Metastable Phase Equilibrium in the Aqueous Quaternary System ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K

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Experimental studies on the metastable solubilities and the physicochemical properties including density, viscosity, refractive index, conductivity, and pH of the aqueous quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K were determined with the method of isothermal evaporation. According to the experimental results, the dry-salt phase diagram, the water diagram, and the physicochemical properties via composition diagrams were plotted. It was found that there is one three-salt cosaturation point of $KCl + K_2SO_4 + K_2B_4O_7 \cdot 4H_2O$, three univariant curves, and three metastable crystallization fields corresponding to potassium chloride, potassium sulfate, and potassium borate tetrahydrate formed in the metastable quaternary system. Neither solid solution nor double salts were found.

Introduction

Salt lakes are widely distributed in the west of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau. Salt Lakes of the Caidamu Basin consist of a series of lakes including Caerhan Lake which produces two million tons of potassium fertilizer per year at present. Dongtai Lake, Xitai Lake, and Yiliping Lake are a subtype of magnesium sulfate brines famous for their abundance of lithium, potassium, magnesium, and boron resources and also for the highest concentration ratio of magnesium to lithium in brines around the world from 500 to 800. The natural salt lake brines are mostly similar with the seawater system. The climate conditions in the region of the Caidamu Basin are generally windy, arid, little rainfall, and great evaporating capacity.[1] To economically exploit the brine and mineral resources, it is important to adequately adopt the local natural resources such as the energy of the wind and sun, i.e., solar pond techniques. Therefore, metastable phase equilibrium research is essential to predict the crystallized path of evaporation of the salt lake brine.

Although a number of papers describing the metastable equilibrium of the seawater system ($Na + K + Mg + Cl + SO_4 + H_2O$) from (293.15 to 373.15) K have been reported,[2–5] the quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K is not reported in the literature to describe the metastable behavior. This is needed to separate and purify the potassium-containing mixture salts. In this paper, the metastable solubilities and the physicochemical properties of the quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K are presented.

Experimental Section

Apparatus and Reagents. The isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermal insulation material box (70 cm long, 65 cm wide, 60 cm high) with an apparatus to control the temperature was installed. The temperature-controlling apparatus is made up of an electric relay, an electrical contact thermograph, and heating lamps. When the solution temperature in the container was under (308.15 ± 0.3) K, the apparatus for controlling the temperature formed a circuit and the heating lamp began to heat. Conversely, the circuit was broken, and the heating lamp stopped working. Therefore, the temperature in the box could always be kept at (308.15 ± 0.3) K. An electric fan installed on the box always worked to accelerate the evaporation quantity of water from solutions. The solid phase minerals were identified using an XP-300 Digital Polarizing Microscopy (Shanghai Caikon Optical Instrument Co., Ltd., China) and an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands).

The chemicals used were of analytical grade and obtained from either the Tianjin Kermel Chemical Reagent Ltd. or the Sinopharm Chemical Reagent Co. Ltd.: potassium chloride (KCl, 99.5 mass %), potassium sulfate (K_2SO_4, 99.0 mass %), and potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$, 99.5 mass %) were recrystallized before use. Doubly deionized water (DDW) with conductivity less than $1 \cdot 10^{-4}\ S \cdot m^{-1}$ was used to prepare the series of artificial synthesized brines and for chemical analysis.

Experimental Method. The isothermal evaporation method was used in this study. According to phase equilibrium composition, the appropriate quantity of salts and DDW were mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high), and then the containers were put into the box for the isothermal evaporation at (308.15 ± 0.3) K. The experimental conditions were: air flowing velocity of (3.5 to 4.0) $m \cdot s^{-1}$, relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) $mm \cdot d^{-1}$. The conditions are reflective of those of the Caidamu Basin. For metastable evaporation reasons, no stirring was applied to the solutions. The crystal behavior of the solid phase was observed periodically. When enough new solid phase appeared, the wet residue mixtures were taken from the solution. Then solids were approximately evaluated with combined chemical analysis, observation using an oil-immersion

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10.1021/je700472p CCC: $40.75

