Metastable Equilibrium of the Salt Lake Brine System $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K

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The metastable phase equilibrium of the quinary system $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ was studied at 273.15 K using an isothermal evaporation method. The solubilities and densities of the equilibrated solution were measured. On the basis of the experimental data, the stereo metastable phase diagram and the projected phase diagram saturated with salt $Na_2B_4O_7$ of the quinary system at 273.15 K were constructed. The projected phase diagram of this system consists of six invariant points, 12 univariant curves, and seven crystallization fields corresponding to the single salts $Na_2SO_4\cdot10H_2O$, K_2SO_4, $K_2B_4O_7\cdot4H_2O$, $Na_2CO_3\cdot10H_2O$, and $K_2CO_3\cdot3/2H_2O$ and double salts $2Na_2SO_4\cdot Na_2CO_3$ and $K_2CO_3\cdot Na_2CO_3\cdot12H_2O$. The double salts $2Na_2SO_4\cdot Na_2CO_3$ and $K_2CO_3\cdot Na_2CO_3\cdot12H_2O$ are formed in the quinary system and also exist in the other quinary or quaternary systems containing the $Na_2CO_3-Na_2SO_4-H_2O$ and $K_2CO_3-Na_2CO_3-H_2O$ ternary subsystems at 273.15 K. The forms of sodium and potassium borate are $Na_2B_4O_5(OH)_4\cdot8H_2O$ and $K_2B_4O_5(OH)_4\cdot2H_2O$, respectively. In contrast to the phase diagrams of its subsystems, the crystallization area of $K_2CO_3\cdot3/2H_2O$ increases clearly in the quinary system.

Introduction

Salt-water system phase diagrams remain a topic of current interest, largely due to the potential for the comprehensive utilization of the saline brines. Salt lakes are widely distributed in the area of the Qinghai-Xizang (Tibet) Plateau and a series of salt lakes in Tibet that are famous for their abundance of sodium, potassium, and lithium, as well as chloride, borate, sulfate, and carbonate, especially the Zabuye Salt Lake. The main components of the brines belong to the complex system ($Li^+ + Na^+ + K^+ + Cl^- + CO_3^{2-} + SO_4^{2-}$ + borate + H_2O).[1] Because of the rainless and windy climate in the saline lake country, natural evaporating technologies are widely used to extract salts from the saline brines. Earlier research has proved that, in the process of evaporation, the equilibrium relationships among the salts in the brines are always metastable.[2,3] Thus, investigations on metastable equilibria are more important than the stable phase equilibria for salts exploited from the saline brines.

A series of work has been done on metastable phase equilibria of saline brines; however, most effort has focused on temperatures above 288 K, including our earlier work aimed at the Zabuye Salt Lake.[4,5] The metastable phase equilibrium at $T =$ 273.15 K is scarcely reported in the literature. The Zabuye Salt Lake region is arid, with high daily evaporation, and its average temperature is about 273 K.[1] Thus, studies on the phase equilibria at 273 K will be more close to reality and will be of great use in exploiting the brine. Compared to phase studies at higher temperatures, studies at 273.15 K are more difficult because of the lower evaporating velocity, stronger viscosity of solution, and longer time to reach the equilibrium.

The experimental phase diagram studies at $T < 273$ K are limited by the freezing point of water at atmospheric pressure. Some researchers[6] have tried to calculate the phase diagram for saline brine systems at lower temperatures by using Pitzer's equation, but it was not possible due to a lack of low-temperature Pitzer single salt parameters and mixture ion interaction parameters. Pitzer and his coworkers[7,8] have established the temperature-dependent equations for the virial coefficients and ion interaction parameters for the simple ternary system NaCl + Na_2SO_4 ($MgCl_2$) + H_2O. These equations work well at temperatures between (298 and 373) K with concentrations up to the saturated solution for NaCl + Na_2SO_4 and NaCl + $MgCl_2$. However, the temperature-dependent equations are not used at lower temperatures, and the Pitzer parameters obtained from the solubility were not set up in the absence of any solubility literature data at temperatures lower than 273.15 K.

The quinary system $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ is one of the basic and characteristic subsystems of the composition of the Zabuye Lake saline brine. We have undertaken studies on this quinary system at 273.15 K, with the hope that the metastable phase diagrams of this system at lower temperature can be obtained and also with the hope that the determined solubility data will help in calculating the lower temperature Pitzer parameters of carbonate and borate.

