Measurement of Solid-liquid Equilibria in Quaternary System Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K

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Abstract In order to utilize the brine resources in China, the solid-liquid equilibria in quaternary system Li⁺, $K^+//SO_4^{2-}$, $B_4O_7^{2-}$ - H_2O at 288 K was studied by the isothermal solution equilibrium method. Solubilities and densities of solutions were determined experimentally. According to the experimental data, the equilibrium phase diagrams, density-composition diagram and corresponding water content diagram of the quaternary system were plotted. Double salt KLiSO₄ was found in the reciprocal quaternary system Li⁺, $K^+//SO_4^{2-}$, $B_4O_7^{2-}$ - H_2O at 288 K. The quaternary system has three invariant points, seven univariant curves and five fields of crystallization. The five crystallization regions correspond to Li₂B₄O₇·3H₂O, Li₂SO₄·H₂O, K₂B₄O₇·4H₂O, K₂SO₄ and KLiSO₄, respectively. The crystallization field of salt Li₂B₄O₇·3H₂O is the largest, whereas that of Li₂SO₄·H₂O is the smallest. The experimental results show that Li₂SO₄·H₂O has a strong salting-out effect on other salts.

Keywords Solid-liquid equilibria; Borate; Double salt; Salting-out effect

1 Introduction

Salt lake brine is a kind of high salinity liquid mineral resources. Salt lakes in China with numerous types and large number, are famous for their rich resources, and are rich in rare elements^[1]. Salt-lake brine, bounded with more than 50 kinds of elements, is a very important liquid mineral resource. Because of the influence of geologic structure, topoclimate, ionic migration, and the characteristic of hydrochemistry, the modern salt lakes are usually provided with zonal aggregation^[2]. The Qinghai-Tibet Plateau, located in the west of China, is the main distribution area of salt lakes in the world. A subtype of sulfate salt lake brine is widely distributed in the area of the Qinghai-Tibet Plateau, which has distinct characteristics from other brine types, and is famous for the high concentrations of lithium, potassium, and boron^[3]. The sulfate salt lake brines on the Qinghai-Tibet Plateau of China belong to the complex seven-compound system^[4].

The evaporation method is often used to exploit the brines and mineral resources. Boron is one of the most important elements in the Earth's crust, and a boron mine is a source of major chemical raw materials. Boron resources of China are rich, but not easy to process^[5]. Effective development and utilization of salt lakes brine will help to make up for the shortage of solid boron mines. Qinghai salt lake is very rich in mineral resources, known as the "salt of the world". The production of these 5 kinds of minerals, including magnesium, potassium, lithium, strontium ore and Glauber salt, run the first place in the country; boron, lake salt and bromine rank second in the country; trona, rubidium and gypsum rank third place in the country; iodine ranks fourth in the whole country; the total reserves of potassium resources reach to 7.06 million tons^[6].

Therefore, deeply carrying out the research of phase equilibrium and phase diagram about potassium, lithium, boron multicomponent system, plays an important role to exploit the potassium, lithium, boron resources in China's salt lakes. So far, many studies have been focused on phase equilibria of systems containing boron.

Sang et al.^[7] studied the equilibrium relationship about a series of ternary systems containing lithium borate or potassium borate at 288 K. The solubility diagram and physicochemical properties of the solution in ternary system Li₂B₄O₇-K₂B₄O₇-H₂O at 25 °C were researched by Yu *et al.*^[8]. Song et al.^[9,10] completed the study on the solubility diagram and physicochemical properties of the solution in quaternary interaction system Li⁺, Mg²⁺//SO₄²⁻, B₄O₇²⁻-H₂O and the sub-system of quaternary system Li+//SO42-, B4O72-H2O at 25 °C. Solubility calculation of ternary systems LiCl-Li_2B_4O_7-H_2O and Li_2B_4O_7-MgCl_2-H_2O at 298 K have been researched^[11,12]. Sun et al.^[13] carried out researching on the phase equilibrium in a sulfate type pentabasic system with Li, Mg, B coexisted. Phase equilibria in ternary system Li₂B₄O₇-MgB₄O₇-H₂O at 323 K^[14] and ternary system $K_2B_4O_7$ -MgB₄O₇-H₂O at 298 K^[15] and 348 K^[16] have also been

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reported.