Table 1. Metastable Equilibrium Solubility of the Quaternary System ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K

	composition of liquid phase w_b (mass %)				composition of liquid phase (g/100 g of dry salt)		
no.	KCl	K_2SO_4	$K_2B_4O_7$	H_2O	KCl	H_2O	equilibrium solid phase
1,E_1	27.57	1.18	0.00	71.25	95.90	247.83	$KCl + K_2SO_4$
2	27.19	1.20	0.71	70.90	93.44	243.64	$KCl + K_2SO_4$
3	27.11	1.16	0.83	70.90	93.16	243.64	$KCl + K_2SO_4$
4	26.84	1.14	1.10	70.92	92.30	243.88	$KCl + K_2SO_4$
5	26.40	1.16	2.20	70.24	88.71	236.02	$KCl + K_2SO_4$
6	25.85	1.12	3.20	69.83	85.68	231.46	$KCl + K_2SO_4$
7	25.45	1.12	4.03	69.40	83.17	226.80	$KCl + K_2SO_4$
8	25.45	1.10	4.45	69.00	82.10	222.01	$KCl + K_2SO_4$
9,E_2	25.52	0.00	5.50	68.98	82.27	222.37	KCl + KB[a]
10	25.46	0.50	5.15	68.89	81.84	221.44	KCl + KB
11	25.38	0.70	5.10	68.82	81.40	220.72	KCl + KB
12	25.32	0.81	5.09	68.78	81.10	220.31	KCl + KB
13	25.14	1.10	4.92	68.84	80.68	220.92	KCl + KB
14,E_3	0.00	6.21	20.18	73.61	0.00	278.93	K_2SO_4 + KB
15	1.57	5.65	19.01	73.77	5.99	281.24	K_2SO_4 + KB
16	2.10	5.57	18.77	73.56	7.94	278.21	K_2SO_4 + KB
17	2.46	5.60	18.48	73.46	9.27	276.79	K_2SO_4 + KB
18	4.02	5.04	17.29	73.65	15.26	279.51	K_2SO_4 + KB
19	5.61	4.49	16.14	73.76	21.38	281.10	K_2SO_4 + KB
20	6.68	4.19	15.35	73.78	25.48	281.39	K_2SO_4 + KB
21	9.41	3.66	13.63	73.30	35.24	274.53	K_2SO_4 + KB
22	11.99	3.01	11.84	73.16	44.67	272.58	K_2SO_4 + KB
23	15.34	2.54	9.53	72.59	55.96	264.83	K_2SO_4 + KB
24	16.71	2.41	8.40	72.48	60.72	263.37	K_2SO_4 + KB
25	20.07	2.03	7.21	70.69	68.47	241.18	K_2SO_4 + KB
26	23.23	1.46	5.50	69.81	76.95	231.24	K_2SO_4 + KB
27,E	25.20	1.12	4.84	68.84	80.87	220.92	K_2SO_4 + KB

[a] KB: $K_2B_4O_7 \cdot 4H_2O$.

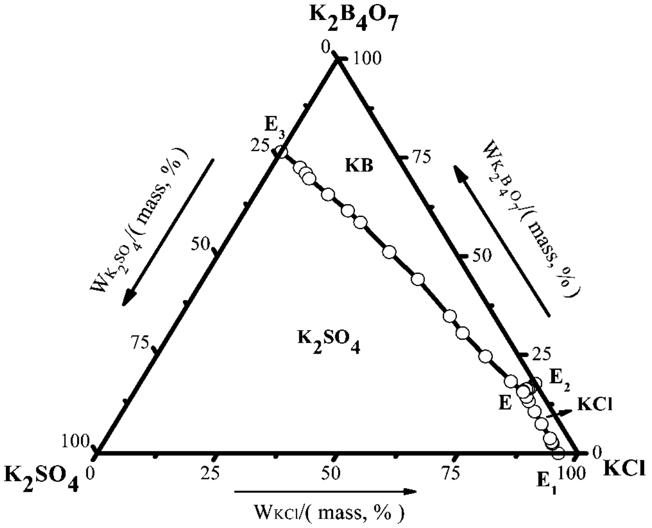


Figure 1. Metastable equilibrium phase diagram of the quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K. ○, experimental point; −, experimental isotherm curve; KB, $K_2B_4O_7 \cdot 4H_2O$.

