J. Chem. Eng. Data **2006,** *51,* 219−222

Liquid−Solid Metastable Equilibria in the Quinary System $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288$ K

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An experimental study on phase equilibria at 288 K in the quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ was done by the isothermal evaporation method. Equilibrium solubility of the solution was measured, and the equilibrium phase diagram for the solution saturated with salt Li_2CO_3 was constructed in which there were three invariant points, seven univariant curves, and five crystallization fields corresponding to potassium chloride, lithium chloride monohydrate ($LiCl \cdot H_2O$), potassium borate pentahydrate ($K_2B_4O_7 \cdot 5H_2O$), hydrated lithium borate ($Li_2B_2O_4 \cdot 16H_2O$), hydrated potassium carbonate ($K_2CO_3 \cdot {}^3/_2H_2O$). No solid solutions or double salts were found. In comparison with the metastable phase diagram of this quinary system at 288 K and its stable phase diagram at 298 K, the size of the salt crystallization fields and the salt crystallization forms were changed. These changes between phase diagrams at different temperature will be very useful for extracting the salts.

Introduction

Alkaline lakes are widely distributed in the area of the Qinghai-Xizhang Plateau. The Zabuye Salt Lake, located in Tibet, is one of the alkaline lakes famous for its high concentrations of sodium, potassium, lithium, and borate,[1] and the composition of its brines mostly belong to the eight-component system $Li^+ + K^+ + Na^+ + Cl^- + CO_3^{2-} + HCO_3^- + SO_4^{2-}$ + borate ($B_4O_7^{2-}$) + H_2O. Although these salt lake brine resources are valuable, nothing has been reported on its comprehensive utilization because the relevant phase relations are lacking.

As a part of the eight-component system, the stable equilibria of some four- or five-component subsystems have been measured.[2−5] In the process of evaporating, the phase equilibria among the salts are always assumed as metastable. Compared with the stable equilibrium, the metastable equilibrium result is more important for the salts exploiting from the liquid resources, which has been proven in practice, just as the exploiting of Searles Salt Lake in the United States and of Chaidamu saline Lake in China.

Recently, a series of metastable equilibrium studies aimed at the subsystems of a complex eight-component system have been reported, such as $Li^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$[6] and $Na^+ + K^+ + Cl^- + SO_4^{2-} + CO_3^{2-} + H_2O$ at 298 K,[7] $Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288 K,[8] $Na^+ + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$ at $T =$ (288 K, 298 K, and 308 K),[9−11] and $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K.[12]

In this paper, the metastable equilibrium of the quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ has been studied. The solubilities of the five-component system at 288 K were measured. This system is a subsystem of the eight-component system of Zabuye brines. Its isothermal dissolution phase diagram at 298 K has been reported, but no report has been found about its phase equilibrium at 288 K. Because the average temperature of Tibet in the summer is about 288 K, the metastable phase equilibrium study at 288 K will be more in accordance with expected conclusions.

Experimental Section

Reagents. The chemicals used were of analytical purity grade and were obtained from either the Beijing Xinghua Chemical Reagent Plant or the Chengdu Chemical Reagent Manufactory. They are lithium borate ($Li_2B_4O_7$, mass fraction 99.0 %), potassium borate ($K_2B_4O_7 \cdot 5H_2O$, mass fraction 99.0 %), lithium chloride ($LiCl \cdot H_2O$, mass fraction 97.0 %), potassium chloride (KCl, mass fraction 99.5 %), lithium carbonate (Li_2CO_3, mass fraction 99.0 %), and potassium carbonate (K_2CO_3, mass fraction 99.0 %). 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 measurement. The thermostatic evaporator was made in Chongqing INBORN Instrument Corporation, China, whose temperature could be controlled to ± 0.1 K. A SIMENS D500 X-ray diffraction analyzer was used for the X-ray diffraction analysis for the solid phase.

Experimental Methods. The isothermal evaporate method was used. The series of mixtures of the quinary system were loaded into clean polyethylene bottles. The mixtures were made up with salts and deionized water, whose quantities were calculated according to the composition of invariant points in the quaternary subsystem. The bottles were placed in the thermostatic evaporator, whose temperature was controlled to (288.15 ± 0.1) K, and exhausted at 20 $m^3 \cdot min^{-1}$ to accelerate the equilibrium of those complexes.