Quaternary system Li^+ , $K^+//SO_4^{2-}$, $B_4O_7^{2-}H_2O$ at 288 K is an important subsystem of the sulfate salt lake brine complex system in the Qinghai-Tibet Plateau of China. So far, the metastable equilibria in quaternary systems Li⁺, K⁺//CO₃²⁻, SO₄²⁻, B4O72-H2O at 273 K^[17], Li2SO4+K2SO4+Li2CO3+K2CO3+H2O at 288 $K^{[18]}$, Li₂SO₄+K₂SO₄+Li₂B₄O₇+K₂B₄O₇+H₂O at 288 K^[19] and Li₂SO₄-Li₂CO₃-Li₂B₄O₇-H₂O at 288 K^[20] have been reported by us, but no report has been found to describe the stable phase equilibria of this quaternary system at 288 K. Three K₂B₄O₇+Li₂B₄O₇+H₂O, ternary subsystems Li₂SO₄+Li₂B₄O₇+H₂O and K₂SO₄+K₂B₄O₇+H₂O of them and K₂B₄O₇-Li₂B₄O₇-MgB₄O₇-H₂O^[21-23] at 288 K have already been reported in our previous studies, which is useful to provide the foundation for this work.

In this work, the phase equilibrium of the quaternary system was studied on the basis of our former researches. We studied quaternary system Li^+ , $\text{K}^+//\text{SO}_4^{-2}$, $\text{B}_4\text{O}_7^{-2}$ -H₂O at 288 K using isothermal solubility equilibrium method. The solubilities and densities of the equilibrated solutions were determined at 288 K. This can further supplement and perfect the above heptatomic system Li^+ , Na^+ , Mg^{2+} , $\text{K}^+//\text{CI}^-$, SO_4^{-2-} , $\text{B}_4\text{O}_7^{-2-}\text{H}_2\text{O}$ and provide basic solubility data for boron resource development.

2 Experimental

2.1 Reagents and Instruments

 $Li_2B_4O_7$ (mass fraction 99%), $K_2B_4O_7$ · $4H_2O$ (mass fraction 99%), Li_2SO_4 · H_2O (mass fraction 98%), K_2SO_4 (mass fraction 99%) were of analytical purity that were obtained from Chengdu Kelong Chemical Reagent Manufactory; deionized water(conductivity less than 1×10^{-5} S/m, pH=6.6) was used to prepare the experimental solutions.

A standard analytical balance of a 110 g capacity and 0.0001 g resolution(AL104, Mettler Toledo Instruments Co., Ltd.) was employed for the determination of the solution density. A biochemical incubator in a temperature range of -15-60 °C with 0.1 °C resolution(SHH-250, Chongqing Inborn Experiment Instrument Co., Ltd.) was employed to control the temperature. An oscillator(HY-5, Jintan Kexi Instrument Co., Ltd.) placed in the incubator(SHH-250) was employed for the sufficient reaction of the samples. An electrothermal blowing dry box(101-0AB, Beijing Zhongxing Weiye Instrument Co., Ltd.) was employed to dry the solid samples.

2.2 Experimental Method

The phase equilibrium of quaternary system Li^+ , $\text{K}^+//\text{SO}_4^{2-}$, $B_4O_7^{2-}$ - H_2O at 288 K was studied by the isothermal solution method. The system points for the quaternary system were compounded by adding the third component gradually to the invariant samples of relevant ternary subsystems at 288 K. The prepared salts were dissolved in 50 mL of deionized water to form the artificial synthesized brines in sealed glass bottles. Then, the bottles were placed in the oscillator(HY-5) which was placed in the incubator(SHH-250) beforehand and the sample

temperature was maintained at (288±0.1) K. The solutions were taken out periodically and analyzed by chemical methods. The sign of the equilibrium is based on the unchanged concentration of the solution. This process took about 40 d. After equilibrium, the liquid and solid phases were separated and taken out. The liquid phases were analyzed quantitatively by chemical methods, and the solid phases were analyzed by X-ray diffraction to ascertain the crystalloid form. The invariant point was determined from the solution compositions and the X-ray diffraction photograph. As the concentration of the third kind of salt increases gradually, the points whose solid phase only contain two kinds of salts connect into univariant curve. Until three salts saturated at the same time, use X-ray diffraction identification to analyze the solid phases. If the solid phase contains three kinds of salts at the same time, it means this point is the eutonic point. In the process of experiment, must pay especial attention to the sample preparation and temperature control, in order to ensure the accuracy of the experimental data. For experimental details, Niu and Cheng^[24] can be referenced.