Table 2. Physicochemical Property Data of the Quaternary System ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K

			conductivity	viscosity	density
no.[a]	pH	n_D	$\kappa/(S \cdot m^{-1})$	$10^{-3}\eta/(pa \cdot s)$	$10^{-3}\rho/(kg \cdot m^{-3})$
1,E_1	6.74	1.3702	ND[b]	0.7148	1.1925
2	8.20	1.3734	ND	0.7208	1.1948
3	9.10	1.3739	ND	0.7238	1.1954
4	9.12	1.3741	ND	0.7383	1.1985
5	9.17	1.3748	ND	0.7519	1.2041
6	9.21	1.3760	ND	0.7878	1.2103
7	9.24	1.3765	ND	0.7958	1.2168
8	9.30	1.3775	ND	0.8138	1.2187
9,E_2	9.58	1.3785	ND	0.8499	1.2272
10	9.57	1.3783	ND	0.8326	1.2251
11	9.50	1.3774	ND	0.8144	1.2193
12	9.49	1.3769	ND	0.8038	1.2168
13	9.45	1.3771	ND	0.8280	1.2185
14,E_3	10.14	1.3730	1.227	1.3908	1.2402
15	10.10	1.3740	1.304	1.4071	1.2387
16	10.04	1.3742	1.318	1.3672	1.2382
17	9.99	1.3745	1.382	1.3055	1.2378
18	9.95	1.3744	1.501	1.2219	1.2362
19	9.92	1.3741	1.703	1.1879	1.2354
20	9.91	1.3745	1.766	1.1370	1.2348
21	9.77	1.3747	1.845	1.1247	1.2341
22	9.80	1.3751	1.980	1.0889	1.2335
23	9.76	1.3756	ND	0.9510	1.2285
24	9.74	1.3759	ND	0.9339	1.2264
25	9.51	1.3768	ND	0.9163	1.2232
26	9.46	1.3773	ND	0.8740	1.2216
27,E	9.40	1.3781	ND	0.8301	1.2206

[a] The no. column corresponds to the no. column in Table 1. [b] ND means not detected.

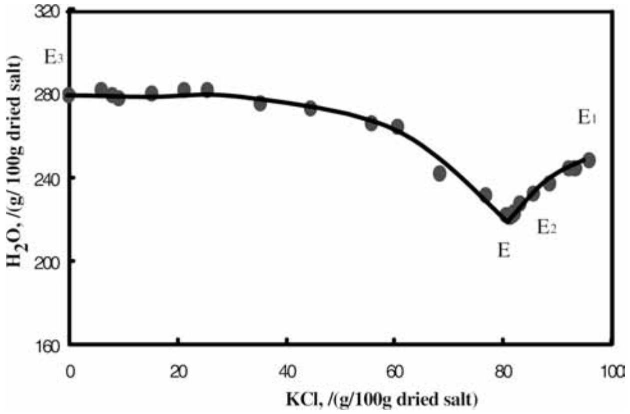
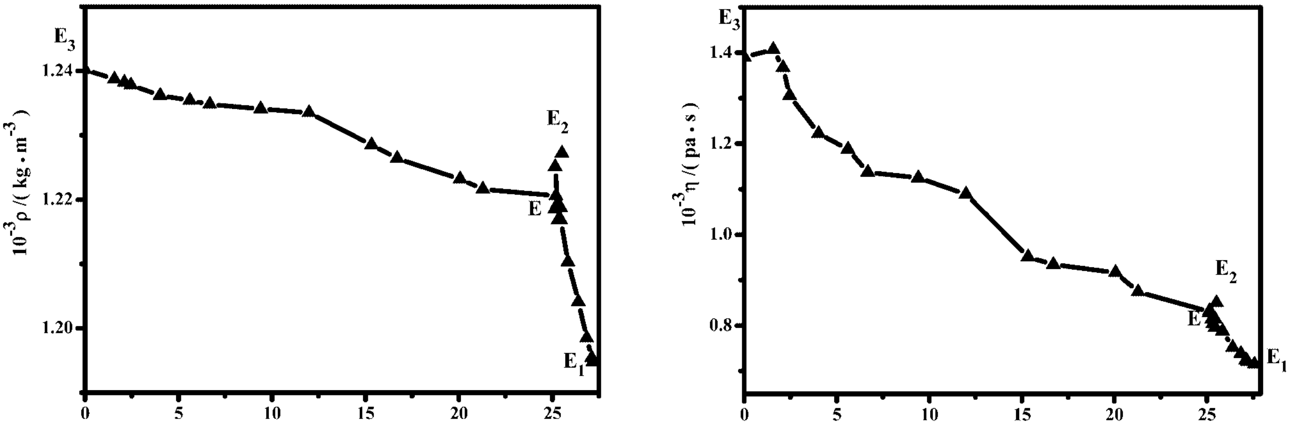