The measuring point depended on the changes of solid phase in the process of evaporate. When enough new solid phases appeared in the complex, the liquid and solid phases were separated by filter. Then a 5.0 mL sample of the clarified solution was taken from the liquid phase and diluted to 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 poured back into the

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10.1021/je050337m CCC: $33.50 © 2006 American Chemical Society
Published on Web 10/28/2005

Table 1. Experimental Values of Solubility and Density (ρ) for the Quinary System $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288.15$ K (Saturated with Li_2CO_3)

	composition of liquid phase, (w(B) × 10^2)						Janëcke index n(B), $n(Na_2^{2+}) + n(CO_3^{2-}) + n(B_4O_7^{2-}) = 100$ mol				
no.	$w(Li^+)$	$w(K^+)$	$w(Cl^-)$	$w(B_4O_7^{2-})$	$w(CO_3^{2-})$	$w(H_2O)$	$n(K_2^{2+})$	$n(Cl^-)$	$n(B_4O_7^{2-})$	equilibrium solid phase	$\rho/(g \cdot cm^{-3})$
1, G_1	0.066	29.38	0.38	0.00	22.51	47.66	98.59	1.41	0.00	$KCl + K_2CO_3 \cdot 3/2H_2O + Li_2CO_3$	1.5581
2	0.067	29.03	0.38	0.24	22.15	48.13	98.16	1.43	0.41	$KCl + K_2CO_3 \cdot 3/2H_2O + Li_2CO_3$	1.5549
3	0.058	28.83	0.39	0.33	21.75	48.24	97.30	1.45	1.25	$KCl + K_2CO_3 \cdot 3/2H_2O + Li_2CO_3$	1.5530
4	0.043	28.55	0.42	0.90	21.39	48.70	96.89	1.57	1.54	$KCl + K_2CO_3 \cdot 3/2H_2O + Li_2CO_3$	1.5511
5	0.039	28.04	0.44	1.24	20.84	49.40	96.21	1.65	2.14	$KCl + K_2CO_3 \cdot 3/2H_2O + Li_2CO_3$	1.5503
6, E_3	0.032	27.82	0.64	1.59	20.33	49.59	95.52	1.73	2.75	$KCl + K_2CO_3 \cdot 3/2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5484
7	0.041	25.78	0.40	1.57	19.02	53.19	95.45	1.62	2.93	$K_2CO_3 \cdot {}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5413
8	0.047	25.43	0.38	1.61	18.77	53.76	95.40	1.56	3.04	$K_2CO_3 \cdot {}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5404
9	0.057	24.56	0.31	1.73	18.16	55.18	95.31	1.31	3.38	$K_2CO_3 \cdot {}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5399
10	0.070	23.91	0.19	2.01	16.29	57.53	95.16	0.82	4.02	$K_2CO_3 \cdot {}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5350
11	0.080	22.37	0.12	2.05	16.62	58.76	95.07	0.54	4.39	$K_2CO_3 \cdot {}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5293
12, G_3	0.084	21.77	0.00	2.35	16.16	59.64	94.85	0.00	5.15	$K_2CO_3 \cdot {}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5246
13, G_2	2.72	1.09	14.63	0.00	0.21	81.35	7.42	92.58	0.00	$LiCl \cdot H_2O + KCl + Li_2CO_3$	1.2763
14	2.09	1.37	11.50	0.16	0.29	84.59	8.16	91.26	0.58	$LiCl \cdot H_2O + KCl + Li_2CO_3$	1.2718
15	1.99	1.48	11.04	0.24	0.31	84.94	10.74	88.37	0.89	$LiCl \cdot H_2O + KCl + Li_2CO_3$	1.2593
16	1.78	1.50	9.89	0.35	0.33	86.15	11.92	86.66	1.42	$LiCl \cdot H_2O + KCl + Li_2CO_3$	1.2455
17	1.73	1.51	9.52	0.48	0.39	86.37	12.33	85.70	1.97	$LiCl \cdot H_2O + KCl + Li_2CO_3$	1.2370
18, E_1	1.57	1.53	8.68	0.48	0.41	87.33	13.48	84.37	2.15	$LiCl \cdot H_2O + KCl + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2319
19	1.77	1.10	9.35	0.55	0.35	86.88	9.44	88.20	2.36	$LiCl \cdot H_2O + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2465
20	2.13	0.90	11.09	0.71	0.26	84.91	6.67	90.69	2.64	$LiCl \cdot H_2O + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2513
21	2.56	0.73	13.21	0.93	0.09	82.48	4.60	92.43	2.97	$LiCl \cdot H_2O + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2589
22	3.49	0.45	17.64	1.14	0.08	77.20	2.43	94.49	3.08	$LiCl \cdot H_2O + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2618
23, G_5	4.37	0.00	21.48	1.74	0.03	72.38	0.00	96.43	3.57	$LiCl \cdot H_2O + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2784
24	1.38	1.65	7.57	0.96	0.47	87.97	15.74	79.63	4.63	$KCl + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2603
25	1.30	1.91	7.16	1.36	0.49	87.78	18.21	75.28	6.51	$KCl + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2586
26	1.11	2.47	6.44	1.86	0.51	87.55	23.50	67.57	8.93	$KCl + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2497
27	0.90	2.65	5.31	2.29	0.57	88.28	27.43	60.61	11.96	$KCl + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O$	1.2412
28, E_2	0.76	2.82	4.71	2.24	0.59	88.88	30.86	56.81	12.33	$KCl + Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O$	1.1541
29	1.00	8.63	7.07	3.66	3.57	76.07	47.25	42.66	10.09	$KCl + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.2674
30	0.964	11.02	6.41	3.41	5.88	72.32	55.64	35.70	8.66	$KCl + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.3360
31	0.445	17.37	5.73	3.43	9.08	63.94	68.35	24.86	6.79	$KCl + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.4927
32	0.356	21.91	4.82	2.39	13.35	57.17	77.07	18.69	4.24	$KCl + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5315
33	0.140	25.78	3.04	2.27	16.93	51.84	85.13	11.09	3.78	$KCl + Li_2CO_3 + K_2B_4O_7 \cdot 5H_2O$	1.5443
34	0.66	3.09	3.98	3.10	0.65	88.52	34.19	48.54	12.27	$Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O$	1.1437
35	0.56	3.31	3.22	3.83	0.77	88.31	37.64	40.38	21.98	$Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O$	1.1409
36	0.46	3.85	1.73	6.71	0.89	86.36	42.15	20.83	37.02	$Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O$	1.1156
37	0.38	4.07	0.66	7.96	1.13	85.80	46.23	8.24	45.53	$Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O$	1.0933
38, G_4	0.35	4.56	0.00	9.00	1.30	84.56	50.15	0.00	49.85	$Li_2CO_3 + Li_2B_2O_4 \cdot 16H_2O + K_2B_4O_7 \cdot 5H_2O$	1.0812