Experimental Section

Reagents and Instruments. The chemicals used were of analytical grade purity and were obtained from the Chengdu Chemical Reagent Plant. They are potassium carbonate (K_2CO_3, 99.0 %), potassium sulfate (K_2SO_4, 99.0 %), potassium borate ($K_2B_4O_7$, 99.5 %), sodium carbonate (Na_2CO_3, 99.0 %), sodium sulfate (Na_2SO_4, 99.0 %), and sodium borate ($Na_2B_4O_7$, 99.5 %). Before being used to make the experimental solution, the potassium and sodium carbonate were pretreated to remove the

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small amount of bicarbonate in them. The commercial potassium carbonate or sodium carbonate was put into a beaker, heated to 470 K, kept the temperature for up to 20 min to remove the bicarbonate, and then cooled to room temperature for use.

Doubly deionized water (electrical conductivity less than $1 \cdot 10^{-4}$ S·m^{-1}, pH = 6.6) was used 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 experiment. The temperature controlling precision is ± 0.1 K.

A Siemens D500 X-ray diffraction analyzer with Ni-filtered Cu Kα radiation was used for the analysis of solid phases. The operating conditions are 35 kV and 25 mA.

An atomic absorption spectrophotometer (type WYD-YII) was employed for the determination of the sodium ion concentration in solution.

Experimental Methods. The isothermal evaporation method was used for the metastable phase equilibria experiments.[9] The experiments were done at (273.15 ± 0.1) K, and a thermostatic evaporator was used for evaporation. Because of the low evaporation temperature, the time for reaching equilibrium was comparatively long. The measuring point depended on the changes of the solid phase in the process of evaporation. When enough new solid phase appeared in the complex, the liquid and solid phases were separated by a rapid filtration method.[4] The composition of solution was determined by an analytical method. The wet crystals in the solid phase were separated from each other according to crystal shape as much as possible, dried at 273.15 K, pestled into a powder, and then analyzed by X-ray diffraction.

The densities of solution were also determined in this study and used for the mass fraction calculation of components. The densities were determined by the specific gravity bottle method with correction for the floating force of air (precision: 0.0001 g·cm^{-3}).[9]

Analytical Methods. The composition of potassium ion was measured by titration with a sodium tetraphenylborate-hexadecyl trimethyl ammonium bromide aqueous solution.[10] The average relative deviation of the determination was less than 0.5 %.

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, with a precision of less than 0.5 %.[10]

The borate ion concentration was determined by a neutralization titration in the presence of propanetriol, with a precision of less than 0.3 %.[10]

The carbonate ion concentration was determined by acid−base neutralization titration, with a precision of less than 0.5 %.[10]

The sodium ion concentration was determined by atomic absorption spectrophotometry, with a precision of less than 0.06 %.[10]

Results and Discussion

The solubilities and densities of the equilibrated solution in the quinary system $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K are tabulated in Table 1. In Table 1, $w(B)$ is the mass fraction of B, and $J(B)$ is the Jänecke index values of B, with $J(K_2^{2+}) + J(SO_4^{2-}) + J(CO_3^{2-}) = 100$. On the basis of the experimental data, the stereo metastable phase diagram and the projected phase diagram saturated with salt $Na_2B_4O_7$ were constructed, as shown in Figures 1 and 2, respectively.

In Figure 1, the six apexes of the regular three-prism denote six pure salts that are Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3, $Na_2B_4O_7$, and $K_2B_4O_7$, respectively. The nine touchlines express the nine ternary subsystems, and points 1 to 11 correspond to the invariant points for these ternary subsystems. Among them, the ternary system $K_2CO_3 + Na_2CO_3 + H_2O$ and $Na_2SO_4 + Na_2CO_3 + H_2O$ are of a complex type, where the double salts $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ and $2Na_2SO_4 \cdot Na_2CO_3$ are formed, respectively.

The upper regular triangle denotes the simple quaternary system $K_2CO_3 + K_2SO_4 + K_2B_4O_7 + H_2O$, with the invariant point N. The down regular triangle denotes the quaternary system $Na_2CO_3 + Na_2SO_4 + Na_2B_4O_7 + H_2O$, with the invariant points E_1 and E_2. The double salt $2Na_2SO_4 \cdot Na_2CO_3$ is found in this subsystem. The three squares denote the three reciprocal quaternary subsystems $Na_2CO_3 + K_2CO_3 + Na_2SO_4 + K_2SO_4 + H_2O$, $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$, and $Na_2CO_3 + K_2CO_3 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$, respectively. The double salts $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ and $2Na_2SO_4 \cdot Na_2CO_3$ are simultaneously found in the quaternary system $Na_2CO_3 + K_2CO_3 + Na_2SO_4 + K_2SO_4 + H_2O$.

