J. Chem. Eng. Data **2011,** *56,* 53–57

Metastable Phase Equilibrium in the Aqueous Quaternary System LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O at 273 K

Hongxia Yang[†] and Ying Zeng*[,†,‡]

College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, and
Mineral Resources Chemistry Key Laboratory of the Higher Education Institutions of Sichuan Province,
Chengdu 610059, People's Republic of China

The metastable phase equilibrium in the quaternary system LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O was studied at $T = 273$ K using an isothermal evaporation method. The solubilities, densities, and pH values were determined experimentally. The crystalloid forms of the solid phase were determined using chemical analysis and an X-ray diffraction method. On the basis of the experimental data, the metastable phase diagram, water diagram, pH value diagram, and density diagram were plotted. The experimental results show that this system is of a simple eutectic type; no double salt or solid solution formed at the investigated temperature. The phase diagram consists of one invariant point, three univariant curves, and three crystallization regions. The three crystallization regions correspond to salts $LiCl\cdot H_2O$, $Li_2SO_4\cdot H_2O$, and $LiBO_2\cdot 8H_2O$. The salt $LiBO_2\cdot 8H_2O$ has the largest crystallization field, whereas the salt $LiCl\cdot H_2O$ has the smallest crystallization field. The salt LiCl has a strong salting-out effect on the salt $Li_2SO_4\cdot H_2O$. Comparisons between the metastable and stable phase diagrams at different temperatures show that the crystallization form of lithium borate has changed. In the stable phase diagrams at $T = (298$ and $288)$ K, the crystallization form of lithium borate is $Li_2B_4O_7\cdot 3H_2O$, while in the metastable phase diagram at $T = 273$ K, the crystallization form of lithium borate is $LiBO_2\cdot 8H_2O$.

Introduction

Salt lakes are widely distributed in the area of the Qinghai-Xizhang (Tibet) plateau. More than 200 salt lakes occupying an area of over 1 km^2 have been found in Tibet. Among them, a series of salt lakes are famous in the world for the high concentration of lithium, sodium, potassium, chloride, sulfate, carbonate, and borate, especially the Zabuye Salt Lake.[1] To economically exploit salt lake brine resources, it is important to adopt the local natural energy such as the sun and the wind; thus, a technique such as solar ponds is widely used. The technology of solar ponds is strongly dependent on the metastable equilibrium solubilities of salts, and therefore, the investigation of metastable equilibrium is of important theoretical and practical significance.

The main components of the Zabuye Salt Lake brine belong to the Li^+, Na^+, K^+, Mg^{2+}//Cl^-, SO_4^{2-}, CO_3^{2-}, borate$-H_2O$ system. By now, a series of papers describing the metastable and stable equilibria have been reported, such as the papers about the quaternary reciprocal systems Li^+, K^+//Cl^-, $SO_4^{2-}-H_2O$ at (323 and 348) K,[2] Li^+, K^+//CO_3^{2-}, $B_4O_7^{2-}-H_2O$ at 273 K,[3] and Li^+, K^+//SO_4^{2-}, $B_4O_7^{2-}-H_2O$ at 273 K[4] and the quinary systems K^+, Na^+, Mg^{2+}//Cl^-, $SO_4^{2-}-H_2O$ from (288 to 308) K,[5−7] Li^+, K^+//Cl^-, CO_3^{2-}, $B_4O_7^{2-}-H_2O$ at 288 K,[8] and Li^+, Na^+, K^+//SO_4^{2-}, $B_4O_7{}^{2-}-H_2O$ at 288 K.[9]

The quaternary system LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O is a subsystem of the Zabuye Salt Lake. The stable phase equilibrium of this system at $T = (288$ and $298)$ K have been reported.[10,11] However, no study on the metastable phase diagram at $T = 273$ K of this system has been reported yet. Actually, the average temperature of the Zabuye Salt Lake region is about 273 K,[1] and the equilibrium relationships among salts in the process of evaporating brines are always metastable;[12,13] thus, studies on the metastable phase equilibria at 273 K will be more close to reality and be of great use in exploiting the brine. In this paper, the metastable phase equilibrium of the quaternary system LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O at $T =$ 273 K is presented. Compared to the phase studies at normal temperature, the studies at 273 K are more difficult because of the lower evaporating velocity, stronger viscosity of solution, and longer time to reach equilibrium.

