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Metastable Phase Equilibrium in the Aqueous Quaternary System ($Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$) at 273.15 K

Ying Zeng,*[†,‡] Fujia Cao,[†] LongGang Li,[§] Xudong Yu,[†] and Xiaofeng Lin[‖]

[†]Department of Geochemistry, College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P. R. China

[‡]Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, P. R. China

[§]The Development and Comprehensive Utilization of Marine Sedimentary Brine, Sichuan Provincial Key Laboratory, Chengdu 610059, P. R. China

[‖]Panzhihua Steel Corporation, Panzhihua 617067, P. R. China

ABSTRACT: The quaternary system ($Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$) is one of the most important and basic subsystems of the brines located in the area of the Qinghai-Xizang (Tibet) Plateau. To make certain the solubility of the lithium, sodium, and borate changes with the temperature, the metastable equilibrium of the quaternary system ($Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$) was investigated at 273.15 K using an isothermal evaporation method. The solubilities of the equilibrated solution were measured using chemical analytical methods. The crystalloid forms of the solid phase were determined using an X-ray diffraction method. This system is of a complex type, with a double salt of sodium and lithium sulfate ($3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$) formed at 273.15 K. The phase diagram of this system consists of three invariant points, seven univariant curves, and five crystallization fields. Comparisons between the phase diagrams of this system at 273.15 K and at 288.15 K show that the crystallization forms and the size of crystallization field of salt have changed. The solubility of salt sodium borate changes with temperature more obviously than that of salt lithium borate. Thus, the crystallization area of $Na_2B_4O_7 \cdot 10H_2O$ becomes bigger obviously, whereas the crystallization area of salt $LiBO_2 \cdot 8H_2O$ becomes smaller at 273.15 K. This difference is beneficial to separate sodium and lithium using an evaporation method, and a rise in temperature is necessary to obtain more lithium borate from the solution.

INTRODUCTION

A series of salt lakes in the west of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau, are famous for their abundance of lithium and borate resources.[1] The main component of these brines can be described as the complex system ($Li^+ + Na^+ + K^+ + Mg^{2+} + Cl^- + CO_3^{2-} + SO_4^{2-}$ + borate anions $+ H_2O$). The evaporation method is often used to exploit the brines and mineral resources. It is well-known that phase equilibria and phase diagrams play an important role in establishing the evaporation process. Earlier researchers found that in the evaporation process of brine the equilibria among the salts are always metastable,[2,3] and therefore, more attention has been focused on the investigation of metastable phase equilibrium and metastable phase diagram.

So far, a lot of work has been done on metastable phase equilibria aimed at different types of brines. The metastable phase equilibria of the seawater system ($Na^+ + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$) were studied at 288.15 K,[4,5] 298.15 K,[6] and 308.15 K[7] using an isothermal evaporating method; the metastable phase equilibria of the sulfate salt lake brines system ($Li^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$) were studied at 298.15 K;[8] and the metastable phase equilibria of the carbonate salt lake brines were studied at 288.15 K and 298.15 K.[9,10] These research results, especially the research results of the seawater system ($Na^+ + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$), have been widely used in the industrial process of salt production, such as extracting schoenite ($MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$) or potassium sulfate ($K_2SO_4$) from the Chaidamu Saline Lake, China. However, most of the effort has focused on temperatures above 288.15 K, including our earlier work aimed at the Zabuye Salt Lake, located at Qinghai-Xizang (Tibet) Plateau.[9,10]

The quaternary system ($Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$) is one of the most important and basic subsystems of the complex system mentioned above. The metastable phase equilibria of this system have been studied at 288.15 K,[11] whereas the metastable phase equilibria of this system at other temperatures are not reported in the literature yet. To make certain the solubility of the lithium, sodium, and borate changes with the temperature, the metastable equilibria of the quaternary system ($Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$) at 273.15 K were investigated. The solubilities and densities of the equilibria solution of this system were measured, and the comparisons between the phase diagram at 273.15 K and 288.15 K have also been made.

EXPERIMENTAL SECTION

Reagents and Apparatus. The chemicals used in this work were of analytical grade purity and from the Peking Xinhua

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Chemical Reagent Plant. They were sodium sulfate (Na_2SO_4, 99.0 % (w/w)), lithium sulfate (Li_2SO_4, 99.0 % (w/w)), sodium borate ($Na_2B_4O_7 \cdot 10H_2O$, 99.5 % (w/w)), and lithium borate ($Li_2B_4O_7$, 99.5 % (w/w)). Doubly deionized water was obtained from a Millipore water system with an electrical conductivity less than $1 \cdot 10^{-4}$ S·m^{-1} and pH = 6.6. For each experiment, the required amounts of the reagents were dissolved in enough deionized water to produce the experimental solutions.