Figure 2, the projected diagram saturated with salt $Na_2B_4O_7$, clearly shows that the metastable phase diagram of the quinary system $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K consists of seven crystallization fields, 12 univariant curves, and six invariant points. The seven crystallization fields correspond to sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), potassium sulfate (K_2SO_4), potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$), sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), potassium carbonate hydrate ($K_2CO_3 \cdot 3/2H_2O$), sodium carbonate−sulfate double salt ($2Na_2SO_4 \cdot Na_2CO_3$), and a potassium−sodium carbonate double salt ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$).

Borates can form different polyanions in aqueous solution. The various species of boron in aqueous solution depend on the pH value, the total concentration of boron and salts, and the kinds of coexistent salts.[11] $B_4O_7^{2-}$ is just a traditional stoichiometric expression for various boric species in solution. In this metastable system at the studied temperature, the equilibrium solid phase of both sodium borate and potassium borate exists as a tetraborate, with the crystallization form $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ and $K_2B_4O_5(OH)_4 \cdot 2H_2O$, respectively.

The crystallization form of sodium carbonate existing in this system is $Na_2CO_3 \cdot 10H_2O$, and neither $Na_2CO_3 \cdot 7H_2O$ nor $Na_2CO_3 \cdot H_2O$ is found.

There are two kinds of double salts formed in this quinary system; those are a sodium carbonate−sulfate double salt ($2Na_2SO_4 \cdot Na_2CO_3$) and a potassium−sodium carbonate double salt ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$). It is worthy to point out that the potassium−sodium sulfate double salt ($3K_2SO_4 \cdot Na_2SO_4$) is formed in the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 288.15 K[4] but exists in neither this system nor the quinary system $Li^+ + Na^+ + K^+ + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K.[12] This result shows that the temperature affects the interaction of sodium and potassium sulfate.

The six invariant points labeled as K_1, K_2, K_3, K_4, K_5, and K_6 are cosaturated with four salts. The saturated salts and the mass fraction composition for the invariant points in this system are listed below.

K_1, saturated with salts $Na_2B_4O_7 \cdot 10H_2O + Na_2SO_4 \cdot 10H_2O + K_2SO_4 + K_2CO_3 \cdot 3/2H_2O$, with $w(Na^+)$ 2.73 %, $w(K^+)$ 0.72 %, $w(SO_4^{2-})$ 4.94 %, $w(CO_3^{2-})$ 1.00 %, $w(B_4O_7^{2-})$ 0.06 %.

K_2, saturated with salts $Na_2B_4O_7 \cdot 10H_2O + K_2B_4O_7 \cdot 4H_2O + K_2SO_4 + K_2CO_3 \cdot 3/2H_2O$, with $w(Na^+)$ 10.73 %, $w(K^+)$ 4.70 %, $w(SO_4^{2-})$ 20.36 %, $w(CO_3^{2-})$ 2.96 %, $w(B_4O_7^{2-})$ 4.97 %.

Table 1. Solubilities and Densities of Solutions in the Quinary System $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K