Experiments

Reagents and Apparatus. All the chemicals used in this work were of analytical purity grade and were obtained from the Chengdu Kelong Chemical Reagent Plant. They were lithium tetraborate ($Li_2B_4O_7$; 99.5 %), lithium chloride (LiCl; 95.0 %), and lithium sulfate ($Li_2SO_4\cdot H_2O$; 99.0 %). Doubly deionized water was obtained from a Millipore water system with an electrical conductivity of less than $1.0\cdot 10^{-4}$ $S\cdot m^{-1}$ and pH 6.60.

An SHH-250-type thermostatic evaporator made by the Chongqing INBORN Instrument Corp., China, was used for the metastable phase equilibrium experiment. There was a temperature-controlling apparatus and a blower accessory equipment in it to control the temperature and the evaporation quantity of the evaporated system. The temperature-controlling precision was ± 0.1 K.

A pXS-1^+ ion activity meter with an uncertainty of 0.01 was used to measure the pH value of the equilibrium solution. A

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* Corresponding author. E-mail: zengyster@gmail.com. Phone: 86-28-84079016. Fax: 86-28-84079074.
[†] Chengdu University of Technology.
[‡] Mineral Resources Chemistry Key Laboratory of the Higher Education Institutions of Sichuan Province.

10.1021/je100748q

Table 1. Solubilities, pH Values, and Densities of the Equilibrium Solutions in the Quaternary System $LiCl + Li_2SO_4 + Li_2B_4O_7 + H_2O$ at 273 K[a]

no.	pH value	density	composition of the equilibrium solution				Janëcke index of the dry salt $J(Li_2Cl_2) + J(Li_2SO_4) + J(Li_2B_4O_7) = 100$ mol				equilibrium solid phase
		$g \cdot cm^{-3}$	100 $w(LiCl)$	100 $w(Li_2SO_4)$	100 $w(Li_2B_4O_7)$	100 $w(H_2O)$	$J(Li_2Cl_2)$	$J(Li_2SO_4)$	$J(Li_2B_4O_7)$	$J(H_2O)$	
1A	7.86	1.2845	0.00	28.04	1.42	70.53	0.000	96.81	3.195	1486	LS + LB
2	7.88	1.2679	0.51	26.72	1.64	71.13	2.304	93.94	3.753	1527	LS + LB
3	8.20	1.2734	0.57	27.32	1.83	70.28	2.514	93.41	4.077	1467	LS + LB
4	8.20	1.2699	0.59	26.09	1.89	71.43	2.726	92.91	4.368	1553	LS + LB
5	8.00	1.2708	0.65	26.23	2.04	71.08	2.971	92.35	4.678	1528	LS + LB
6	7.92	1.2485	2.43	23.55	2.36	71.67	11.15	83.42	5.432	1550	LS + LB
7	8.02	1.2457	3.65	21.46	3.09	71.80	16.79	76.10	7.118	1554	LS + LB
8	8.44	1.2353	4.42	19.75	3.77	72.06	20.50	70.70	8.795	1575	LS + LB
9	7.69	1.1859	10.46	11.56	1.99	76.00	51.33	43.77	4.902	1757	LS + LB
10	7.60	1.1651	13.83	7.12	2.50	76.56	67.21	26.70	6.093	1753	LS + LB
11	7.12	1.1667	16.78	4.21	2.99	76.02	77.93	15.09	6.979	1663	LS + LB
12	7.42	1.1617	19.46	1.83	3.55	75.16	85.90	6.235	7.867	1562	LS + LB
13	6.71	1.1844	25.13	0.66	3.41	70.81	91.89	1.849	6.264	1220	LS + LB
14E	5.40	1.2475	39.71	0.01	0.08	60.20	99.87	0.026	0.104	713.2	LS + LB + LI
15B	5.70	1.2479	39.44	0.01	0.00	60.55	99.98	0.021	0.000	722.9	LI + LS
16C	5.29	1.2458	39.71	0.00	0.08	60.21	99.90	0.000	0.105	713.4	LB + LI
17	5.39	1.2474	39.71	0.01	0.08	60.20	99.87	0.026	0.104	713.2	LB + LI
18	5.30	1.2439	39.52	0.01	0.08	60.39	99.88	0.018	0.104	718.9	LB + LI
19	5.31	1.2469	39.39	0.01	0.08	60.52	99.88	0.016	0.103	722.9	LB + LI