2.3 Analytical Method

Borate ion concentration($B_4O_7^{2-}$) was measured by means of basic titration(0.05 mol/L NaOH) in the presence of mannitol with a phenolphthalein solution as the indicator(uncertainty of 0.3%, mass fraction). Sulfate ion(SO_4^{2-}) concentration was measured by a method of alizarin red S volumetry(precision: 0.5%, mass fraction). Potassium ion concentration(K^+) was determined by a sodium tetraphenylborate(STPB)-hexadecyl trimethyl ammonium bromide(CTAB) titration(uncertainty of 0.5%, mass fraction). Lithium ion concentration(Li^+) was evaluated on an ion balance and assisted by ICP-OES(uncertainty of 0.5%, mass fraction). Each analysis was repeated thrice to estimate the reproducibility. The densities of the equilibrated solutions were determined *via* the pycnometer method(with a precision of 0.0002 g·cm³)^[25].

3 Results and Discussion

The experimental results of phase equilibrium in quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K are listed in Table 1, where ion concentrations are expressed in mass fraction w(B), and it expresses the B salt in grams per 100 g of the equilibrated solution, that is, g/(100 g of solution); J(B) is the Janeäcke index values of B, with $J(2K^+)+J(2Li^+)=100$ mol; ρ is the density of the equilibrated solution expressed in gram per cubic centimeter, that is, g/cm³. Fig.1 is the phase diagram of quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K that was plotted on the basis of the experimental data. Fig.2 is the water content diagram of quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K, with the value of $J(2Li^+)$ as the abscissa and Fig.3 is the partial enlarged drawing.

It is seen from Table 1 and Fig.1 that in this quaternary system there is no solid solution but complex salt KLiSO₄ generated at the investigated temperature. There are three invariant points, seven univariant curves, and five crystallization regions in the phase diagram. Seven univariant curves are E1-F1, E2-F1, E3-F2, E4-F3, E5-F3, F1-F2, and F2-F3.

The five crystallization regions correspond to $Li_2B_4O_7$; $3H_2O$, Li_2SO_4 ; H_2O , $K_2B_4O_7$; $4H_2O$, potassium sulfate K_2SO_4 and $KLiSO_4$, respectively. The crystallization field of the salt $Li_2B_4O_7$; $3H_2O$ is the largest, whereas that of Table 1. Solubilities and despites of solution in a

 Li_2SO_4 ·H₂O is the smallest. Salt $Li_2B_4O_7$ has the lowest solubility, which means that it can be easily separated from the solution, whereas other salts have higher solubility.