A SHH-250 type thermostatic evaporator made by the Chongqing INBORN Instrument Corporation, China, was used for the metastable phase equilibrium experiments. The equipment has a temperature-controlling apparatus with a blower accessory to control the temperature and the evaporation quantity of the evaporating system. The evaporation rate is (4.0 to 5.5) mm·d^{-1}, the temperature with an operating range of (258.15 to 373.15) K, and the temperature precision is ± 0.1 K.

A DX-2700 X-ray diffractometer with Cu Kα radiation was used to analyze the crystalloid form of the solid phases. The operating conditions were 40 kV and 30 mA.

A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, supplied by Mettler Toledo Instruments Co., Ltd.) was employed for the determination of the density of solution.

An inductively coupled plasma optical emission spectrometer (ICP-OES, Type Optima5300V) made by P.E. Corporation, U.S.A., was employed for the determination of lithium and sodium ion concentration in solution.

Experimental Method. The isothermal evaporation method was employed in this study. The required amounts of reagent, calculated according to the solubility of the salt at 273.15 K and the solubility data of the invariant point of the ternary subsystem, were dissolved into 1000 mL of deionized water to produce the initial evaporating solutions. A series of prepared experimental solutions of the quaternary system were loaded into clean opened polyethylene containers (24 cm long, 14 cm wide, and 7 cm high). The containers were placed in a thermostatic evaporator. The temperature of the solution inside the evaporator was controlled to (273.15 ± 0.1) K and measured by a J thermocouple with an operating range of (258.15 to 373.15) K and a system precision of ± 0.1 K. When enough new solid appeared in the evaporating containers, the liquid and solid phases were separated by filtration. The obtained wet crystals in the solid phase were dried at 273.15 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 50 mL final volume in a volumetric flask filled with deionized water to analyze the concentration of liquid-phase components. Another 5.0 mL sample of the clarified solution was taken to determine the density. The remainder of the solution was loaded back into the polyethylene containers, placed in the thermostatic evaporator, and continued to be evaporated to reach the next measuring point. This same procedure was repeated until the solution was fully evaporated.

The densities of solution were determined in this study and used for the mass fraction calculation of liquid components. The specific gravity bottle method with correction of air floating force was used. The precision of the density measure was 0.0001 g·cm^{-3}. The sample was obtained at 273.15 K and measured at 293.15 K. The excursion caused by the temperature difference was calibrated by using a multipoint temperature revision method.[12]

Analytical Methods. 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, excess of a Ba−Mg mixture solution (contents 0.01 mol·L^{-1} $BaCl_2$ and 0.005 mol·L^{-1} $MgCl_2$) was added quantitatively to give a $BaSO_4$ precipitate. The excess $BaCl_2$ 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 0.5 %. The ion concentration measurement was repeated up to three times to estimate the reproducibility.

The borate ion concentration was determined by neutralization titration in the presence of propanetriol (precision: ± 0.3 %).[13] Boric acid is a weak acid and only partially neutralized by direct titration with a sodium hydroxide standard solution. To improve the measure accuracy, an appropriate amount of polyhydric alcohol like propanetrial is added into the solution before titration to form boron hydroxyl complexes with high dissociation constant.

The sodium and lithium ion concentration was determined by inductively coupled plasma optical emission spectrometry, with the precision less than 0.06 %.

RESULTS AND DISCUSSION

Phase Diagram at 273.15 K. The experimental results of solubilities and densities for the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ at 273.15 K were measured and are tabulated in Table 1. In Table 1, $w(B)$ is the mass fraction of B, and $n(B)$ is the mole number of B, with $n(Li_2^{2+}) + n(Na_2^{2+}) = n(B_4O_7^{2-}) + n(SO_4^{2-}) = 100$ mol. $J(B)$ is the Janëcke index values of B, with $J(Li_2^{2+}) + J(Na_2^{2+}) = J(B_4O_7^{2-}) + J(SO_4^{2-}) = 100$. The calculating formula for $J(B)$ is

$$J(B) = \frac{n(B)}{n(Li_2^{2+}) + n(Na_2^{2+})} \cdot 100 \qquad (1)$$

The calculating formula for water concentration is

$$J(H_2O) = \frac{w(H_2O)}{18 \cdot [n(Li_2^{2+}) + n(Na_2^{2+})]} \cdot 100 \qquad (2)$$

With the data of the Janëcke index $J(B)$, the experimental solubility isothermal metastable phase diagram of the system at 273.15 K was constructed, as shown in Figure 1.