[a] Key: LI, $LiCl \cdot H_2O$, LS, $Li_2SO_4 \cdot H_2O$, LB, $LiBO_2 \cdot 8H_2O$; $w(A)$, mass fraction of component A, $J(A)$, Janëcke index of the dry salt.

Siemens D500 X-ray diffractometer with Ni-filtered Cu Kα radiation was used to analyze the crystalloid form of the solid phase.

An inductively coupled plasma optical emission spectrometer (type 5300 V, Perkin-Elmer, United States) was employed for the determination of the lithium ion concentration in solution.

Experimental Methods. The isothermal evaporation method was employed in this study. According to the phase equilibrium composition and the solubility of the single salt at $T = 273$ K, an appropriate quantity of salts was dissolved into doubly deionized water as a series of artificially synthesized brines and loaded into clean opened polyethylene containers (24 cm long, 14 cm wide, and 7 cm high). The containers were placed in the SHH-250-type thermostatic evaporator to evaporate. The temperature of the solution inside the evaporator was controlled to (273 ± 0.1) K and measured by a J thermocouple with an operating range of (258 to 373) K, with a system precision of ± 0.1 K. When enough new solid appeared in the evaporating containers, the liquid and solid phases were separated by rapid filtration. The obtained wet crystals were dried at 273 K, pestled into a powder, and then analyzed by X-ray diffraction to determine the crystalloid form of the solid phase. At the same time, a 5.0 mL sample of the clarified solution was taken from the liquid phase and diluted to a 100 mL final volume with deionized water in a volumetric flask to analyze the concentration of the liquid-phase components. Another 5.0 mL sample of the clarified solution was taken and placed in the weighing bottle to determine the density. Meanwhile, the pH value of the solution was measured by the pXS-1^+ ion activity meter. The remainder of the solution was loaded back into the polyethylene containers and placed in the thermostatic evaporator, and evaporation was continued to reach the next measuring point. The same procedure was repeated until the solution was fully evaporated. The densities of the solution were determined in this study and used for the mass fraction calculation of the liquid components.

Analytical Methods. The lithium ion concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (precision less than 0.06 %, type 5300 V ICP-OES instrument). The borate ion concentration was determined by neutralization titration in the presence of mannite (precision ± 0.3 %). The chlorine ion concentration was measured by titration with a silver nitrate standard solution (precision ± 0.3 %).[14] 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 quantitative excess of a Ba−Mg mixture solution (contents 0.01 $mol \cdot L^{-1}$ $BaCl_2$ and 0.005 $mol \cdot L^{-1}$ $MgCl_2$) was added to give