Table 1	Solubilities and densities of solution in quaternary sy	stem Li ⁺ , K ⁺ //SO ₄ ²⁻ , B ₄ O ₇ ²⁻ -H ₂ O at 288 K [*]
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No.	Composition of solution, <i>w</i> (B)(%)			Jänecke index, $J/(\text{mol}\cdot 100 \text{ mol}^{-1} \text{ dry-salt})$ $J(2\text{K}^+)+J(2\text{Li}^+)=100 \text{ mol}$			Equilibrium	Solution densi-	
	${\rm B_4O_7}^{2-}$	$\mathrm{SO_4}^{2-}$	\mathbf{K}^+	Li ⁺	2Li ⁺	$\mathrm{SO_4}^{2-}$	H_2O	solid	ty, $\rho/(g \cdot cm^{-3})$
1(E1)	8.67	0.00	3.42	0.17	21.69	0.00	8706.07	KB+LB	1.0631
2	7.06	2.78	4.68	0.201	19.50	38.85	6366.22	KB+LB	1.1715
3	7.06	4.01	5.66	0.203	16.81	47.81	5293.50	KB+LB	1.1970
4	7.14	4.07	5.76	0.202	16.51	47.92	5210.52	KB+LB	1.2027
5(F1)	7.07	4.10	5.73	0.205	16.78	48.35	5224.64	KS+KB+LB	1.2106
6(E2)	6.48	4.07	6.56	0.000	0.00	44.30	5470.52	KB+KS	1.1864
7	6.55	3.77	5.81	0.097	8.61	48.18	5708.17	KB+KS	1.1211
8	6.59	3.69	5.76	0.099	8.84	47.53	5756.33	KB+KS	1.1185
9	6.84	3.74	5.75	0.129	11.18	46.87	5592.18	KB+KS	1.1430
10	7.16	3.86	5.74	0.178	14.89	46.54	5344.76	KB+KS	1.1719
11	7.17	3.89	5.72	0.187	15.56	46.71	5320.47	KB+KS	1.1952
12(E3)	0.00	15.23	4.76	1.352	61.28	100	3531.92	KS+LK	1.1781
13	0.35	12.53	4.28	1.084	58.82	98.06	3442.10	KS+LK	1.1653
14	0.74	12.18	4.21	1.079	59.08	96.11	3472.22	KS+LK	1.1667
15	1.23	12.02	4.29	1.086	58.81	93.82	3418.53	KS+LK	1.1678
6	1.56	12.16	4.40	1.116	58.83	92.39	3372.15	KS+LK	1.1773
17	1.56	11.93	4.33	1.096	58.79	92.29	3355.08	KS+LK	1.1749
18(F2)	1.55	12.06	4.35	1.109	58.98	92.42	3338.40	KS+LK+LB	1.1824
19(E4)	0.00	23.64	1.05	3.23	94.50	100	1639.66	LK+LS	1.2508
20	0.33	20.76	0.68	2.915	96.05	98.61	1951.94	LK+LS	1.2291
21	0.65	20.89	0.78	2.945	95.53	97.72	1907.92	LK+LS	1.2297
22	1.07	20.69	0.79	2.952	95.49	96.49	1896.11	LK+LS	1.2345
23	1.25	20.72	0.73	2.982	95.82	96.01	1879.88	LK+LS	1.2396
24	1.24	20.68	0.77	2.969	95.62	96.02	1884.54	LK+LS	1.2403
25	1.28	20.83	0.74	2.998	95.78	95.93	1864.48	LK+LS	1.2441
26(E5)	1.42	15.37	0.00	2.354	100.00	94.17	2671.54	LS+LB	1.2222
27	1.40	15.00	0.47	2.212	96.34	94.15	2756.42	LS+LB	1.2362
28	1.39	14.92	0.80	2.143	93.81	94.16	2764.26	LS+LB	1.2369
29	1.41	14.88	1.37	2.037	89.35	94.11	2751.32	LK+LB	1.2398
30	1.40	14.89	1.40	2.031	89.07	94.14	2750.39	LK+LB	1.2420
31(F3)	1.42	14.78	1.43	2.013	88.78	94.02	2768.30	LK+LS+LB	1.2433

* Uncertainty: $B_4O_7^{2-}$, 0.3%; SO_4^{2-} , 0.5%; K^+ , 0.5%; Li^+ , 0.5%. Points E1, E2, E3, E4 and E5 are the invariant points of ternary subsystems $Li_2B_4O_7-K_2B_4O_7-H_2O$, $K_2SO_4-K_2B_4O_7-H_2O$, $Li_2SO_4-K_2SO_4-H_2O$, $Li_2SO_4-K_2SO_4-H_2O$ and $Li_2SO_4-Li_2B_4O_7-H_2O$ at 288 K; points F1, F2 and F3 are three invariant points of this quaternary system at 288 K. LS: $Li_2SO_4+H_2O$; KB: $K_2B_4O_7-4H_2O$; LB: $Li_2B_4O_7-H_2O$, $Li_2SO_4+K_2SO_4-H_2O$; KB: $K_2B_4O_7-4H_2O$; LB: $Li_2B_4O_7-H_2O$ at 288 K; points F1, F2 and F3 are three invariant points of this quaternary system at 288 K. LS: $Li_2SO_4+H_2O$; KB: $K_2B_4O_7-4H_2O$; LB: $Li_2B_4O_7$; LK: $KLiSO_4$; KS: K_2SO_4 .