[a] w(B), mass fraction.

polyethylene bottle and continued to be evaporated until it reached another measured point. A part of the wet crystals was analyzed directly after the equilibrium solution was filtered out. Then the other wet crystals in solid phase were separated from each other according to crystal shapes as much as possible, dried at 288 K, pestled into a power, and then analyzed by X-ray diffraction.

The crystallization of the solid phase was identified by X-ray diffraction using a SIEMENS D500 X-ray diffractometer with Ni-filtered Cu Ka radiation, operating at 35 kV and 25 mA.

The densities of solution were also determined in this study and used for the mass fraction calculation of components. The specific gravity bottle method correction for floating force of air (precision: $0.0001\ g \cdot cm^{-3}$) was used. The operation process was the same as pycnometric density. The weighing bottle of 10 cm^3 volumes was dried beforehand by baking and flushing with dry nitrogen and stored in a stoppered bottle. Then 5 mL of liquids was placed in the weighing bottle. The weighing bottle and the weighing bottle with liquids were weighted with a standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, supplied by Mettler Toledo Instruments (Shanghai) Co., Ltd.). All the measurements were done at (288.15 ± 0.1) K.

Analytical Methods. The potassium ion concentration was measured by titration with a sodium tetraphenylborate−hexadecyl trimethylammonium bromide aqueous solution. The average relative deviation of the determination was less than 0.5 %. Lithium ion concentration was determined by atomic absorption spectrometry (Type WYD-YΠ). The uncertainty was less than 0.06 %. Borate ion concentration was determined by a neutralization titration with the existence of propanetriol. The uncertainty was less than 0.3 %.[14] The chlorate ion concentration was measured by titration with a standard solution of $AgNO_3$ in the presence of three drops of a solution of composition of 10 g K_2CrO_4 in 100 cm^3 water. The uncertainty was less than 0.1 %. The carbonate ion concentration was determined by a method of acid−base titration. The uncertainty was less than 0.5 %.[13]

Results and Discussions

Metastable Phase Diagram at 288 K. The phase equilibrium experimental results of solubilities for quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K were measured and tabulated in Table 1. In Table 1, w(B) is the mass fraction of B and n(B) is the Janëcke index values of B, with $n(K_2^{2+}) + n(Cl_2^{2-}) + n(B_4O_7^{2-}) = 100$ mol. 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.