Figure 2. Water-phase diagram of the quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K.

of XP-300D Digital Polarizing Microscopy, and further identification with X-ray diffraction. Meanwhile, a 5.0 mL sample of the clarified solution was taken from the liquid phase of each polyethylene container through a filter pipet and then diluted to a 250.0 mL final volume in a volumetric flask filled with DDW for quantitative analysis of the composition of the liquid phase. Some of the filtrate was used to measure the relative physicochemical properties. The remainder of the solution continued to be evaporated to reach a new metastable equilibrium point.

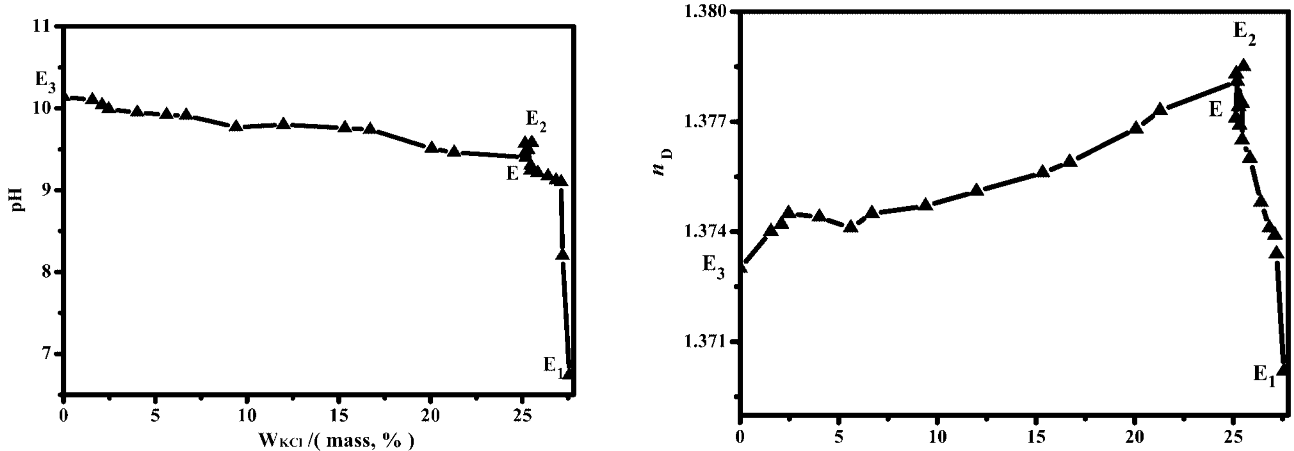
Analytical Method. The composition of K^+ and SO_4^{2-} in the liquids and their corresponding wet solid phases were analyzed by the gravimetric methods of sodium tetraphenyl borate and barium chloride, respectively, both with precisions within ± 0.05 mass %. The Cl^- ion concentration was determined by titration with a mercury nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue with a precision of $\leq \pm$ 0.3 mass %.[6]

A PHS-3C precision pH meter supplied by the Shanghai Precision & Scientific Instrument Co., Ltd. was used to measure the pH of the equilibrium aqueous solutions (precision of ± 0.01). The pH meter was calibrated with standard buffer solutions, either potassium dihydrogen phosphate and sodium dihydrogen phosphate (pH 6.84) or borax (pH 9.18); the densities (ρ) were measured with a density bottle method with a precision of ± 0.2 mg. The viscosities (η) were determined using an Ubbelohde capillary viscometer, which was placed in a thermostat at (308.15 ± 0.1) K. No fewer than five flow times for each equilibrium liquid phase were