Fig.1 Dry-salt solubility diagram of quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K

Points F1, F2 and F3 are the invariant points for quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K. Invariant point F1 is saturated with salts K₂SO₄, K₂B₄O₇·4H₂O and Li₂B₄O₇·3H₂O. The mass fraction composition of the corresponding liquid phase is $w(Li^+)=0.205\%$, $w(K^+)=5.73\%$,



Fig.2 Water contents of saturated solutions in quaternary system Li^+ , $K^+//SO_4^{2-}$, $B_4O_7^{2-}$ -H₂O at 288 K

 $w(SO_4^{2-})=4.10\%$, $w(B_4O_7^{2-})=7.07\%$. Invariant point F2 is saturated with salts K₂SO₄, KLiSO₄ and Li₂B₄O₇·3H₂O. The mass fraction composition of the corresponding liquid phase is $w(Li^+)=1.109\%$, $w(K^+)=4.35\%$, $w(SO_4^{2-})=12.06\%$, $w(B_4O_7^{2-})=1.55\%$. Invariant point F3 is saturated with salts Li₂SO₄·H₂O,

KLiSO₄ and Li₂B₄O₇·3H₂O. The mass fraction composition of the corresponding liquid phase is $w(\text{Li}^+)=2.013\%$, $w(\text{K}^+)=1.43\%$, $w(\text{SO}_4^{-2-})=14.78\%$, $w(\text{B}_4\text{O}_7^{-2-})=1.42\%$.

Fig.2 shows that the water content increases on the uninvariant curves F1E1 and F2E3; remains unchanged on the uninvariant curve F3E5, and decreases on the other uninvariant curves with an increase of the Jänecke index value of $J(2\text{Li}^+)$. It reaches the maximum value at the point E1 and the minimum value at the point E4.



Fig.3 Partial enlarged diagrams of Fig.2

In order to reflect the changes in density, the density diagram of the system is constructed in Fig.4. According to Fig.4 and Table 1, the densities of the equilibrium liquids reach the highest at the invariant points, respectively. The equilibrium liquid has the largest density at the invariant point F3 and the density of the equilibrium liquid at the invariant point F2 is the lowest among the three invariant points. This may be because there is double salt KLiSO₄ generated at the invariant point F3. The double salt gradually decomposed after the invariant point F2 and the solid phase transformed into K_2SO_4 and $Li_2B_4O_7$ ·3H₂O.

According to the research, it takes a long time to reach



Fig.4 Density-composition relations of solutions in quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K

equilibrium because the dissolution behavior of the boric acid salt in aqueous solution is extremely complex. The main existed forms of boric acid group differ at different pH or salt concentration. Its aqueous solution often has multiparticle coexisted and always generate a supersaturated solution, boric acid group often exists as $[B_2O_5(OH)_4]^{2-}$. It easily forms a double salt in the salt-water system containing SO_4^{2-} at room temperature.

Comparing the stable phase diagram with the metastable phase diagram of quaternary system at 288 K^[21] shows the shapes of them are similar. They all have three invariant points, seven univariant curves and five fields of crystallization, and the salts all have the same crystallization forms. However, the solubilities of Li₂SO₄·H₂O, K₂B₄O₇·4H₂O, K₂SO₄, Li₂B₄O₇ are decreased in the stable phase diagram, and the crystallization regions in the stable phase diagram are larger than those in the metastable phase diagram. Moreover, no matter in stable or metastable phase equilibrium, Li₂SO₄·H₂O has strong salting out effect on other salts.

4 Conclusions

The solid-liquid equilibria in the reciprocal quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K were studied *via* the isothermal solution saturation method. Solubilities, densities and corresponding equilibrium solids were determined. According to the experimental data, the phase diagram, corresponding water content diagram and density diagram of the quaternary system were plotted. The double salt KLiSO₄ was found in reciprocal quaternary system Li⁺, K⁺//SO₄²⁻, B₄O₇²⁻-H₂O at 288 K. The quaternary system has three invariant points, seven univariant curves, five fields of crystallization Li₂B₄O₇·3H₂O, Li₂SO₄·H₂O, K₂B₄O₇·4H₂O, K₂SO₄ and KLiSO₄. The experimental results show that Li₂SO₄·H₂O has a strong salting-out effect on other salts.

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