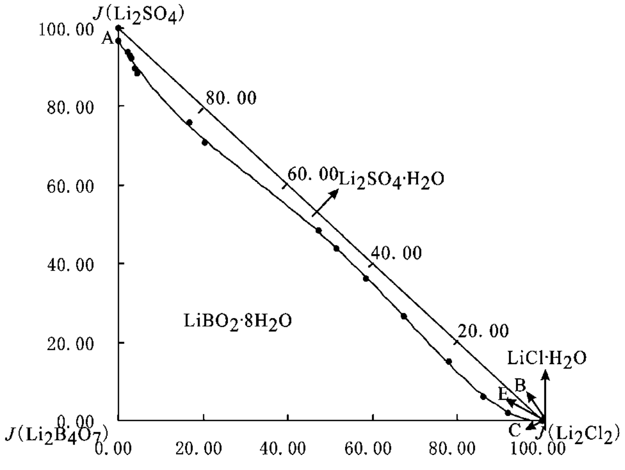

Figure 1. Metastable phase diagram of the quaternary system $LiCl + Li_2SO_4 + Li_2B_4O_7 + H_2O$ at 273 K.

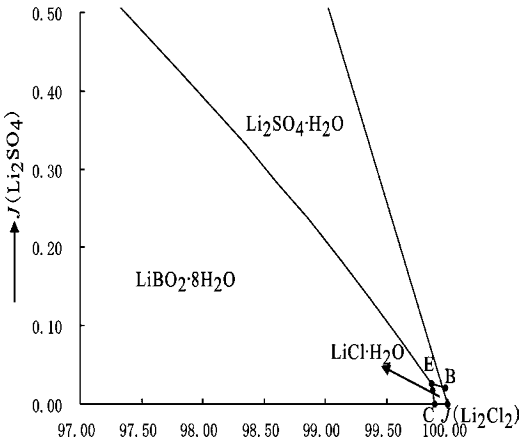

Figure 2. Partially enlarged diagram of Figure 1.

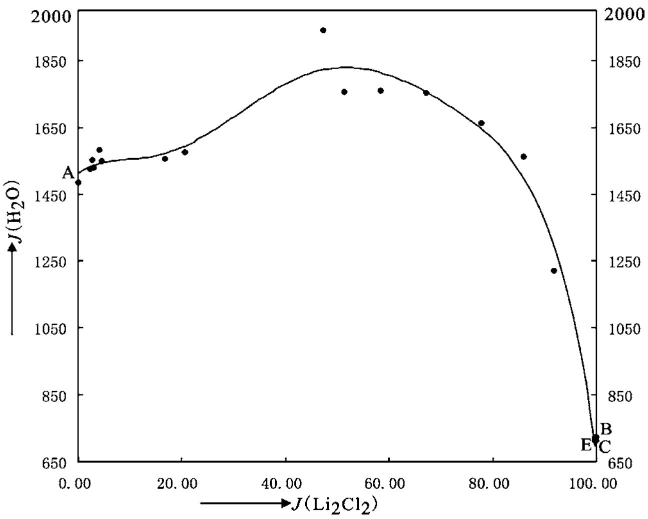

Figure 3. Water-content diagram of the quaternary system LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O at 273 K.

a $BaSO_4$ precipitate. The $BaCl_2$ solution was then titrated with EDTA standard solution in the presence of mixed K−B (acid chrome blue K−naphthol green B) indicator. The precision of the measurements was better than 1 %. The ion concentration measurement was repeated up to three times to estimate the reproducibility.

Results

Phase Diagram at 273 K. The experimental results of the solubilities and physicochemical properties such as pH values and densities of the equilibrium solution in the quaternary system LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O at 273 K are tabulated in Table 1. In Table 1, w(A) is the mass fraction of component A, and J(A) is the Janëcke index value of component A, calculated with 100 mol of dry salt as the benchmark; that is, $J(Li_2Cl_2)$ + $J(Li_2SO_4)$ + $J(Li_2B_4O_7)$ = 100 mol. With the Janëcke index value, the metastable phase diagram at 273 K was plotted, as shown in Figure 1. Figure 2 is a partially enlarged diagram of Figure 1. Figure 3 is the water-content diagram of this system.