The metastable equilibrium phase diagram of the system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ at 273.15 K consists of five crystallization fields, seven univariant curves, and three invariant points. The five crystallization fields correspond to four single salts, $LiBO_2 \cdot 8H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Na_2SO_4 \cdot 10H_2O$, and $Li_2SO_4 \cdot H_2O$, and one double salt, $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$. The seven univariant curves, namely, curves AE_3, BE_3, CE_1, DE_1, EE_2, E_1E_2, and E_2E_3, are cosaturated with two salts, respectively.

There are four ternary subsystems of the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ that are ternary systems $Li_2SO_4 + Na_2SO_4 + H_2O$, $Li_2B_4O_7 + Na_2B_4O_7 + H_2O$, $Li_2SO_4 + Li_2B_4O_7 + H_2O$, and $Na_2SO_4 + Na_2B_4O_7 + H_2O$. In Figure 1, points A, B, C, D, and E are five invariant points of the four ternary systems of this quaternary system, cosaturated with two salts, respectively. Among these four ternary systems, system $Li_2SO_4 + Na_2SO_4 + H_2O$ is of a complex type, has two invariant points D and E, with the double salt $3Na_2SO_4 \cdot Li_2SO_4 \cdot$

Table 1. Experimental Values of Solubility and Density of the Equilibrium Solution in the Quaternary System $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ at 273.15 K[a]

	composition of solution, $w(B)\cdot 10^2$					Janëcke index of dry salt						
						$J(Li_2^{2+}) + J(Na_2^{2+}) = J(SO_4^{2-}) + J(B_4O_7^{2-}) = 100$					density	
No.	$w(Na^+)$	$w(B_4O_7^{2-})$	$w(SO_4^{2-})$	$w(Li^+)$	$w(H_2O)$	$J(Li_2^{2+})$	$J(Na_2^{2+})$	$J(SO_4^{2-})$	$J(B_4O_7^{2-})$	$J(H_2O)$	$(g\cdot cm^{-3})$	solid phase
1,A	0.00	1.19	19.98	2.99	75.84	100.0	0.00	96.44	3.56	1956	1.1780	LiS + LiB
2	0.95	1.26	23.66	3.25	70.88	91.89	8.11	96.81	3.19	1545	1.2332	LiS + LiB
3,E_3	1.06	1.85	26.03	3.61	67.45	91.86	8.14	95.78	4.22	1323	1.2593	LiS + LiB + NaB
4,B	0.21	2.24	0.00	0.14	97.41	68.83	31.17	0.00	100.0	36930	1.0199	LiB+ NaB
5	0.23	1.19	0.77	0.15	97.66	68.36	31.64	51.09	48.91	34319	1.0178	LiB+ NaB
6	0.32	1.58	1.67	0.29	96.14	75.01	24.99	63.05	36.95	19176	1.0319	LiB+ NaB
7	0.30	1.45	1.75	0.29	96.21	76.20	23.80	66.09	33.91	19495	1.0263	LiB+ NaB
8	0.39	1.88	6.62	1.01	90.10	89.56	10.44	85.04	14.96	6161	1.0787	LiB+ NaB
9,C	1.88	0.52	3.59	0.00	94.01	0.00	100.0	91.77	8.23	12774	1.0442	NaB+ NaS
10	1.52	0.55	6.28	0.50	91.15	52.15	47.85	94.85	5.15	7330	1.0842	NaB+ NaS
11	1.64	0.60	6.81	0.54	90.41	52.17	47.83	94.83	5.17	6735	1.0870	NaB+ NaS
12	1.43	0.72	6.88	0.63	90.34	59.34	40.66	93.91	6.09	6561	1.0901	NaB+ NaS
13	1.38	0.81	7.50	0.74	89.57	63.98	36.02	93.73	6.27	5971	1.0968	NaB+ NaS
14, E_1	1.49	0.89	9.91	1.06	86.65	70.21	29.79	94.73	5.27	4426	1.1124	NaB+ NaS+ NaLiS
15,D	2.08	0.00	22.65	2.67	72.60	80.96	19.04	100.0	0.00	1698	1.2280	NaS+ NaLiS
16,E	1.80	0.00	25.25	3.13	69.82	85.21	14.79	100.0	0.00	1466	1.2668	NaLiS + LiS
17,E_2	2.43	3.12	27.64	3.28	63.53	81.72	18.28	93.47	6.53	1221	1.2588	NaLiS + LiS + NaB

[a] Note: NaS—$Na_2SO_4\cdot 10H_2O$, LiS—$Li_2SO_4\cdot H_2O$, NaLiS—$3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O$, NaB—$Na_2B_4O_7\cdot 10H_2O$, LiB—$LiBO_2\cdot 8H_2O$.