	density	composition of equilibrium solution, $w(B)\cdot10^{-2}$					Jänecke index of dry salt, mol/100 mol dry salt $J(K_2^{2+}) + J(CO_3^{2+}) + J(SO_4^{2+}) = 100$						equilibrium
no.	$g\cdot cm^{-3}$	$w(Na^+)$	$w(K^+)$	$w(SO_4^{2-})$	$w(CO_3^{2-})$	$w(B_4O_7^{2-})$	$w(H_2O)$	$J(Na_2^{2+})$	$J(K_2^{2+})$	$J(SO_4^{2-})$	$J(CO_3^{2-})$	$J(H_2O)$	solid phase[a]
1, K_2	1.1006	10.73	4.70	20.36	2.96	4.97	56.28	72.51	18.73	65.93	15.34	972.0	nb+kb+ks+kc
2	1.1104	10.90	4.89	20.67	3.14	4.94	55.46	71.73	18.98	65.18	15.84	932.7	nb+kb+ks
3	1.1052	10.88	5.53	20.7	3.38	5.46	54.05	68.99	20.68	62.89	16.43	875.8	nb+kb+ks
4	1.1326	10.95	5.43	20.55	3.5	5.49	54.08	69.60	20.35	62.59	17.06	878.5	nb+kb+ks
5	1.1348	10.47	5.86	19.94	3.57	5.50	54.66	66.49	21.95	60.67	17.38	887.0	nb+kb+ks
6	1.1610	10.71	6.78	20.46	4.22	5.58	52.25	62.86	23.47	57.54	18.99	783.7	nb+kb+ks
7	1.1555	9.54	8.7	20.08	4.33	5.80	51.55	52.79	28.39	53.24	18.37	729.0	nb+kb+ks
8	1.1477	10.36	6.72	20.2	4.48	4.04	54.20	60.67	23.21	56.68	20.11	811.1	nb+kb+ks
9	1.1477	4.43	8.17	12.21	2.63	4.69	67.87	34.92	37.99	46.12	15.89	1367	nb+kb+ks
10	1.1438	2.31	7.95	8.29	1.72	5.77	73.96	23.15	46.99	39.80	13.21	1894	nb+kb+ks
11	1.1326	0.46	7.08	5.23	0.52	5.83	80.88	6.50	58.95	35.42	5.63	2919	nb+kb+ks
12, L_1	1.1286	0.17	5.33	3.26	0.00	5.92	85.32	3.61	66.80	33.20	0.00	4634	nb+kb+ks
13, L_2	1.1329	2.13	3.91	8.79	0.00	0.79	84.38	32.68	35.38	64.62	0.00	3308	nb+ks+ns
14	1.1013	6.32	3.85	16.87	0.35	0.81	71.80	59.50	21.38	76.12	2.50	1727	nb+ks+ns
15	1.0992	8.10	3.67	21.36	0.62	0.89	65.36	62.91	16.81	79.51	3.68	1297	nb+ks+ns
16	1.0979	11.42	3.59	26.2	0.92	0.91	56.96	74.27	13.77	81.64	4.59	946.7	nb+ks+ns
17	1.0925	10.55	3.13	23.83	0.92	0.94	60.63	75.52	13.21	81.74	5.05	1109	nb+ks+ns
18	1.0949	10.83	3.03	24.28	0.93	0.92	60.01	76.62	12.64	82.31	5.04	1085	nb+ks+ns
19	1.0815	10.63	2.79	23.53	0.96	0.88	61.21	77.84	12.05	82.56	5.39	1145	nb+ks+ns
20	1.0847	10.50	2.92	23.38	0.97	0.93	61.30	76.82	12.60	81.96	5.44	1146	nb+ks+ns
21	1.1116	12.21	2.63	26.4	1.06	0.97	56.73	81.33	10.33	84.26	5.41	965.6	nb+ks+ns
22	1.1298	10.82	3.90	24.84	1.20	1.00	58.24	71.55	15.21	78.71	6.08	984.2	nb+ks+ns
23	1.1440	11.27	4.05	25.61	1.47	0.87	56.73	71.39	15.13	77.73	7.14	918.3	nb+ks+ns
24	1.1395	11.01	3.90	24.75	1.55	0.86	57.93	71.74	14.99	77.27	7.74	964.6	nb+ks+ns
25	1.1654	10.63	4.89	24.97	1.67	0.90	56.94	65.91	17.88	74.18	7.94	902.2	nb+ks+ns
26	1.1138	5.85	2.38	12.58	2.11	0.73	76.35	64.65	16.62	71.37	12.01	2156	nb+ks+ns
27	1.1025	4.15	1.42	8.19	1.18	0.54	84.52	73.24	14.78	69.32	15.90	38128	nb+ks+ns
28	1.0730	2.31	0.59	4.1	0.88	0.08	92.04	77.33	11.65	65.77	22.59	7874	nb+ks+ns
29	1.0742	2.32	0.58	4.05	0.91	0.07	92.07	77.84	11.48	65.11	23.41	7895	nb+kc+ks
30	1.0722	2.44	0.61	4.31	0.93	0.06	91.65	77.76	11.46	65.81	22.72	7464	nb+kc+ks
31, K_1	1.0691	2.73	0.72	4.94	1.00	0.06	90.55	76.72	11.93	66.52	21.55	6503	nb+ns+kc+ks
32	1.1033	11.63	1.78	19.08	3.53	1.13	62.85	90.16	8.14	70.88	20.98	1245	nb+ns+kc
33	1.0961	4.87	1.15	8.06	1.80	1.05	83.07	82.26	11.46	65.23	23.31	3586	nb+ns+kc
34	1.0825	3.43	0.96	6.98	1.63	0.79	86.21	66.47	10.97	64.78	24.25	4269	nb+ns+kc
35	1.0714	2.46	0.72	4.24	1.09	0.06	91.43	74.73	12.90	61.72	25.39	7098	nb+ns+kc
36	1.0753	3.09	0.73	5.06	1.40	0.06	89.66	78.66	10.95	61.70	27.35	5833	nb+ns+kc
37	1.1038	13.78	4.90	23.41	5.93	3.06	48.92	73.87	15.49	60.14	24.37	670.2	nb+kb+kc