There are three isothermal evaporation curves in Figure 1, namely, curves AE, BE, and CE, indicating the cosaturation of two salts. Points A, B, and C, cosaturated with two salts, are three invariant points of the three ternary subsystems of the quaternary system LiCl + Li_2SO_4 + $Li_2B_4O_7$ + H_2O.

The phase diagram of the quaternary system consists of three crystallization fields, one invariant point, and three univariant curves. No double salt or solid solution is formed in this system at the investigated temperature. The invariant point labeled E is cosaturated with three salts. Figure 4 is the X-ray diffraction photograph of the equilibrated solid phase corresponding to invariant point E, which shows the salts $LiBO_2\cdot 8H_2O$, $LiCl\cdot H_2O$, and $Li_2SO_4\cdot H_2O$ coexist. The mass fraction composition of the corresponding liquid phase is 100 w(LiCl) = 39.71, 100 $w(Li_2SO_4)$ = 0.01, and 100 $w(Li_2B_4O_7)$ = 0.08. The three crystallization regions correspond to the three single salts $LiCl\cdot H_2O$, $Li_2SO_4\cdot H_2O$, and $LiBO_2\cdot 8H_2O$. The salt $LiBO_2\cdot 8H_2O$ has the largest crystallization field, while the salt $LiCl\cdot H_2O$ has the smallest crystallization field. The salt $LiCl\cdot H_2O$ has a strong salting-out effect on the salt $Li_2SO_4\cdot H_2O$.

Density and pH Value of the Equilibrium Solution. In this system, the solubility of the salt lithium chloride is greater than that of lithium sulfate and lithium borate; therefore, the concentration of LiCl is the main factor affecting the solution

