JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

Metastable Phase Equilibrium and Solution Properties of the Quaternary System Li^+, $K^+//Cl^-$, and $SO_4^{2-}-H_2O$ at 273.15 K

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ABSTRACT: The metastable phase equilibria of the quaternary system Li^+, $K^+//Cl^-$, and $SO_4^{2-}-H_2O$ was studied at 273.15 K using an isothermal evaporation method. The solubilities and densities of the equilibrated solution were determined. According to the experimental data, the metastable phase diagram, the water-content diagram, density diagram, and pH value diagram were plotted. This quaternary system is of a complex type; the double salt $KLiSO_4$ was found at the studied temperature. The metastable phase diagram consists of three invariant points, seven uninvariant curves, and five salt crystallization regions. Potassium sulfate has the largest crystallization field and can be easily separated from the solution in this system at 273.15 K using an evaporation method. Comparisons between the metastable and the stable phase diagram at different temperatures show that the crystallization forms of the salts are the same, whereas the crystallization field of salt K_2SO_4 becomes obviously larger with the temperature decrease. If more pure potassium sulfate needs to be separated as much as possible, a fall in temperature is necessary.

INTRODUCTION

Salt lakes are widely distributed in the west of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau. Zabuye Salt Lake (84°04' E, 31°21' N) is located in Tibet with an area of 247 km^2, at a high altitude of 4422 m. The average annual precipitation of Zabuye Salt Lake is 196.2 mm, but the annual evaporation is 2269 mm.[1] The concentration of the main components in the Zabuye Salt Lake brine is shown in Table 1.[2] The main components of the Zabuye Salt Lake brine can be described as the complex system Li^+, Na^+, K^+, $Mg^{2+}//Cl^-$, SO_4^{2-}, CO_3^{2-}, and borate$-H_2O$, and the evaluated economic value of the Zabuye Salt Lake brine resource is more than 200 billion Chinese yuan.[1] Because the climatic conditions in the Zabuye Salt Lake region are windy and arid, with high daily evaporation, to exploit salt-lake brine resources, natural energies such as the energy of the sun or the wind are often used to evaporate the brines. Thus, techniques like solar ponds are widely used. It is well-known that metastable phase equilibrium research is essential to predict the crystallized path of evaporation of the salt lake brine, and therefore, the investigation of metastable equilibrium solubilities is of theoretical and practical importance.

The average temperature of Tibet in summer is about 288 K, so most of the effort has focused at a temperature of 288 K, such as the papers about the quinary systems Na^+, K^+, $Mg^{2+}//Cl^-$, and $SO_4^{2-}-H_2O$,[3] Li^+, Na^+, $K^+//CO_3^{2-}$, and $B_4O_7^{2-}-H_2O$,[4] Li^+, $K^+//Cl^-$, CO_3^{2-}, and $B_4O_7^{2-}-H_2O$,[5] and Li^+, Na^+, $K^+//SO_4^{2-}$, and $B_4O_7^{2-}-H_2O$[6] and their corresponding subsystems. In the Zabuye Salt Lake region, the average annual temperature is about 273.15 K;[1] thus, studies on the phase equilibria at 273.15 K will be more closely related to reality and be of great use in exploitation of the brine. By now, a series of papers describing metastable phase equilibria have been reported at a temperature of 273.15 K, such as papers about the quaternary systems Na^+, $K^+//Cl^-$, and $B_4O_7^{2-}-H_2O$,[7] $K^+//Cl^-$, SO_4^{2-}, and $B_4O_7^{2-}-H_2O$,[8] and Na^+, $K^+//Cl^-$, and $CO_3^{2-}-H_2O$,[9] and the quinary system Li^+, Na^+, $K^+//SO_4^{2-}$, and $B_4O_7^{2-}-H_2O$.[10]

Table 1. Main Chemical Composition of Zabuye Salt Lake Brines[2]

component	Na^+	K^+	Li^+	Cl^-	SO_4^{2-}	B_2O_3	CO_3^{2-}	note
composition ($g\cdot L^{-1}$)	122.5	48.1	1.17	181.3	13.1	10.3	33.6	spring brines
	129.6	40.9	1.05	156.2	38.6	11.0	44.2	autumn brines