38	1.1077	13.10	4.96	21.58	5.73	2.73	51.90	74.19	16.56	58.56	24.88	751.1	nb+kb+kc
39	1.1129	13.34	5.25	25.28	4.66	2.52	48.95	71.02	16.48	64.49	19.03	666.0	nb+kb+kc
40	1.1237	13.8	5.87	27.27	4.61	2.21	46.24	68.78	17.25	65.12	17.63	589.0	nb+kb+kc
41	1.1102	12.14	1.87	18.32	5.33	1.29	61.05	86.92	7.90	62.85	29.26	1117	nb+kb+kc
42	1.1181	12.37	1.99	18.48	5.60	1.34	60.22	86.37	8.19	61.83	29.98	1074	nb+kb+kc
43, K_4	1.1134	3.87	0.99	0.45	5.48	0.13	89.08	77.39	11.68	4.31	84.01	4552	nb+kc+nc+nsc
44	1.1262	1.93	5.51	0.57	6.04	0.93	85.02	23.67	39.88	3.35	56.77	2665	nb+nc+knc
45	1.1449	3.58	6.90	0.44	9.64	1.12	78.32	30.68	34.87	1.81	63.33	1715	nb+nc+knc
46	1.1459	4.20	5.49	0.43	9.01	1.08	79.79	40.57	31.28	1.99	66.73	1970	nb+nc+knc
47	1.1687	8.10	3.08	0.67	12.09	1.11	74.95	71.01	15.92	2.81	81.26	1679	nb+nc+knc
48	1.1857	11.75	2.36	0.59	16.34	1.11	67.85	82.74	9.80	1.99	88.21	1221	nb+nc+knc
49, F_1	1.2561	16.15	2.19	0.00	14.88	0.95	65.83	127.17	10.17	0.00	89.83	1325	nb+nc+nkc
50, K_6	1.1201	12.42	2.13	18.81	5.63	1.15	59.86	85.15	8.61	61.79	29.59	1049	nb+ns+nsc+kc
51	1.0532	13.85	2.39	20.3	6.67	1.40	55.39	85.23	8.67	59.86	31.47	871.1	nb+ns+nsc
52	1.137	13.53	2.38	19.38	6.87	1.24	56.60	84.79	8.80	58.20	33.01	906.5	nb+ns+nsc
53	1.1591	13.16	2.67	18.48	7.19	1.23	57.27	82.55	9.88	55.55	34.58	918.1	nb+ns+nsc
54	1.1678	13.92	2.87	19.05	7.95	1.28	54.93	82.29	10.01	53.96	36.03	829.9	nb+ns+nsc
55	1.1542	12.05	1.91	13.21	6.65	5.89	60.29	95.98	8.97	50.41	40.62	1227	nb+ns+nsc
56	1.1305	11.32	1.24	9.92	6.22	8.52	62.78	110.40	7.13	46.37	46.50	1565	nb+ns+nsc
57	1.1183	11.54	0.21	8.21	6.58	9.07	64.39	126.78	1.36	43.21	55.43	1808	nb+ns+nsc
58	1.1034	3.78	0.88	0.50	5.25	0.12	89.47	79.02	10.85	5.01	84.14	4780	nb+nc+nsc
59	1.0927	4.26	0.47	0.53	4.60	2.53	87.61	104.98	6.82	6.35	86.83	5518	nb+nc+nsc
60	1.0882	7.35	0.35	0.79	6.69	6.90	77.92	128.63	3.61	6.67	89.72	3485	nb+nc+nsc
61	1.1286	13.07	2.27	19.08	6.40	1.23	57.95	84.94	8.70	59.41	31.89	962.4	nb+kc+nsc
62	1.2153	13	3.68	17.98	8.00	1.40	55.94	76.84	12.83	50.92	36.25	845.0	nb+kc+nsc
63	1.1288	7.82	1.97	10.44	4.77	1.09	73.91	79.62	11.83	50.94	37.24	1923	nb+kc+nsc
64	1.1268	4.25	1.52	4.08	3.83	0.85	85.47	73.43	14.31	38.80	46.89	3774	nb+kc+nsc
65	1.1217	4.90	1.39	4.11	4.60	0.76	84.24	77.58	12.97	31.20	55.83	3409	nb+kc+nsc
66	1.1192	4.79	1.21	2.95	5.09	0.76	85.20	79.44	11.83	23.42	64.75	3611	nb+kc+nsc
67	1.1165	4.71	1.04	1.29	6.00	0.37	86.59	80.77	10.51	10.64	78.85	3795	nb+kc+nsc
68	1.1210	8.65	9.39	16.81	7.46	1.33	56.36	44.79	28.68	41.71	29.62	745.8	nb+kc+knc
69	1.1163	4.59	8.51	8.33	6.91	1.07	70.59	32.08	35.08	27.89	37.03	1261	nb+kc+knc
70	1.0927	2.56	7.70	4.03	6.36	1.00	78.35	22.56	40.04	17.01	42.95	1764	nb+kc+knc
71	1.0467	1.62	0.67	0.54	1.95	0.87	94.35	75.39	18.39	12.04	69.57	11221	nb+kc+nc
72	1.0549	1.79	0.72	0.52	2.22	0.91	93.84	75.34	17.87	10.49	71.64	10094	nb+kc+nc
73	1.0595	1.87	0.86	0.66	2.36	0.86	93.39	71.03	19.26	12.01	68.72	9065	nb+kc+nc
74	1.0716	2.14	1.02	0.78	2.75	0.88	92.43	69.40	19.51	12.12	68.37	7660	nb+kc+nc
75	1.0729	2.23	1.11	0.81	2.92	0.86	92.07	67.96	19.95	11.83	68.22	7170	nb+kc+nc
76	1.0876	2.45	1.54	0.97	3.43	0.89	90.72	61.21	22.69	11.61	65.70	5792	nb+kc+nc
77	1.1095	1.44	1.19	0.62	2.27	0.35	94.13	52.57	25.62	10.85	63.53	8782	nb+kc+nc
78	1.1083	1.49	2.32	0.57	3.20	0.46	91.96	36.39	33.41	6.67	59.92	5739	nb+kc+nc

