Liquid−Solid Equilibrium for Quaternary System $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at 288 K

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An experimental study on phase equilibria at 288 K in the quaternary system $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ was done by the isothermal evaporation method. Equilibrium solubilities and properties such as density, electrical conductivity, and pH of the solution were measured, and the equilibrium phase diagram was constructed in which there were two invariant points, six univariant curves, and four crystallization fields corresponding to borax ($Na_2B_4O_7{\cdot}10H_2O$), sodium sulfate, potassium sulfate, and potassium borate quahydrate ($K_2B_4O_7{\cdot}4H_2O$). No solid solutions or double salts were found.

Introduction

Alkaline lakes are widely distributed in the area of the Qinghai-Xizhang Plateau. The Zabuye Salt Lake, located in Tibet, is one of the alkaline lakes famous for its high concentrations of sodium, potassium, lithium, and borate.[1] It is reported that Zabuye Salt Lake brine contains 1.35×10^2 g·L^{-1} sodium, 38.56 g·L^{-1} potassium, 1.72 g·L^{-1} lithium, 39.83 g·L^{-1} carbonate ion, 3.99×10^2 mg·L^{-1} bicarbonate ion, 44.77 g·L^{-1} sulfate ion, 1.66×10^2 g·L^{-1} chloride ion, and 11.57 g·L^{-1} B_2O_3[1]. The brines mostly belong to the complex eight-component system of $Li^+ + K^+ + Na^+ + Cl^- + CO_3^{2-} + HCO_3^- + SO_4^{2-}$ + borate ($B_4O_7^{2-}$) + H_2O. It is reported that the economic value of the Zabuye Salt Lake is more than 200 billion RMB.[1] Although this salt lake brine resource is valuable, nothing has been reported on its comprehensive utilization because the relevant phase relations are lacking.

As a part of the complex eight-component system, the stable equilibria of some four- or five-component subsystems have been measured.[2−5] In the process of evaporation, the phase equilibria among the salts are always assumed to be metastable. Compared with the stable equilibrium, the metastable equilibrium result is more important for the salts exploited from the liquid resources, which has been proven in practice. For example, the stable and metastable phase equilibria studies that were done by Teeple[6] have been used in the comprehensive exploiting of the Searles Salt Lake in the U.S., and the metastable phase diagrams of $Na^+ + K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$ at 298 K[7] and 308 K[8] have been used to extract schoenite ($MgSO_4{\cdot}K_2SO_4{\cdot}6H_2O$) or potassium sulfate from the Chaidamu saline Lake, China. Also, other systems' metastable phase diagrams have been reported, such as $Li^+ + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$[9] and $Na^+ + K^+ + Cl^- + SO_4^{2-} + CO_3^{2-} + H_2O$[10] at 298 K. But the average temperature of Tibet in summer is about 288 K, so the metastable phase equilibrium study at 288 K will be of great value to exploiting brines.

In this paper, the metastable equilibrium of quaternary system $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ has been studied. The solubility and physicochemical properties data of the four-component system at 288 K were measured. This system is a subsystem of the eight-component system of Zabuye brines. So far, no report has been found about its phase equilibrium at 288 K.

Experimental Section

Reagents. The chemicals used were of analytical purity grade and were obtained from either the Shanghai Chemical Reagent Plant or the Chengdu Chemical Reagent Manufactory. They are sodium sulfate (Na_2SO_4, 99.0 mass %), potassium sulfate (K_2SO_4, 99.5 mass %), potassium borate ($K_2B_4O_7$, 99.5 mass %) and borax ($Na_2B_4O_7{\cdot}10H_2O$, 99.5 mass %). Doubly deionized water (electrical conductivity less than 1×10^{-4} S·m^{-1} at pH 6.6) was used to prepare the experimental solutions.

Instruments. An ET-Q-type thermostatic vibrator attached to an air-exhaust fan was used for the phase equilibrium measurement. The thermostatic vibrator was made at the Jiangsu Yitong Analytical Instrument Corporation, China, and its temperature could be controlled to ±0.1 K. A Simens D500 X-ray diffraction analyzer was used for the X-ray diffraction analysis of the solid phase.

Experimental Methods. The isothermal evaporation method was used in this study. The series of complexes of the quaternary system were loaded into clean polyethylene bottles. The bottles were placed in the thermostatic vibrator, whose temperature was controlled to (288.15 ± 0.1) K, and rotated at 120 rpm and exhausted at 20 m^3·min^{-1} to accelerate the equilibrium of those complexes. The measured points depended on the changes in the solid phase during the process of evaporation. When enough new solids appeared in the complex, the solids were separated from the solutions. The solid phase was detected by X-ray diffraction, and 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. The remainder of the solution continued to be evaporated and reached another measured point.

