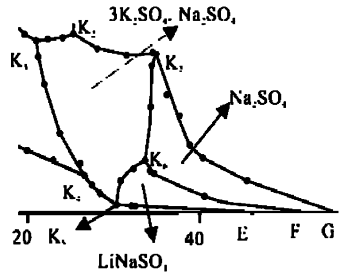

Figure 2. Partial enlarged diagram of Figure 1.

basic conditions, the potassium ion can act with kalignost to form a potassium tetraphenylboron ($K[B(C_6H_5)_4]$) precipitate. Ten minutes later, the excess of the kalignost solution was titrated with 0.35 % hexadecyl trimethyl ammonium bromide in the presence of turpentine oil as a precipitate protecting agent and titan yellow as indicator. The average relative deviation of the determination was less than 0.5 %.

Lithium ion and sodium ion concentrations were determined by atomic absorption spectrometry. The uncertainty was less than 0.06 %. Borate ion concentration was determined by a neutralization titration using propanetriol. The uncertainty was less than 0.3 %.[8]

The sulfate ion concentration was determined by titration with a standard solution of EDTA in the presence of an excess Ba−Mg mixture solution. First, a Ba−Mg mixture solution (containing 0.01 $mol \cdot L^{-1}$ $BaCl_2$ and 0.005 $mol \cdot L^{-1}$ $MgCl_2$) was added to give a $BaSO_4$ precipitate. The remaining $BaCl_2$ in the solution was titrated with EDTA standard solution in the presence of mixed K−B (acid chrome blue K + naphthol green B) indicator. The uncertainty was less than 1 %.

Results and Discussion

The measured phase equilibrium experimental results of solubilities for the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288 K are tabulated in Table 1. The concentration of each solution component is given both in mass fractions and Janëcke index values, shown as *w*(B) and *n*(B) (with $n(Na_2^{2+}) + n(K_2^{2+}) + n(SO_4^{2-}) = 100$ mol), respectively. Table 1 also presents the solid-phase composition being in equilibrium with the studied solution. On the basis of the Janëcke index *n*(B), the experimental solubility isothermal metastable phase diagram of the system at 288 K was plotted, as shown in Figure 1. Figure 2 is a partial enlarged phase diagram of Figure 1.

The phase diagram of the quinary system shown in Figure 1 (saturated with $Li_2B_2O_4 \cdot 16H_2O$) consists of 8 crystallization fields, 7 invariant points (points K_1 to K_7) and 14 univariant curves. The eight crystallization fields correspond to potassium tetraborate pentahydrate ($K_2B_4O_7 \cdot 5H_2O$), borax ($Na_2B_4O_7 \cdot 10H_2O$), potassium sulfate, lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), sodium sulfate, lithium−potassium sulfate double salt ($Li_2SO_4 \cdot K_2SO_4$), lithium−sodium sulfate double salt ($Li_2SO_4 \cdot Na_2SO_4$), and potassium−sodium sulfate double salt ($3K_2SO_4 \cdot Na_2SO_4$). The crystallization area of borax is obviously larger than that of the other salts, which indicates that the borax salt is more easily saturated and crystallized from solution.

The equilibria solid phases and the mass fraction composition of the liquid phase of the invariant points are shown in Table 2. Every invariant point is saturated with four kinds of salts. On the basis of X-ray analysis of the solid phases, the crystallization forms for lithium and potassium borate were $K_2B_4O_7 \cdot 5H_2O$ and $Li_2B_2O_4 \cdot 16H_2O$, respectively, which are usually $K_2B_4O_7 \cdot 4H_2O$ and $Li_2B_4O_7 \cdot 3H_2O$ in stable equilibrium at 298 K.