The phase diagram of the quinary system in Figure 1 consists of five crystallization fields, three invariant points (point E_1, E_2, E_3), and seven univariant curves. The five crystallization fields are corresponding to potassium chloride, lithium chloride monohydrate ($LiCl \cdot H_2O$), potassium borate pentahydrate ($K_2B_4O_7 \cdot 5H_2O$), hydrated lithium borate ($Li_2B_2O_4 \cdot 16H_2O$), and hydrated potassium carbonate ($K_2CO_3 \cdot {}^3/_2H_2O$). The crystallization areas

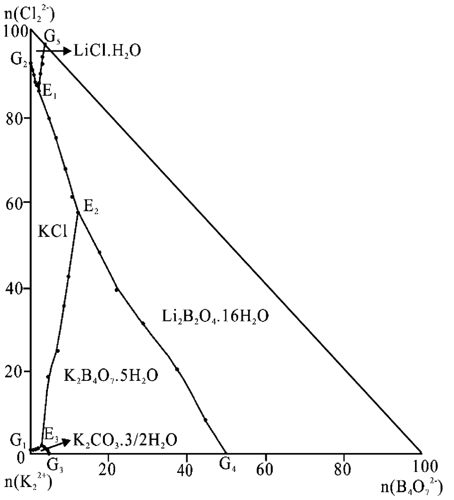

Figure 1. Metastable equilibrium phase diagram of the quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K (saturated with Li_2CO_3).

of potassium and lithium borate are larger than that for the other salts, which indicate that the potassium and lithium borate are easy to be saturated and crystallized from solution.

Invariant point E_1 was saturated with salts $LiCl{\cdot}H_2O + KCl + Li_2CO_3 + Li_2B_2O_4{\cdot}16H_2O$, and the mass fraction composition of corresponding liquid phase is $w(Li^+) = 1.57$ %, $w(K^+) = 1.53$ %, $w(Cl^-) = 8.68$ %, $w(B_4O_7^{2-}) = 0.48$ %, and $w(CO_3^{2-}) = 0.41$ %. Invariant point E_2 was saturated with salts $KCl + Li_2B_2O_4{\cdot}16H_2O + Li_2CO_3 + K_2B_4O_7{\cdot}5H_2O$, and the mass fraction composition of corresponding liquid phase is $w(Li^+) = 0.76$ %, $w(K^+) = 2.82$ %, $w(Cl^-) = 4.71$ %, $w(B_4O_7^{2-}) = 2.24$ %, and $w(CO_3^{2-}) = 0.59$ %. Invariant point E_3 was saturated with salts $KCl + K_2CO_3{\cdot}{}^3/_2H_2O + Li_2CO_3 + K_2B_4O_7{\cdot}5H_2O$, and the mass fraction composition of corresponding liquid phase is $w(Li^+) = 0.032$ %, $w(K^+) = 27.82$ %, $w(Cl^-) = 0.64$ %, $w(B_4O_7^{2-}) = 1.59$ %, and $w(CO_3^{2-}) = 20.33$ %.

G_1 and G_2 are two invariant points for the subsystem $Li^+ + K^+ + Cl^- + CO_3^{2-} + H_2O$, G_3 and G_4 are two invariant points for the subsystem $Li^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$, and G_5 is the invariant point for the simple subsystem $Li^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$. These invariant points for quaternary subsystem are all cosaturated with three salts.

Comparison between the Metastable and Stable Equilibrium Phase Diagram. Figure 2 is the stable equilibrium phase diagram for the quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298$ K,[14] also saturated with Li_2CO_3. The phase diagram consists of three invariant points (E_1^1, E_2^1, E_3^1), seven univariant curves, and five crystallization fields corresponding to potassium chloride, lithium chloride monohydrate ($LiCl{\cdot}H_2O$), potassium borate pentahydrate ($K_2B_4O_7{\cdot}4H_2O$), hydrated lithium borate ($Li_2B_4O_7{\cdot}3H_2O$), and hydrated potassium carbonate ($K_2CO_3{\cdot}{}^3/_2H_2O$). The mass fraction composition of liquid phase of invariant point E_1^1 is $w(Li^+) = 4.16$ %, $w(K^+) = 1.93$ %, $w(Cl^-) = 22.84$ %, $w(B_4O_7^{2-}) = 0.28$ %, and $w(CO_3^{2-}) = 0.01$ %. The mass fraction composition of liquid phase of invariant point E_2^1 is $w(Li^+) = 2.18$ %, $w(K^+) = 4.98$ %, $w(Cl^-) = 14.56$ %, $w(B_4O_7^{2-}) = 1.65$ %, and $w(CO_3^{2-}) = 0.33$ %. The mass fraction composition of liquid phase of invariant point E_3^1 is $w(Li^+) = 0.31$ %, $w(K^+) = 27.62$ %, $w(Cl^-) = 0.84$ %, $w(B_4O_7^{2-}) = 1.42$ %, and $w(CO_3^{2-}) = 21.17$ %.