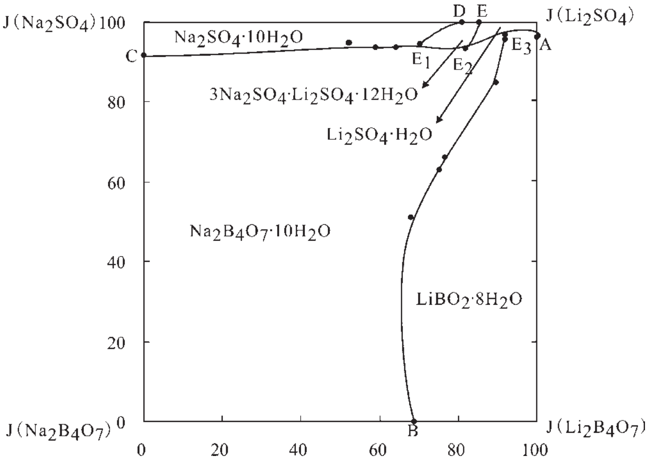
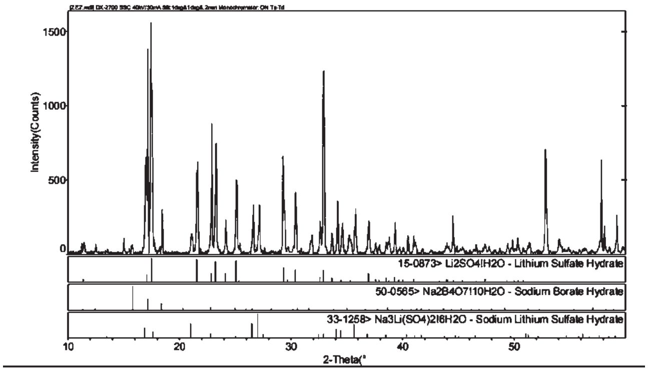


Figure 1. Metastable phase equilibrium diagram of the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ at 273.15 K.



Chemical Formula	$Na_2B_4O_7\cdot 10H_2O$	$Li_2SO_4\cdot H_2O$	$3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O$
D spacing, Å	5.68	5.08	3.30
Score	16	17	27

Figure 2. X-ray diffraction pattern of the invariant point E_2 ($Na_2B_4O_7\cdot 10H_2O + Li_2SO_4\cdot H_2O + 3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O$).

$12H_2O$ formed. The double salt $3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O$ is also found in the investigated quaternary system.

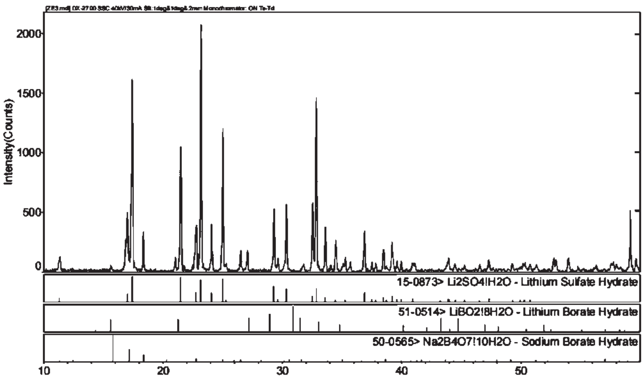
There are three invariant points in Figure 1, labeled as E_1, E_2, and E_3. The invariant points are cosaturated with three salts, and the equilibrated solid phases of the invariant points were confirmed with X-ray diffraction analysis. Figure 2 gives the X-ray diffraction pattern of the invariant point E_2, which is saturated with salts $Li_2SO_4\cdot H_2O$, $Na_2B_4O_7\cdot 10H_2O$, and $3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O$. Figure 3 gives the X-ray diffraction pattern of the invariant point E_3, which is saturated with salts $Li_2SO_4\cdot H_2O$, $Na_2B_4O_7\cdot 10H_2O$ and $LiBO_2\cdot 8H_2O$. The saturated salts and the mass fraction composition for the three invariant points are listed below.