Table 1 Continued

no.	density $g \cdot cm^{-3}$	composition of equilibrium solution, $w(B) \cdot 10^{-2}$ $w(Na^+)$	$w(K^+)$	$w(SO_4^{2-})$	$w(CO_3^{2-})$	$w(B_4O_7^{2-})$	Jänecke index of dry salt, mol/100 mol dry salt $J(K_2^{2+}) + J(CO_3^{2+}) + J(SO_4^{2+}) = 100$ $w(H_2O)$	$J(Na_2^{2+})$	$J(K_2^{2+})$	$J(SO_4^{2-})$	$J(CO_3^{2-})$	$J(H_2O)$	equilibrium solid phase[a]
79	1.0939	1.96	3.17	0.96	4.10	0.75	89.06	35.81	34.15	8.40	57.45	4159	nb+kc+nc
80	1.0872	1.54	3.82	0.89	4.07	0.83	88.85	26.55	38.82	7.38	53.80	3915	nb+kc+nc
81, K_3	1.0766	1.26	4.75	0.92	4.36	0.92	87.79	19.14	42.54	6.69	50.76	3407	nb+kc+knc+nc
82	1.0732	10.84	2.64	19.55	3.38	1.43	62.16	80.20	11.52	69.31	19.17	1175	nb+kb+knc
83	1.0803	10.92	2.75	19.71	3.46	1.50	61.66	79.60	11.82	68.84	19.34	1149	nb+kb+knc
84	1.0970	11.72	3.96	21.02	4.59	1.54	57.17	73.59	14.66	63.24	22.10	917.3	nb+kb+knc
85, K_5	1.1552	11.82	6.32	20.78	6.50	2.00	52.58	63.32	19.97	53.34	26.70	719.8	nb+kb+kc+nkc
86	1.1552	9.43	10.58	20.51	6.74	2.22	50.52	44.41	29.38	46.28	24.33	608.0	nb+kb+knc
87	1.1552	6.78	15.67	20.82	6.90	2.48	47.35	27.66	37.71	40.71	21.59	493.7	nb+kb+knc
88	1.2117	5.02	17.21	18.45	7.42	2.16	49.74	20.34	41.13	35.82	23.05	515.1	nb+kb+knc
89	1.3251	3.10	17.43	7.77	8.56	1.78	61.36	15.07	49.98	18.10	31.91	762.5	nb+kb+knc
90	1.3749	2.15	18.78	2.84	13.8	0.81	61.62	9.34	48.12	5.91	45.97	684.2	nb+kb+knc
91, F_2	1.4289	1.87	21.05	0.00	18.31	0.73	58.04	7.07	46.93	0.00	53.07	560.7	nb+kb+knc
92, F_3	1.5578	1.11	28.53	0.00	23.10	0.60	46.66	3.21	48.72	0.00	51.28	345.3	kb+kc+knc
93, M_1	1.1529	5.29	4.16	5.77	3.04	0.00	81.74	70.08	32.50	36.63	30.87	2767	ns+nsc+ks
94, M_4	1.3518	2.94	25.90	1.56	21.42	0.00	48.18	9.06	47.08	2.30	50.62	379.5	ks+knc+kc
95, M_2	1.3086	5.69	4.13	5.24	3.60	0.00	81.34	73.83	31.61	32.58	35.81	2697	nc+nsc+ks
96, M_3	1.1561	2.19	16.15	0.00	14.88	0.95	65.83	10.46	45.50	0.00	54.50	803.7	nc+knc+nb
97, N	1.4968	0.00	27.10	0.93	18.53	2.06	51.38	0.00	52.17	1.45	46.37	428.6	kc+ks+kb
98, E_1	1.1069	9.27	0.00	5.37	5.02	9.60	70.74	144.35	0.00	40.07	59.93	2815	nb+ns+nsc
99, E_2	1.0857	7.87	0.00	1.75	5.38	9.80	75.20	158.57	0.00	16.90	83.10	3872	nb+nc+nsc