In comparison with Figure 1 and Figure 2, we can see that although the numbers of invariant points, crystallization fields, and unvariant curves are the same, there are many differences existing in these two diagrams.

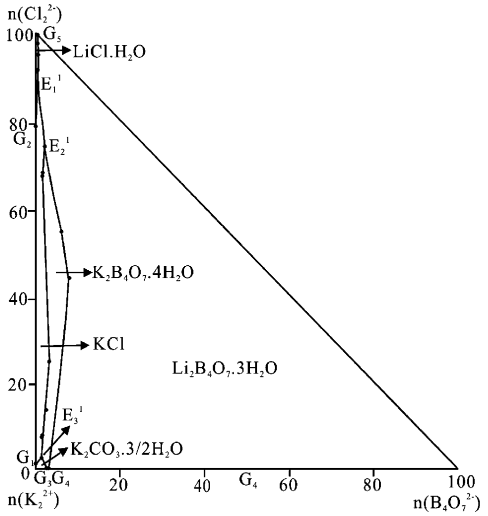

Figure 2. Isothermal dissolution equilibrium phase diagram of the quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 298 K (saturated with Li_2CO_3).

One of the differences was the salt crystallization form. The crystallization forms for lithium and potassium borate were $K_2B_4O_7{\cdot}4H_2O$ and $Li_2B_4O_7{\cdot}3H_2O$ in stable equilibrium at $T = 298$ K for this quinary system, which were changed to $K_2B_4O_7{\cdot}5H_2O$ and $Li_2B_2O_4{\cdot}16H_2O$ in metastable equilibrium at $T = 288$ K, respectively.

The other difference was the size of the salt crystallization fields. The crystallization fields for salts $K_2B_4O_7{\cdot}5H_2O$, KCl and $LiCl{\cdot}H_2O$ at 288 K were all obviously bigger than that at 298 K, which indicated that the solubilities values of these three salts were decreased with the temperature lowered. On the contrary, the crystallization field for salt lithium borate became small. Relatively, the variations on the crystallization fields of lithium borate and potassium borate were larger than that of the other salts. This fact implied that the temperature influence on the lithium and potassium borate solubility was more strongly marked than that of the other lithium and potassium salts. This feature will be very useful for borate salts extracting.

Borates in the Solution. 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 co-existent salts.[15] $B_4O_7^{2-}$ is just the traditional stoichiometric expression for various boric species in solution. In this metastable equilibriua, the equilibrium solid phase of lithium borate exists with diborate, and that for potassium borates exists with tetraborate.

Conclusions

Metastable equilibria of the quinary system $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288$ K were studied by isothermal evaporation method. The solubility and densities of equilibrium solutions were determined.

The equilibrium phase diagram for this system at 288 K consists of three invariant points, seven univariant curves, and five crystallization fields corresponding to potassium chloride, lithium chloride monohydrate ($LiCl{\cdot}H_2O$), potassium borate pentahydrate ($K_2B_4O_7{\cdot}5H_2O$), hydrated lithium borate ($Li_2B_2O_4{\cdot}16H_2O$), and hydrated potassium carbonate ($K_2CO_3{\cdot}{}^3/_2H_2O$). No solid solutions or double salts were found.

The results also show that the temperature has a considerably high influence on the crystallization forms and the solubility of salts. The crystallization forms for lithium and potassium borate in this quinary system were $K_2B_4O_7{\cdot}5H_2O$ and $Li_2B_2O_4{\cdot}16H_2O$

in metastable equilibrium at $T = 288$ K, which were $K_2B_4O_7 \cdot 4H_2O$ and $Li_2B_4O_7 \cdot 3H_2O$ in stable equilibrium at $T = 298$ K, respectively. Meanwhile, with the decrease of temperature, the crystallization fields for salts $K_2B_4O_7 \cdot 5H_2O$, KCl, and $LiCl \cdot H_2O$ became bigger, whereas that for salt lithium borate became smaller. These results will be very useful for extracting the salts.

Acknowledgment

The authors thank the Editor and the anonymous reviewers for their good comments on the manuscript.

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Received for review August 20, 2005. Accepted September 25, 2005. This work received support from the National Natural Science Foundation of China (No. 40303010).

JE050337M