Point E_1 is saturated with salts $Na_2SO_4\cdot 10H_2O + 3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O + Na_2B_4O_7\cdot 10H_2O$. The mass fraction composition of the corresponding liquid phase is $w(Na^+) = 1.49$ %, $w(Li^+) = 1.06$ %, $w(B_4O_7^{2-}) = 0.89$ %, and $w(SO_4^{2-}) = 9.91$ %.

Point E_2 is saturated with salts $Li_2SO_4\cdot H_2O + 3Na_2SO_4\cdot Li_2SO_4\cdot 12H_2O + Na_2B_4O_7\cdot 10H_2O$. The mass fraction composition of the corresponding liquid phase is $w(Na^+) = 2.43$ %, $w(Li^+) = 3.28$ %, $w(B_4O_7^{2-}) = 3.12$ %, and $w(SO_4^{2-}) = 27.64$ %.

Point E_3 is saturated with salts $Li_2SO_4\cdot H_2O + Na_2B_4O_7\cdot 10H_2O + LiBO_2\cdot 8H_2O$. The mass fraction composition of the corresponding liquid phase is $w(Na^+) = 1.06$ %, $w(Li^+) = 3.61$ %, $w(B_4O_7^{2-}) = 1.85$ %, and $w(SO_4^{2-}) = 26.03$ %.

The crystallization field of the salt $Na_2B_4O_7 \cdot 10H_2O$ is the largest, which indicates that sodium borate is easier to saturate and crystallize than the other four salts from solution at the investigated temperature.



Chemical Formula	$LiBO_2 \cdot 8H_2O$	$Li_2SO_4 \cdot H_2O$	$Na_2B_4O_7 \cdot 10H_2O$
D spacing, Å	3.06	5.08	5.68
Score	29	17	16

Figure 3. X-ray diffraction pattern of the invariant point E_3 ($LiBO_2 \cdot 8H_2O + Li_2SO_4 \cdot H_2O + Na_2B_4O_7 \cdot 10H_2O$).

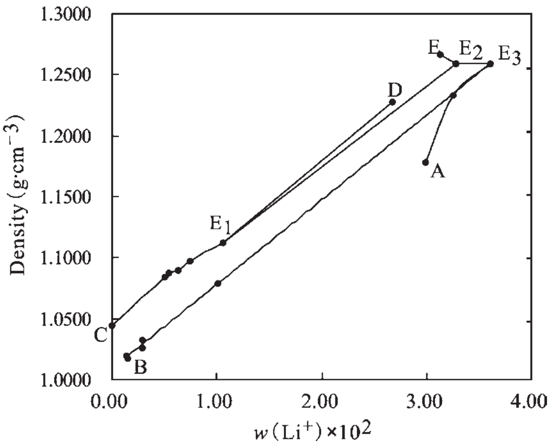


Figure 4. Density vs composition diagram of the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ at 273.15 K.

In Figure 4, the ordinate is the density of equilibrated solution, and the abscissa is the mass fraction of lithium. Figure 4 shows that the density changes regularly with the composition of lithium in the solution. In this system, the solubility of lithium sulfate is greater than that of the other salts; therefore, the concentration of lithium sulfate is the main factor affecting the solution density. The density increases with the increase of concentration of lithium and reaches a maximum value at the invariant point E_3. At the univariant curves CE_1 and BE_3 (cosaturated with salt lithium borate and sodium borate and salt sodium sulfate and sodium borate, respectively), because of the rapid condensing of salt Li_2SO_4, the density of the solution varies with greater range along with the change of lithium composition, while at the other univariant curves, the density of the solution varies with lesser range.

The water content diagram of the system is constructed in Figure 5. In Figure 5, the ordinate is the Jänecke index of water (mol H_2O/100 mol dry salt), and the abscissa is the mass fraction of lithium. Figure 5 shows that the water content changes regularly with a composition of lithium ion and reaches the smallest value at the invariant point E_3. At the univariant curves CE_1 and BE_3, the solution is dilute and has rapid evaporating rate at the early stage of evaporating. Along with the evaporating process, the evaporating rate is slowed down with an increase of lithium sulfate concentration.