The quaternary system Li^+, $K^+//Cl^-$, and $SO_4^{2-}-H_2O$ is a subsystem of the Zabuye Salt Lake brine. The stable phase equilibria of this system at (323 and 348) K[11] have been reported, whereas the metastable phase diagram of this system has not been found yet. In this paper, the metastable phase equilibrium of the quaternary system Li^+, $K^+//Cl^-$, and $SO_4^{2-}-H_2O$ at 273.15 K is presented. Compared to the phase studies at 298 K or higher temperature, studies at 273.15 K are more difficult because of the lower evaporating velocity, stronger viscosity of solution, and longer time to reach equilibrium.

EXPERIMENTAL SECTION

Apparatus and Reagents. The chemicals used in this work were of analytical purity grade and from the Chengdu Chemical Reagent Plant. They were lithium sulfate (Li_2SO_4, 99.0 % (w/w)), potassium sulfate (K_2SO_4, 99.0 % (w/w)), lithium chloride (LiCl, 99.5% (w/w)), and potassium chloride (KCl, 99.5 % (w/w)). Doubly deionized water was obtained from a Millipore water system with an electrical conductivity less than $1\cdot10^{-4}$ $S\cdot m^{-1}$ and pH = 6.6. For each experiment, the required

Received: August 16, 2010
Accepted: January 3, 2011
Published: January 19, 2011

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 temperature-controlling precision was ± 0.1 K.

A Siemens D500 powder X-ray diffractometer with Ni-filtered Cu Kα radiation was used to analyze the crystalloid forms of the solid phases. The operating conditions were 35 kV and 25 mA. A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, supplied by the Mettler Toledo Instruments Co., Ltd.) was employed for the determination of the solution density.

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Experimental Method. The isothermal evaporation method was employed in this study. The required amounts of reagent, calculated according to the solubility of salts at 273.15 K and the solubility data of the invariant points of the ternary subsystems, 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 bottles. The bottles 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 bottles, the liquid and solid phases were separated by filtration. The obtained wet crystals in the solid phase were separated from each other according to crystal shapes as much as possible. Each kind of solid sample was divided into two parts. One was analyzed by chemical methods to obtain the composition of salt. The other was 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 100 mL final volume in a volumetric flask filled with deionized water to analyze the liquid-phase components. Another 5.0 mL sample of the clarified solution was taken to determine the density and pH value. The remainder of the solution continued to be evaporated to reach the next measuring point. The same procedure was repeated until the solution was fully evaporated. This process took about (15 to 20) days.

The densities of solution were determined using a specific gravity bottle method with a correction of air floating force.[12] The sample was obtained at 273.15 K and measured at 298 K. The excursion caused by the temperature difference was calibrated by using a multipoint temperature-revision method.[13]

The pH values of the equilibrated solution were determined using a pXS-1$^+$ pH meter which was calibrated with standard buffer solutions of a mixed phosphate of potassium dihydrogen phosphate and sodium hydrogen phosphate (pH 6.86) as well as potassium hydrogen phthalate (pH 4.00).

Analytical Method. The composition of potassium in the liquids and their corresponding wet solid phases were analyzed by using a sodium tetraphenylborate (STPB)- hexadecyl trimethyl ammonium bromide (CTAB) back-titration method with the existence of propanetriol, with a precision within 0.5 % (by mass).[14]

The lithium ion concentration was determined by inductively coupled plasma emission spectrometry (precision: less than 0.06 % (by mass), type ICP-OES 5300 V).

The chlorine ion concentration was determined by titration with a silver nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue with a precision of 0.3 % (by mass).[14]

The sulfate ion concentration was determined by titration with a standard solution of ethylenediaminetetraacetic acid (EDTA) in the presence of an excess Ba−Mg mixture solution.[14] The precision of the measurements was better than 1 %.