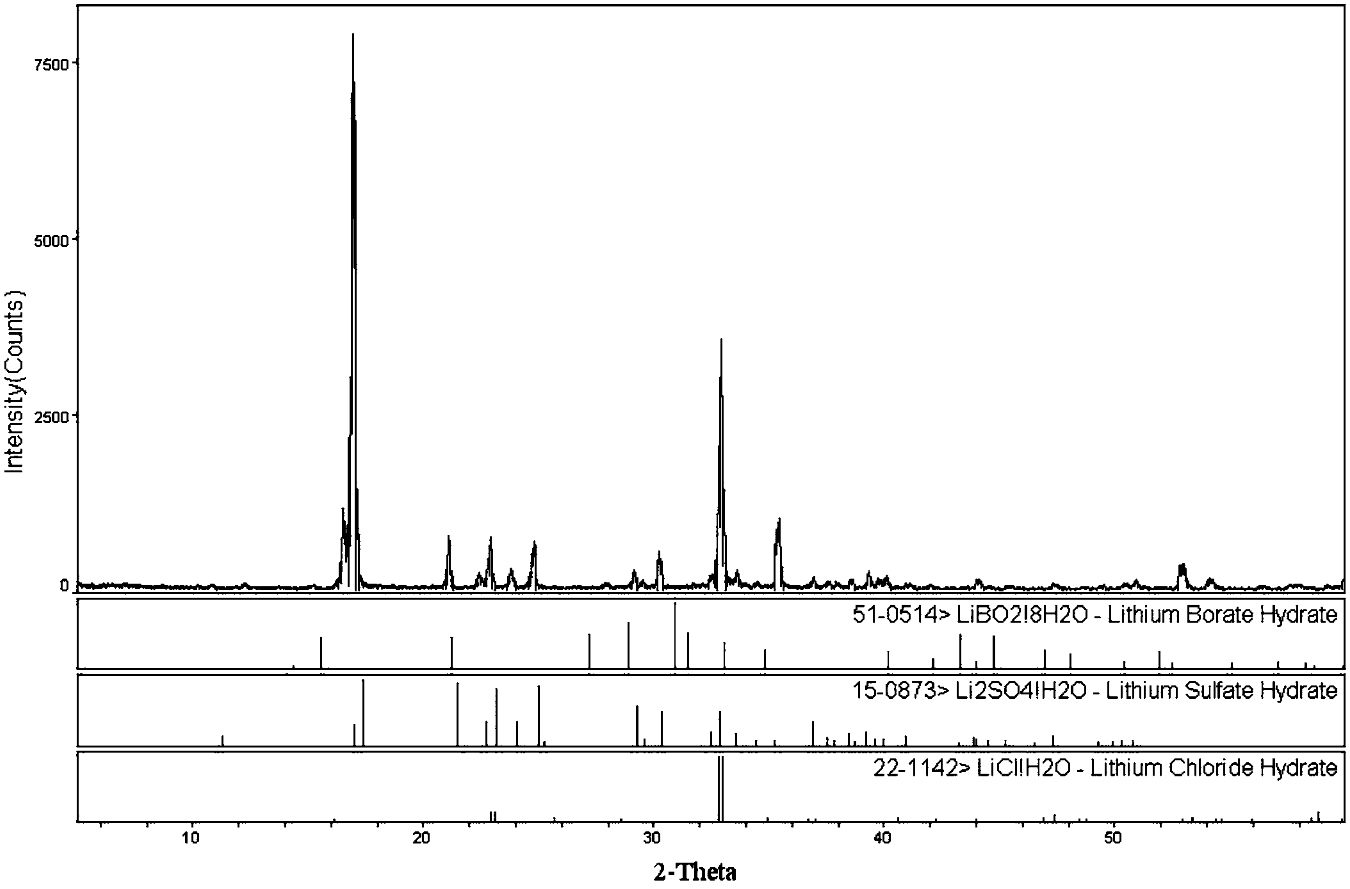

Figure 4. X-ray diffraction photograph of the invariant point E ($LiBO_2\cdot 8H_2O$ + $Li_2SO_4\cdot H_2O$ + $LiCl\cdot H_2O$).

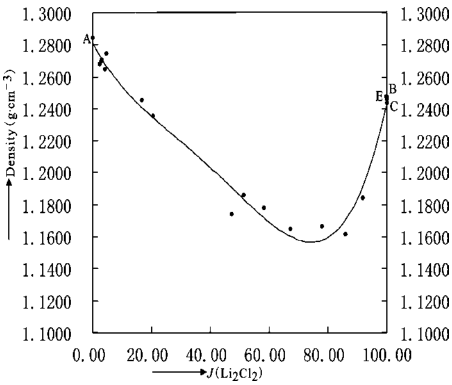

Figure 5. Density value vs composition diagram of the quaternary system $LiCl + Li_2SO_4 + Li_2B_4O_7 + H_2O$ at 273 K.

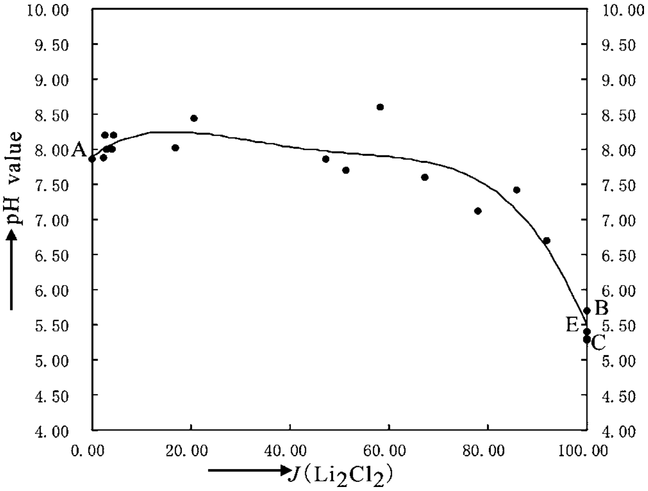

Figure 6. pH value vs composition diagram of the quaternary system $LiCl + Li_2SO_4 + Li_2B_4O_7 + H_2O$ at 273 K.

density and pH value. Figure 5 is the density vs composition diagram of the equilibrated solution. The density of the system changed regularly with the content change of lithium chloride. On the univariant curve AE, with an increase of $J(Li_2Cl_2)$, the density value first decreases to a minimum and then increases to the invariant point E, whereas it increases on the univariant curve BE and decreases on the univariant curve CE.