Comparison with the Metastable Phase Diagrams at (273.15 and 288.15) K. The matastable phase equilibrium of the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ has been studied at 288.15 K.[11] Comparisons between the two phase diagrams at different temperatures shows that the crystallization fields and the crystallization forms have changed. The crystallization form of lithium borate is $Li_2B_4O_7 \cdot 3H_2O$ at 288.15 K, whereas that is lithium metaborate ($LiBO_2 \cdot 8H_2O$) at 273.15 K, with the crystallization forms $Li[B(OH)_4] \cdot 6H_2O$, as shown in Figure 3. The crystallization form of sodium sulfate has also changed; it is $Na_2SO_4 \cdot 10H_2O$ at 273.15 K, whereas that is Na_2SO_4 at 288.15 K. Although the double salt of sodium and lithium sulfate is formed in the quaternary system both at 273.15 K and at 288.15 K, the crystallization form of the double salt has changed from $Na_2SO_4 \cdot Li_2SO_4$ at 288.15 K to $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ at 273.15 K.

The metastable phase diagrams of this quaternary system at different temperatures all have three invariant points. The mass

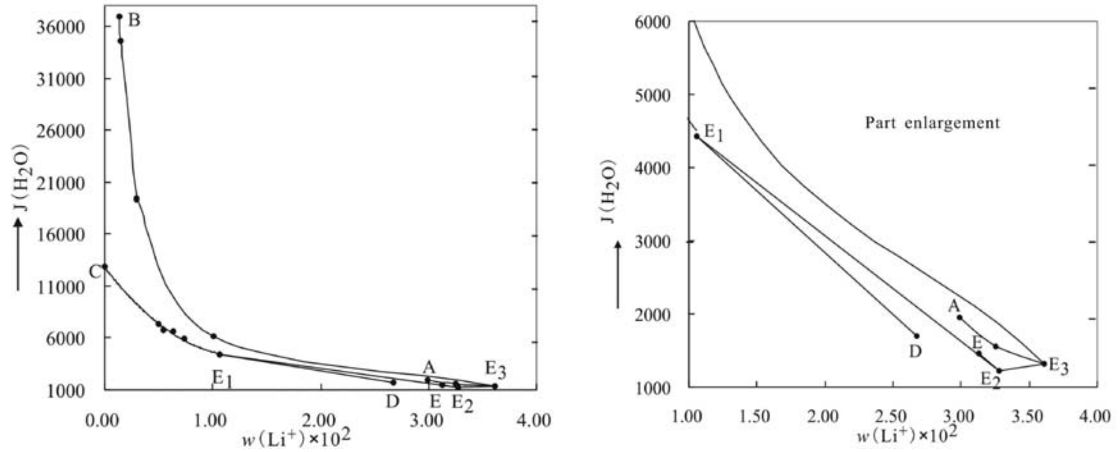


Figure 5. Water-content diagram of the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ at 273.15 K.

fraction compositions of the solution and the solid phases corresponding with the three invariant points have obviously changed. At 288.15 K, the three invariant points all saturated with salt $Li_2B_4O_7 \cdot 3H_2O$, while at 273.15 K, with the crystallization field of salt $LiBO_2 \cdot 8H_2O$ becoming smaller and that of salt $Na_2B_4O_7 \cdot 10H_2O$ becoming larger, there is only one invariant point saturated with salt $LiBO_2 \cdot 8H_2O$. The results show that the solubility of salt sodium borate changes with temperature more obviously than that of salt lithium borate. This information can be used to separate sodium borate and lithium borate.

CONCLUSION

Metastable phase equilibrium in the quaternary system $Li_2SO_4 + Na_2SO_4 + Li_2B_4O_7 + Na_2B_4O_7 + H_2O$ was investigated at 273.15 K using an isothermal evaporation method. Solubilities and densities of the solution were determined experimentally. On the basis of the experimental data, the metastable phase diagram, the water content diagram, and the density vs composition diagram were constructed. This system is of a complex type, and the double salt of sodium and lithium borate is formed at the investigated temperature. There are three invariant points, seven univariant curves, and five crystallization fields in the metastable phase diagram. The five crystallization fields correspond to sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), sodium tetraborate decahydrate (borax, $Na_2B_4O_7 \cdot 10H_2O$), lithium metaborate octahydrate ($LiBO_2 \cdot 8H_2O$), and a sodium and lithium sulfate double salt ($3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$), respectively. The salt borax has the largest crystallization field and can be easily separated from the solution at 273.15 K. Comparisons between the phase diagram at 273.15 K and the one at 288.15 K show that the crystallization forms and crystallization fields of the salts in this system change with temperature, and the solubility of salts changes obviously with temperature. This result is beneficial to separate the sodium and lithium borate from the investigated system.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zengyster@gmail.com.

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