RESULTS AND DISCUSSION

Phase Diagram at 273.15 K. The experimental results of solubilities and densities of the equilibrated solution in the quaternary system Li^+, K^+//Cl^-, and SO_4^{2-}−H_2O at 273.15 K are tabulated in Table 2. In Table 2, $w(B)$ is the mass fraction of B, $J(B)$ is the Jänecke index value of B, and $n(B)$ is the mole number of B, with $n(Li_2^{2+}) + n(K_2^{2+}) = n(Cl_2^{2-}) + n(SO_4^{2-}) = 100$ mol. The molar masses of the elements used in this calculation are adopted from an International Union of Pure and Applied Chemistry (IUPAC) Technical Report.[15] The formula for $J(B)$ is,

$$J(B) = \frac{n(B)}{n(Li_2^{2+}) + n(K_2^{2+})} \cdot 100 \qquad (1)$$

The calculating formula for the water concentration is,

$$J(H_2O) = \frac{100 - \sum w(B) \cdot 100}{18 \cdot [n(Li_2^{2+}) + n(K_2^{2+})]} \cdot 100 \qquad (2)$$

With the data of the Jänecke index $J(B)$, the experimental solubility isothermal metastable phase diagram of the system at 273.15 K is plotted in Figure 1. Figure 2 is the partial enlarged diagram of Figure 1, and Figure 3 is the water-content diagram.

The phase diagram of the quaternary system consists of three invariant points, seven univariant curves, and five crystallization fields. The five crystallization fields correspond to the single salt lithium chloride monohydrate ($LiCl \cdot H_2O$), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), a lithium−potassium sulfate double salt ($KLiSO_4$), potassium sulfate (K_2SO_4), and potassium chloride (KCl), respectively. There are seven isothermal evaporation curves in Figure 1, namely, curves AE_1, BE_1, CE_3, DE_3, FE_2, E_1E_2, and E_2E_3, indicating the cosaturation of two salts. Points A, B, C, D, and F, cosaturated with two salts, are five invariant points of four ternary subsystems of the quaternary system Li^+, K^+//Cl^-, and SO_4^{2-}−H_2O, respectively.

By the phase rule, the simplest methods to judge the type of invariant point is whether the point lies in the triangle which is formed by cosaturated solid-phase salts in the phase diagram or not. The commensurate invariant point lies in the triangle, whereas the incommensurate invariant point lies out the triangle. In this phase diagram, the three invariant points labeled as E_1, E_2, and E_3 are cosaturated with three salts. The point E_1 lies in the triangle which is formed by corresponding solid-phase salts $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$, and KCl, so E_1 is a commensurate invariant point. While the points E_2 or E_3 lie out the triangle which is formed by each corresponding solid-phase salts, E_2 and E_3 are incommensurate invariant points.

The metastable equilibrated solid phases of the invariant points were confirmed with X-ray diffraction analysis. Figure 4

Table 2. Solubilities, pH Values, and Densities of the Equilibrated Solutions in the Quaternary System Li^+, K^+//Cl^-, and $SO_4^{2-}-H_2O$ at 273 K[a]