There are three kinds of double salts formed in this quinary system: a lithium−potassium sulfate double salt ($Li_2SO_4 \cdot K_2SO_4$), a lithium−sodium sulfate double salt ($Li_2SO_4 \cdot Na_2SO_4$), and a potassium−sodium sulfate double salt ($3K_2SO_4 \cdot Na_2SO_4$). It is worthy to point out that the potassium−sodium sulfate double salt ($3K_2SO_4 \cdot Na_2SO_4$) is not formed in the quaternary system $Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288 K.[4] This result shows that the presence of lithium ion in the aqueous solution affects the interaction of sodium and potassium sulfate.

Borates can form different polyanions in solution. The various species of boron in aqueous solution depend on the pH value, the total concentration of boron and salts, and the kinds of coexistent salts.[9] $B_4O_7^{2-}$ is just the traditional stoichiometric expression for various boric species in solution. In this metastable system, the equilibrium solid phase of lithium borate exists as a diborate and that of potassium borate exists as a tetraborate.

Table 2. Equilibria Solid Phases and Mass Fraction Composition of Liquid Phase of Invariant Points in the Quinary System $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288.15$ K

	composition of liquid phase, ($w(B) \times 10^2$)						
no.	$w(Li^+)$	$w(Na^+)$	$w(K^+)$	$w(SO_4^{2-})$	$w(B_4O_7^{2-})$	$w(H_2O)$	equilibrium solid phase
K_1	0.181	1.22	3.94	3.37	5.80	86.87	$Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O + Na_2B_4O_7 \cdot 10H_2O + K_2SO_4$
K_2	1.267	3.22	3.27	15.96	5.74	70.54	$Li_2B_2O_4 \cdot 16H_2O + K_2SO_4 + Na_2B_4O_7 \cdot 10H_2O + 3K_2SO_4 \cdot Na_2SO_4$
K_3	1.449	2.59	3.14	16.80	4.03	71.99	$Li_2B_2O_4 \cdot 16H_2O + K_2SO_4 + Li_2SO_4 \cdot K_2SO_4 + 3K_2SO_4 \cdot Na_2SO_4$
K_4	2.595	4.93	0.97	27.57	3.03	61.61	$Li_2B_2O_4 \cdot 16H_2O + Li_2SO_4 \cdot H_2O + Li_2SO_4 \cdot K_2SO_4 + 3K_2SO_4 \cdot Na_2SO_4$
K_5	2.303	5.44	0.24	26.15	2.33	63.54	$Li_2B_2O_4 \cdot 16H_2O + Li_2SO_4 \cdot H_2O + Li_2SO_4 \cdot Na_2SO_4 + 3K_2SO_4 \cdot Na_2SO_4$
K_6	1.339	5.70	1.40	22.20	1.10	68.27	$Li_2B_2O_4 \cdot 16H_2O + Li_2SO_4 \cdot Na_2SO_4 + Na_2SO_4 + 3K_2SO_4 \cdot Na_2SO_4$
K_7	0.428	4.35	2.88	13.40	3.53	75.41	$Li_2B_2O_4 \cdot 16H_2O + Na_2SO_4 + 3K_2SO_4 \cdot Na_2SO_4 + Na_2B_4O_7 \cdot 10H_2O$

Conclusions

Metastable equilibria of the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288 K were studied using the isothermal evaporation method. The solubility and densities of the equilibrium solutions were determined.

The equilibrium phase diagram for this system at 288 K consists of 7 invariant points, 14 univariant curves, and 8 crystallization fields corresponding to potassium tetraborate pentahydrate ($K_2B_4O_7 \cdot 5H_2O$), borax ($Na_2B_4O_7 \cdot 10H_2O$), potassium sulfate, lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), sodium sulfate, lithium−potassium sulfate double salt ($Li_2SO_4 \cdot K_2SO_4$), lithium−sodium sulfate double salt ($Li_2SO_4 \cdot Na_2SO_4$), and potassium−sodium sulfate double salt ($3K_2SO_4 \cdot Na_2SO_4$). Three kinds of double sulfate salts (lithium and potassium, lithium and sodium, and potassium and sodium) formed in this quinary system. The crystallization form of lithium borate in this quinary system was $Li_2B_2O_4 \cdot 16H_2O$.

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