[a] nc: $Na_2CO_3 \cdot 10H_2O$; ns: $Na_2SO_4 \cdot 10H_2O$; kc: $K_2CO_3 \cdot 3/2H_2O$; ks: K_2SO_4; nsc: $2Na_2SO_4 \cdot Na_2CO_3$; knc: $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$; kb: $K_2B_4O_7 \cdot 4H_2O$.

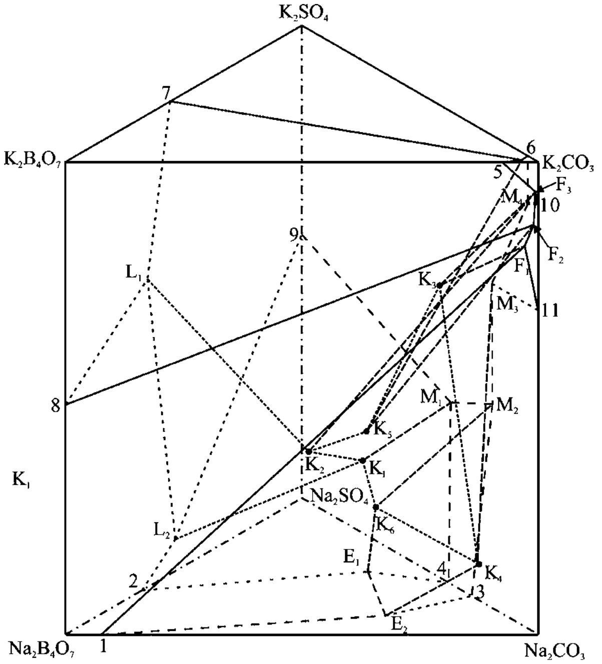

Figure 1. Stereo phase diagram of quinary system $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K.

K_3, saturated with salts $Na_2B_4O_7 \cdot 10H_2O + Na_2CO_3 \cdot 10H_2O + K_2CO_3 \cdot 3/2H_2O + K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$, with $w(Na^+)$ 1.26 %, $w(K^+)$ 4.57 %, $w(SO_4^{2-})$ 0.92 %, $w(CO_3^{2-})$ 4.36 %, $w(B_4O_7^{2-})$ 0.92 %.

K_4, saturated with salts $Na_2B_4O_7 \cdot 10H_2O + K_2CO_3 \cdot 3/2H_2O + 2Na_2SO_4 \cdot Na_2CO_3 + Na_2CO_3 \cdot 10H_2O$, with $w(Na^+)$ 3.87 %, $w(K^+)$ 0.99 %, $w(SO_4^{2-})$ 0.45 %, $w(CO_3^{2-})$ 5.48 %, $w(B_4O_7^{2-})$ 0.13 %.