	density		composition of equilibrium solution, $w(B)\cdot 10^2$				Jänecke index of dry salt $n(Li_2^{2+}) + n(K_2^{2+}) = n(Cl_2^{2-}) + n(SO_4^{2-}) = 100$ mol					equilibrium solid phase
no.	$g\cdot cm^{-3}$	pH value	$w(Li^+)$	$w(K^+)$	$w(Cl^-)$	$w(SO_4^{2-})$	$J(Li_2^{2+})$	$J(K_2^{2+})$	$J(Cl_2^{2-})$	$J(SO_4^{2-})$	$J(H_2O)$	
1,A	1.2586	7.60	6.49	0.97	34.29	0.00	97.42	2.58	100.00	0.00	673.7	LI+KI
2	1.2353	4.90	5.84	0.88	30.83	0.02	97.41	2.59	99.97	0.04	798.2	LI+KI
3	1.2338	4.60	5.98	0.89	31.57	0.01	97.44	2.56	99.97	0.03	772.6	LI+KI
4,E_1	1.2365	4.60	5.88	0.88	31.05	0.02	97.42	2.57	99.96	0.04	789.0	LI+KI+LS
5,B	1.2479	5.70	6.57	0.00	32.87	0.01	100.00	0.00	99.94	0.06	722.9	LI+LS
6	1.2338	4.60	5.98	0.89	31.57	0.01	97.44	2.56	99.97	0.03	768.3	LI+LS
7	1.2305	4.80	5.96	0.89	31.45	0.02	97.43	2.57	99.96	0.04	772.8	LI+LS
8	1.2294	8.00	5.89	0.88	31.11	0.03	97.42	2.58	99.93	0.07	791.2	KI+LS
9	1.2305	5.80	5.88	0.89	31.01	0.04	97.40	2.60	99.91	0.09	789.8	KI+LS
10,E_2	1.2243	8.00	5.79	0.89	30.58	0.04	97.35	2.65	99.90	0.10	812.2	KS+KI+ LS
11	1.2376	6.10	3.19	0.69	2.07	20.27	96.31	3.69	12.11	87.89	1716	LS+KS
12	1.2060	5.70	3.07	0.77	2.93	18.36	95.75	4.25	17.76	82.24	1799	LS+KS
13	1.2329	6.20	2.80	0.79	5.17	13.45	95.26	4.74	34.21	65.79	2038	LS+KS
14	1.1596	6.50	2.98	0.75	9.81	8.37	95.74	4.26	61.30	38.70	1933	LS+KS
15,C	1.2366	8.42	3.69	0.82	0.00	22.51	96.21	3.79	0.00	100.00	1730	LS+LKS
16	1.2593	7.98	3.14	0.71	0.29	22.35	96.16	3.84	1.75	98.25	1734	LS+LKS
17	1.2774	8.90	3.40	0.75	0.36	24.09	96.24	3.76	1.97	98.03	1557	LS+LKS
18	1.2752	9.10	3.46	0.62	0.37	24.31	96.91	3.09	2.03	97.97	1537	LS+LKS
19	1.2664	8.90	3.37	0.59	0.41	23.63	96.98	3.02	2.30	97.70	1596	LS+LKS
20	1.2658	8.50	3.31	0.59	0.45	23.13	96.94	3.06	2.59	97.41	1636	LS+LKS
21	1.2489	7.40	3.17	0.60	0.62	21.93	96.76	3.24	3.70	96.30	1733	LS+LKS
22	1.2442	7.30	3.28	0.63	1.48	21.57	96.70	3.30	8.51	91.49	1659	LS+LKS
23	1.2400	6.80	3.22	0.68	1.76	20.85	96.41	3.59	10.26	89.74	1695	LS+LKS
24,E_3	1.2514	7.73	3.39	0.73	2.03	21.73	96.35	3.65	11.21	88.79	1579	LS+LKS+KS
25,D	1.1622	8.82	1.41	3.52	0.00	14.06	69.19	30.81	0.00	100.00	3076	KS+LKS
26	1.1863	8.38	1.61	3.50	0.61	14.67	72.23	27.77	5.36	94.64	2749	KS+LKS
27	1.1847	8.29	2.00	2.73	0.84	16.11	80.54	19.46	6.61	93.39	2429	KS+LKS
28	1.1933	8.48	2.49	1.82	1.19	17.96	88.56	11.44	8.24	91.76	2096	KS+LKS
29	1.2287	7.95	3.33	0.77	1.86	21.59	96.08	3.92	10.42	89.58	1610	KS+LKS
30,F	1.1530	6.10	0.00	13.04	11.37	0.45	0.00	100.00	97.16	2.84	2529	KS+KI
31	1.1520	6.00	0.05	11.42	10.24	0.53	2.26	97.74	96.30	3.70	2884	KS+KI
32	1.1536	6.40	0.18	10.88	10.40	0.60	8.70	91.30	95.89	4.11	2844	KS+KI
33	1.1534	6.50	0.23	10.61	10.42	0.58	10.89	89.11	96.07	3.93	2850	KS+KI
34	1.1560	7.48	0.30	10.39	10.58	0.59	14.08	85.92	96.06	3.94	2808	KS+KI
35	1.1521	7.32	0.72	9.19	11.26	1.08	30.61	69.39	93.35	6.65	2547	KS+KI
36	1.1511	7.64	1.39	7.08	12.21	1.86	52.56	47.44	89.87	10.13	2255	KS+KI
37	1.1483	7.92	1.93	5.33	13.36	1.92	67.21	32.79	90.39	9.61	2075	KS+KI
38	1.1443	7.70	2.80	3.30	16.48	1.24	82.74	17.26	94.72	5.28	1734	KS+KI
39	1.1497	7.59	3.30	2.40	18.40	1.00	88.57	11.43	96.12	3.88	1549	KS+KI
40	1.1702	6.01	4.16	1.67	22.50	0.57	93.35	6.62	98.16	1.84	1229	KS+KI
41	1.1819	6.74	4.43	1.43	23.94	0.20	94.61	5.36	99.38	0.62	1151	KS+KI