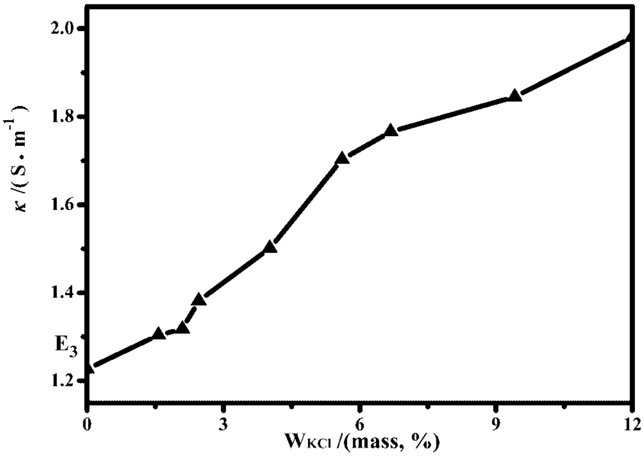
(a) density value-composition

(b) viscosity-composition



(c) pH-composition

(d) refractive index-composition



(e) conductivity-composition

Figure 3. Property−composition diagram for the metastable quaternary system: (a) density vs composition; (b) viscosity vs composition; (c) pH vs composition; (d) refractive index vs composition; (e) conductivity vs composition. ▲, experimental data point; —, experimental relationship diagram.

measured with a precision of 0.1 s; the results calculated were the average. The uncertainty of the flow time measurements was ± 0.2 s. An Abbe refractometer (model WZS-1) was used for measuring the refractive index (n_D) with an accuracy of ± 0.0001. Conductivities (κ) were measured with an Orion 145A+ conductivity meter (Thermo Electron Corporation, America) with a precision of ± 0.001 S•m^{-1}. Measurements for the physicochemical properties of density, refractive index, and pH were conducted in a thermostat that electronically controlled the set temperature at (308.15 ± 0.1) K.

Results and Discussion

The experimental data on the metastable solubilites and the relevant physicochemical properties of the quaternary system

($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K are presented in Tables 1 and 2, respectively. The ion concentration values in the metastable equilibrium solution are expressed in mass fraction. According to the experimental data in Table 1, the metastable equilibrium phase diagram of the system at 308.15 K is shown in Figure 1.

The metastable phase diagram of the system in Figure 1 consists of three crystallization zones corresponding to potassium chloride (KCl), potassium sulfate (K_2SO_4), and potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$). Point E is an invariant point, which is saturated with the three salts $K_2B_4O_7 \cdot 4H_2O + K_2SO_4 + KCl$, and the mass fraction composition (mass %) of the corresponding liquid phase is KCl 25.20, K_2SO_4 1.12, $K_2B_4O_7$ 4.84. There are three isotherm evaporation curves corresponding to curves E_1E, E_2E, and E_3E, indicating the cosaturation of two salts. The crystallization area of potassium sulfate is the largest, and the crystallized zone of potassium chloride is the smallest. These results indicate that potassium sulfate is easy to saturate and crystallize from solution and that potassium chloride has a high solubility. Neither a solid solution nor double salts formed in the system.

Figure 2 is the relevant water-phase diagram of the system at 308.15 K. Figure 2 shows that the mass values of water (g/100 g of dry salt) change with the mass values of potassium chloride (g/100 g of dry salt) and reach the smallest value at invariant point E.

On the basis of the experimental data in Table 2, relationships between the solution physicochemical properties (density, pH, conductivity, refractive index, and viscosity) and mass fraction of potassium chloride are found, as shown in Figure 3. It can be seen that the physicochemical properties change regularly with the mass fraction changes of potassium chloride.

Conclusions

Metastable equilibria of the quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K were studied by an isothermal evaporation method. Solubilities and physicochemical properties were determined experimentally. According to the experimental data, the metastable equilibrium phase diagram and the water diagram of the system were determined. The results show that there is neither a solid solution nor double salts formed in this quaternary system.

Acknowledgment

The authors hope to thank Professor Z.H. Gao and Ms. P. Wang in Qinghai Institute of Salt Lakes for their kind help. Thanks also go to the Editor and the anonymous reviewers for their critical comments on the manuscript.

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Received for review August 20, 2007. Accepted November 24, 2007. Financial support from the National Natural Science Foundation of China (Grant 40773045), the "A Hundred Talents Program" of Chinese Academy of Sciences (Grant 0560051057), and the Specialized Research Fund for the Doctoral Program of Chinese Higher Education (Grant 20060616004) is greatly acknowledged.

JE700472P