The pH value vs composition diagram is plotted in Figure 6. The pH value of the system also changed regularly with the content change of lithium chloride; with an increase of $J(Li_2Cl_2)$, the pH value of the solution decreases on the univariant curve AE and BE, whereas it increases on the univariant curve CE.

Discussion

Comparison of the Metastable and Stable Phase Diagrams. Different experimental methods or investigated temperatures lead to different crystalline regions and crystal forms. Commonly, the metastable phase diagram is used to describe the relationships of the solubility between water and salts during the process of isothermal evaporation, while the stable phase diagram focuses on these relationships during the process of isothermal solution.

The stable phase diagrams of the quaternary system $LiCl + Li_2SO_4 + Li_2B_4O_7 + H_2O$ have been studied at 288 K[10] and at 298 K.[11] Compared with the two stable phase diagrams at different temperatures, the result shows that the salts in this system have the same crystallization forms, but the crystallization fields have slight changes. The crystallization field of the salt $LiCl \cdot H_2O$ is larger at 288 K than at 298 K, whereas the crystallization field of $Li_2SO_4 \cdot H_2O$ and $Li_2B_4O_7 \cdot 3H_2O$ is smaller at 288 K than at 298 K.

Comparison between the metastable phase diagram at 273 K and stable phase diagram at 288 K shows that lithium borate has different crystallization forms. In the metastable phase diagram at 273 K the lithium borate is $LiBO_2 \cdot 8H_2O$, whereas in the stable phase diagram at 288 K it is $Li_2B_4O_7 \cdot 3H_2O$. The regional distributions of the crystallization field in the metastable and stable phase diagrams are almost the same; lithium borate has the largest field, and $LiCl \cdot H_2O$ has the smallest field.

Salting-Out Effect of LiCl. The experimental results show that the salt LiCl has a salting-out effect on the salt lithium borate ($Li_2B_4O_7 \cdot 3H_2O$ or $LiBO_2 \cdot 8H_2O$) and has a strong salting-out effect on the salt Li_2SO_4. The effect is likely caused not only by the larger polarization of the lithium ion, but also by the structural similarity of LiCl and H_2O.[15,16] Because of the structural similarity between LiCl and H_2O, the salt LiCl is easy to dissolve and has a large solubility. The large solubility of LiCl in aqueous solution causes a series of changes in the properties of the solution, such as increasing the polarity of the solution, decreasing the dielectric constant, and strengthening the electrostatic action, and also with a high common-ion effect, all these changes are beneficial to salting out. Thus, the salt LiCl has a strong salting-out effect and the role of making other hydrates dehydrate.[17]

Conclusion

Metastable phase equilibrium in the quaternary system $LiCl + Li_2SO_4 + Li_2B_4O_7 + H_2O$ at 273 K was studied using an isothermal evaporation method. The solubilities and physicochemical properties such as the pH value and densities were determined experimentally. This system is of a simple common saturation type; no double salt or solid solution is formed. There are three univariant curves, one invariant point, and three single-salt crystallization regions in the phase diagram. The three single-salt crystallization regions are $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$, and $LiBO_2 \cdot 8H_2O$. In this system, the crystallization form of lithium borate is $LiBO_2 \cdot 8H_2O$. The crystallization field of the salt $LiBO_2 \cdot 8H_2O$ is the largest, while that of the salt LiCl is the smallest.

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Received for review July 16, 2010. Accepted November 6, 2010. Financial support for this work was provided by the National Natural Science Foundation of China (Grant 40673050), the Doctoral Fund of the Ministry of Education of China (Grant 20070616008), the Scholarship Leaders Training Fund from Sichuan Province, and the Program for New Century Excellent Talents in University (Grant NCET-08-0900).

JE100748Q