[a] LS: $Li_2SO_4\cdot H_2O$; LKS: $LiKSO_4$; KS: K_2SO_4; KI: KCl; LI: $LiCl\cdot H_2O$. $w(B)$: mass fraction of B, $J(B)$: Jänecke index of dry salt.

gives the X-ray diffraction photograph of the invariant point E_3, which shows that at the invariant point E_3, the salts $Li_2SO_4\cdot H_2O$, K_2SO_4, and $KLiSO_4$ coexisted. The saturated salts and the mass fraction composition for the three invariant points are listed below.

Point E_1 is saturated with salts $LiCl\cdot H_2O + Li_2SO_4\cdot H_2O +$ KCl. The mass fraction composition of the corresponding liquid phase is $w(Li^+) = 5.88$ %, $w(K^+) = 0.88$ %, $w(Cl^-) = 31.05$ %, and $w(SO_4^{2-}) = 0.02$ %.

Point E_2 is saturated with salts $Li_2SO_4\cdot H_2O + K_2SO_4 +$ KCl. The mass fraction composition of the corresponding liquid phase is $w(Li^+) = 5.79$ %, $w(K^+) = 0.89$ %, $w(Cl^-) = 30.58$ %, $w(SO_4^{2-}) = 0.04$ %.

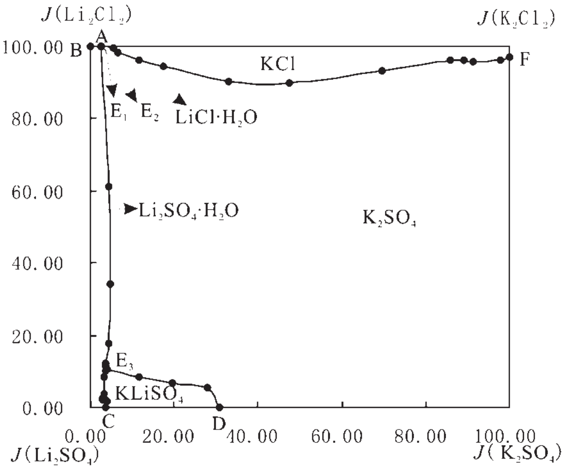


Figure 1. Metastable phase diagram of the quaternary system Li^+, K^+//Cl^-, and SO_4^{2-}—H_2O at 273.15 K.

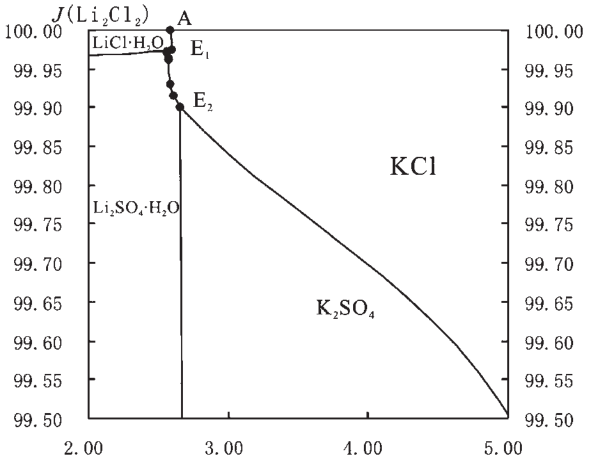


Figure 2. Partial enlarged diagram of Figure 1.