K_5, saturated with salts $Na_2B_4O_7 \cdot 10H_2O + K_2CO_3 \cdot 3/2H_2O + K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O + K_2B_4O_7 \cdot 4H_2O$, with $w(Na^+)$ 11.82 %, $w(K^+)$ 6.32 %, $w(SO_4^{2-})$ 20.78 %, $w(CO_3^{2-})$ 6.50 %, $w(B_4O_7^{2-})$ 2.00 %.

K_6, saturated with salts $Na_2B_4O_7 \cdot 10H_2O + K_2CO_3 \cdot 3/2H_2O + 2Na_2SO_4 \cdot Na_2CO_3 + Na_2SO_4 \cdot 10H_2O$, with $w(Na^+)$ 12.42 %, $w(K^+)$ 2.13 %, $w(SO_4^{2-})$ 18.81 %, $w(CO_3^{2-})$ 5.63 %, $w(B_4O_7^{2-})$ 1.15 %.

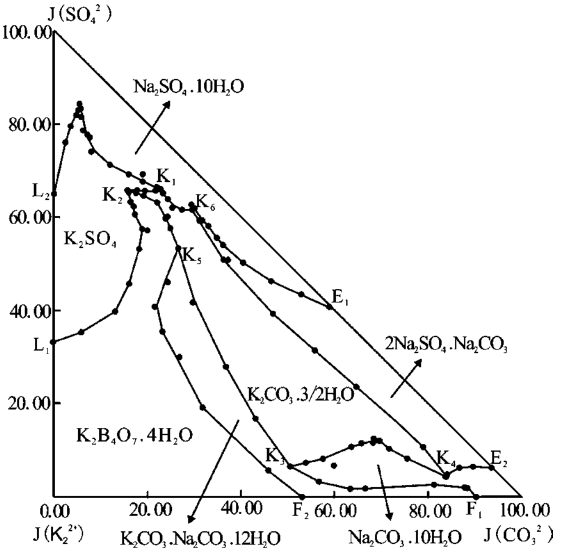

Figure 2. Projected diagram of quinary system $Na^+ + K^+ + CO_3^{2-} + SO_4^{2-} + B_4O_7^{2-} + H_2O$ at 273.15 K (saturated with $Na_2B_4O_7 \cdot 10H_2O$).

In the equilibrated solution corresponding to invariant point K_1, the order of the ion concentration is $SO_4^{2-} > Na^+ > CO_3^{2-} > K^+ > B_4O_7^{2-}$, with the largest concentration of SO_4^{2-} present only in the salt K_2SO_4 among the equilibrated solid phases, so the invariant point K_1 is an incongruent invariant point. Similarly K_2, K_3, K_5, and K_6 are incongruent invariant points. However, in the equilibrated solution corresponding to invariant point K_4, the order of the ion concentration is $CO_3^{2-} > Na^+ > K^+ > SO_4^{2-} > B_4O_7^{2-}$, with the largest concentration of CO_3^{2-} present in the salts $K_2CO_3 \cdot 3/2H_2O$, $2Na_2SO_4 \cdot Na_2CO_3$, and $Na_2CO_3 \cdot 10H_2O$ among the equilibrated solid phases, so invariant point K_4 is a congruent invariant point. At the congruent invariant point K_4, four salts simultaneously precipitated, whereas at the invariant points K_1, K_2, K_3, K_5, and K_6, dissolving conversion occurred, with one salt dissolving and the other three salts precipitating.

On the basis of the measured density data of the equilibrated solution tabulated in Table 1, we concluded that, at the univariant curves, the density of the solution smoothly changes with the $J(CO_3^{2-})$. Comparisons between this system and the ternary or quaternary subsystems containing potassium carbonate show that, in this quinary system, the contribution of salt potassium carbonate to the density has been reduced, and the crystallization field of salt $K_2CO_3 \cdot 3/2H_2O$ enlarges clearly.[13]

Conclusions

The projected phase diagram saturated with the salt $Na_2B_4O_7$ of this system at 273.15 K consists of six invariant points, 12 univariant curves, and seven crystallization fields corresponding to the single salts $Na_2SO_4 \cdot 10H_2O$, K_2SO_4, $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot 3/2H_2O$, $K_2B_4O_7 \cdot 4H_2O$, and double salts $2Na_2SO_4 \cdot Na_2CO_3$ and $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$. The crystallization forms of sodium and potassium borate are $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ and $K_2B_4O_5(OH)_4 \cdot 2H_2O$, respectively. In contrast to the subsystems containing potassium carbonate, the crystallization area of $K_2CO_3 \cdot 3/2H_2O$ increases clearly in the quinary system.

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