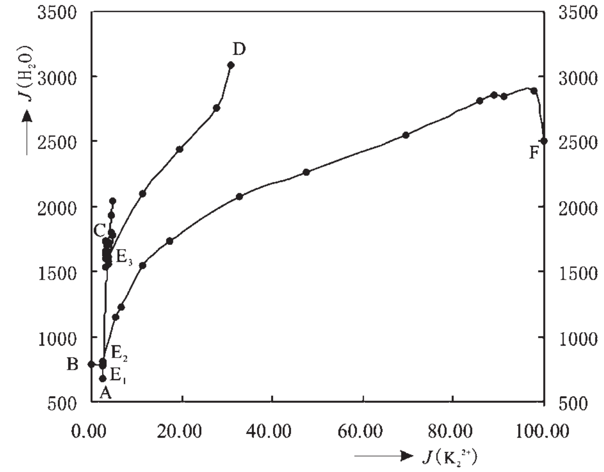
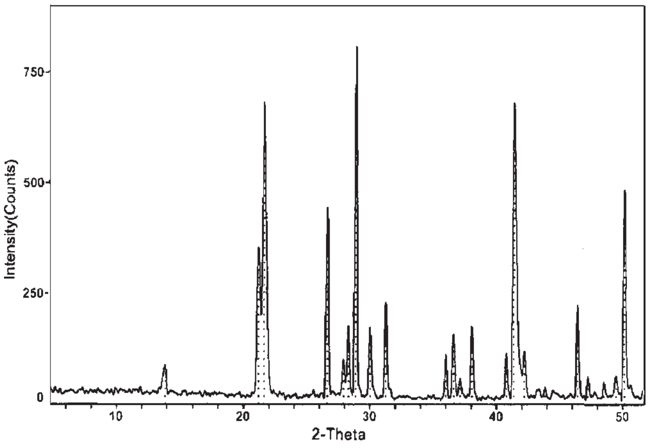


Figure 3. Water-content diagram of the quaternary system Li^+, K^+// Cl^-, and SO_4^{2-}—H_2O at 273.15 K.



Chemical Formula	$Li_2SO_4 \cdot H_2O$	K_2SO_4	$KLiSO_4$
Dspacing	4.10	2.86	3.10
Score	21	31	29

Figure 4. X-ray diffraction photograph of the invariant point E_3 ($Li_2SO_4 \cdot H_2O$ + $KLiSO_4$ + K_2SO_4).

Point E_3 is saturated with salts $Li_2SO_4 \cdot H_2O$ + $KLiSO_4$ + K_2SO_4. The mass fraction composition of the corresponding liquid phase is $w(Li^+)$ = 3.39 %, $w(K^+)$ = 0.73 %, $w(Cl^-)$ = 2.03 %, $w(SO_4^{2-})$ = 21.73 %.

The crystallization field of the salt $LiCl \cdot H_2O$ is the smallest, while the crystallization field of the salt K_2SO_4 is the largest. These results indicate that potassium sulfate is easier to saturate and crystallize than the other four salts from solution at 273.15 K.

Figure 3 is the water-content diagram of the quaternary system. At the invariant point E_1, the system has the lowest water content. Invariant point E_1 is a congruent eutonic point and the evaporating end point of the whole system. At this point, the salts $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$ and KCl can be salted out simultaneously, without any dissolving conversion action.

Density and pH Value of the System. The density versus composition diagram is plotted in Figure 5. The density increases with a decrease of the potassium ion content at the univariant curves. Especially on the univariant curve FE_2, as the potassium ion content decreases from 13.04 % to 0.89 %, the density increases from 1.1530 $g \cdot cm^{-3}$ to 1.2243 $g \cdot cm^{-3}$.

Figure 6 is the pH value versus composition diagram. The pH value of the system also changes regularly with the content change of the potassium ion. On the univariant curve FE_2, as the potassium ion content changes from 13.04 % to 0.89 %, the corresponding pH value increases from 6.10 to 8.00.

Comparison between the Metastable and the Stable Phase Diagrams. The stable phase diagram of the quaternary system Li^+, K^+//Cl^-, and SO_4^{2-}—H_2O has been studied at (323 and 348) K.[11] Comparing the two stable phase diagrams at different temperatures, it is easy to observe that the crystallization field of the double salt $KLiSO_4$ is obviously larger at 348 K than at 323 K, whereas the crystallization field of the salt K_2SO_4 is smaller at 348 K than at 323 K.

A comparison between the metastable phase diagram at 273.15 K and the stable phase diagram at (323 and 348) K[11] shows that, although the salts in this system, including the double salt, have the same crystallization forms, which are $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$, $KLiSO_4$, K_2SO_4, and KCl, the crystallization fields of the salts have changed. The crystallization field of salt K_2SO_4 becomes obviously larger with the temperature decrease,

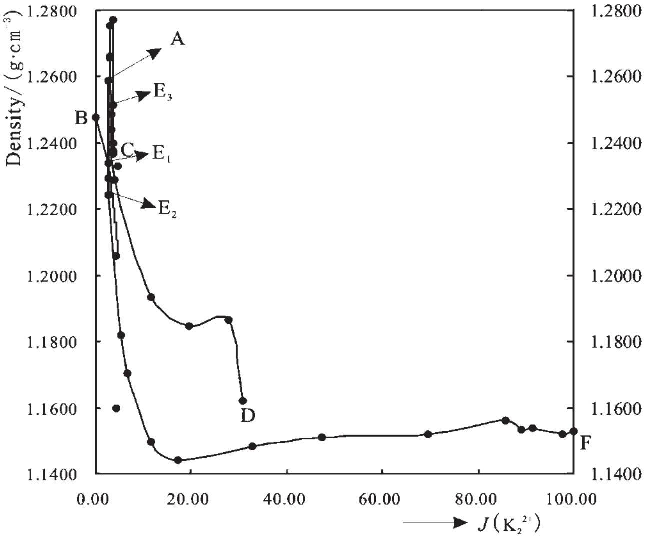


Figure 5. Density value vs composition diagram of the quaternary system Li^+, K^+//Cl^-, and $SO_4^{2-}-H_2O$ at 273.15 K.

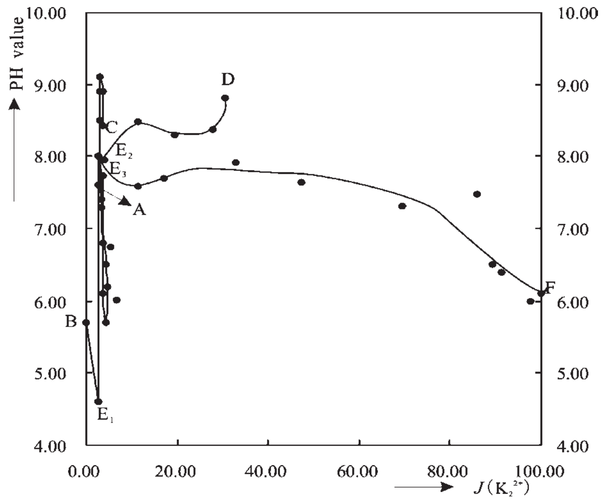


Figure 6. pH value vs composition diagram of the quaternary system Li^+, K^+//Cl^-, and $SO_4^{2-}-H_2O$ at 273.15 K.

whereas that of the double salt $KLiSO_4$ becomes smaller, while the crystallization fields of the other salts change slightly. By reason of this, the metastable phase diagram at 273.15 K and the stable phase diagrams at higher temperatures ((323 and 348) K) have different saturated salts at incommensurate invariant points. The incommensurate invariant points are cosaturated with salts $Li_2SO_4 \cdot H_2O + K_2SO_4 + KCl$ and $Li_2SO_4 \cdot H_2O + KLiSO_4 + K_2SO_4$ at 273.15 K and with salts $KLiSO_4 + K_2SO_4 + KCl$ and $Li_2SO_4 \cdot H_2O + KLiSO_4 + KCl$ at higher temperatures ((323 and 348) K).[11] The results show that a fall in temperature is necessary for more pure potassium sulfate to be separated.

■ CONCLUSIONS

Metastable phase equilibrium in the quaternary system Li^+, K^+//Cl^-, and $SO_4^{2-}-H_2O$ was studied at 273.15 K using an isothermal evaporation method. The solubility and physicochemical properties such as densities and pH values were determined experimentally. This system is of a complex type. The double salt $KLiSO_4$ was found in this system at 273.15 K. There are three invariant points, seven uninvariant curves, and five salt crystallization regions corresponding to KCl, $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$, K_2SO_4, and $KLiSO_4$ in the phase diagram. Among the three invariant points, point E_1 is a commensurate invariant point, while points E_2 and E_3 are incommensurate invariant points. The crystallization field of salt $LiCl \cdot H_2O$ is the smallest, while the crystallizing field of the salt K_2SO_4 is the largest. More pure potassium sulfate can be obtained with decreasing temperature.

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Funding Sources

Financial support for this work was provided by the National Nature Science Foundation of China (No. 40673050), the Doctoral Fund of Ministry of Education of China (20070616008), the Scholarship Leaders Training Fund from Sichuan Province (2008-140), and the Program for New Century Excellent Talents in University (NCET-08-0900).

■ REFERENCES

(1) Zheng, M. P.; Liu, W. G.; Xiang, J. *Qinghai-Xizang Plateau Saline Lakes* (in Chinese); Beijing Science and Technology Press: Beijing, China, 1989; pp 192−270.

(2) Nie, Z.; Bu, L. Z.; Zheng, M. P.; Zhang, Y. S. Phase Chemistry Study on Brine from the Zabuye Carbonate Type Salt Lake in Tibet. *Acta Geol. Sin.* **2010**, *84*, 587–592.

(3) Jin, Z. M.; Zhou, H. N.; Wang, L. S. Studies on the Metastable Phase Equilibrium of Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}-H_2O Quinary System at 288 K. *Chem. J. Chin. Univ.* **2002**, *23*, 690−694 (in Chinese).

(4) Sang, S. H.; Yin, H. A.; Tang, M. L. (Liquid + Solid) Phase Equilibria in the Quinary System $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K. *J. Chem. Eng. Data* **2005**, *50*, 1557–1559.

(5) Zeng, Y.; Shao, M. Liquid-Solid Metastable Equilibria in the Quinary System $Li^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at T = 288 K. *J. Chem. Eng. Data* **2006**, *51*, 219–222.

(6) Zeng, Y.; Lin, X. F.; Ni, S. J.; Zhang, C. J. 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. *J. Chem. Eng. Data* **2007**, *52*, 164–167.

(7) Zeng, Y.; Wang, R. L.; Lin; X. F.; Peng, Y. Metastable Phase Equilibria of the Quaternary System Na^+, K^+//Cl^-, $B_4O_7^{2-}$-H_2O at 273 K. *Acta Phys.-Chim. Sin.* **2008**, *24*, 471−474 (in Chinese).

(8) Peng, Y.; Zeng, Y.; Feng, S. Metastable Equilibria in the Quaternary System $KCl + K_2SO_4 + K_2B_4O_7 + H_2O$ at 273 K. *Geochim. Cosmochim. Acta* **2009**, *73*, A1010.

(9) Zeng, Y.; Liu, J. M.; Zheng, Z. Y. Metastable Phase Equilibrium in the Quaternary System $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ at 273 K. *J. Chem. Eng. Data* **2010**, *55*, 1310–1313.

(10) Zeng, Y.; Lin, X. F. Solubility and Density Measurements of Concentrated $Li_2B_4O_7 + Na_2B_4O_7 + K_2B_4O_7 + Li_2SO_4 + Na_2SO_4 + K_2SO_4 + H_2O$ Solution at 273.15 K. *J. Chem. Eng. Data* **2009**, *54*, 2054–2059.

(11) Ren, K. W.; Song, P. S. A Study on Equilibrium Solubilities in the Quaternary Reciprocal System of Li^+, K^+//Cl^-, SO_4^{2-} - H_2O at 50 °C and 75 °C. *Chin. J. Appl. Chem.* **1994**, *11*, 7–10.

(12) Zeng, Y.; Zheng, Z. Y. Metastable Phase Equilibria for the Quaternary System $Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K. *J. Chem. Eng. Data* **2010**, *55*, 1623–1627.

(13) Xu, G. L. The Determination and Application of the Temperature Correction Coefficient for the Density of Vinyl Acetate. *Fujian Anal. Test.* **1999**, *8*, 1104–1108.

(14) Institute of Qinghai Salt-Lake of Chinese Academy of Sciences (in Chinese). *Analytical Methods of Brines and Salts*, 2nd ed.; Chinese Science Press: Beijing, 1984; pp 75−80.

(15) Wieser, M. E.; Berglund, M. Atomic weights of the elements 2007. (IUPAC Technical Report). *Pure Appl. Chem.* **2009**, *81*, 2131–2156.