In this paper, the $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ system has been studied. The mixture properties of salts $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7$ will be

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Table 1. Solubility of an Equilibrium Solution of the Quaternary System Na_2SO_4 + K_2SO_4 + $Na_2B_4O_7$ + $K_2B_4O_7$ + H_2O at 288 K

	comp. of solution, $w(B) \times 10^2$[a]				Janëcke index, $n(B)$[b] $n(Na_2^{2+}) + n(K_2^{2+}) = 100$ mols			
no.	$w(K^+)$	$w(SO_4^{2-})$	$w(B_4O_7^{2-})$	$w(Na^+)$	$n(Na_2^{2+})$	$n(SO_4^{2-})$	$n(H_2O) \times 10^{-3}$	solid phase
1, E_1	0.00	7.72	0.82	3.94	100.00	93.83	5.669	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
2	0.01	8.78	0.74	4.41	99.82	95.05	4.967	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
3	0.26	9.02	0.72	4.38	96.58	95.29	4.822	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
4	0.42	9.91	0.81	4.73	95.00	95.16	4.307	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
5	0.90	10.41	0.82	4.70	89.85	95.34	4.062	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
6	1.76	13.20	0.85	5.53	84.22	96.16	3.055	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
7	1.79	12.68	1.08	5.34	83.57	95.00	3.161	$Na_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
8, E_2	1.41	0.00	6.09	0.98	54.18	0.00	12.94	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
9	1.54	0.54	6.20	1.19	56.64	12.24	11.039	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
10	1.52	0.97	5.24	1.12	55.72	23.06	11.54	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
11	1.58	1.35	4.81	1.14	55.15	31.11	11.24	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
12	1.73	2.05	4.42	1.27	55.55	42.85	10.08	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
13	1.84	3.07	3.60	1.45	57.32	57.92	9.060	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
14	1.86	3.40	3.34	1.52	58.11	62.17	8.766	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
15	2.17	6.59	1.95	2.46	65.86	84.50	5.937	$K_2B_4O_7{\cdot}4H_2O + Na_2B_4O_7{\cdot}10H_2O$
16, E_3	8.07	5.75	6.73	0.00	0.00	58.01	4.271	$K_2B_4O_7{\cdot}4H_2O + K_2SO_4$
17	6.25	6.10	6.01	1.03	21.84	62.12	4.374	$K_2B_4O_7{\cdot}4H_2O + K_2SO_4$
18	4.68	6.20	4.15	1.45	34.46	70.74	5.080	$K_2B_4O_7{\cdot}4H_2O + K_2SO_4$
19	3.23	6.44	2.70	1.98	51.13	79.42	5.633	$K_2B_4O_7{\cdot}4H_2O + K_2SO_4$
20	2.82	7.86	1.93	2.68	61.73	86.80	4.989	$K_2B_4O_7{\cdot}4H_2O + K_2SO_4$
21, E	2.41	7.88	1.67	2.85	66.85	88.41	5.093	$K_2B_4O_7{\cdot}4H_2O + K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
22	1.94	9.40	1.06	3.68	76.37	93.46	4.448	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
23	1.90	9.85	0.98	3.89	77.69	94.19	4.250	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
24	1.91	10.65	0.98	4.26	79.13	94.63	3.895	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
25	1.82	10.99	0.85	4.44	80.62	95.43	3.792	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
26	1.68	11.92	0.85	4.97	83.44	95.78	3.454	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
27	1.74	12.08	0.85	5.01	83.07	95.81	3.396	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
28, F	1.76	12.78	0.86	5.34	83.76	96.01	3.175	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O + Na_2SO_4$
29, E_4	1.62	12.11	0.00	4.84	83.53	100.00	3.587	$K_2SO_4 + Na_2SO_4$
30	1.74	12.37	0.28	4.98	82.94	98.63	3.428	$K_2SO_4 + Na_2SO_4$
31	1.72	12.48	0.28	5.05	83.31	98.61	3.390	$K_2SO_4 + Na_2SO_4$
32	1.78	12.78	0.64	5.26	83.37	97.00	3.221	$K_2SO_4 + Na_2SO_4$
33	1.76	11.67	0.98	4.84	82.35	95.05	3.505	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
34	1.74	8.38	0.88	3.25	76.01	93.93	5.126	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
35	1.72	11.64	0.89	4.83	82.69	95.46	3.537	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$
36	1.86	11.49	0.95	4.69	81.05	95.11	3.577	$K_2SO_4 + Na_2B_4O_7{\cdot}10H_2O$

[a] $w(B)$ − mass fraction. [b] $n(b)$ − Janëcke index.

useful in industrial sectors. A survey of the literature indicates that no physical property data of these mixtures have been studied earlier. This prompted us to undertake a study on the measurement of the pH value, density, viscosity, and refractive index of solutions at each measured phase point.

An electronic digital acidometer with a readability of ±0.01 units (PHS-3C, supplied by Jiangshu Electronic-Analytical Instrument Factory, China) was used for the pH measurements.

The densities of solution were determined by the specific gravity bottle method with a correction for the floating force of air (precision: 0.0001 $g{\cdot}cm^{-3}$). The operational process was the same as for the pycnometric density determination; the only difference was that the gravity bottle was substituted for the pycnometer. Weighing bottles of 10 cm^3 volume were dried beforehand by baking and flushing with dry nitrogen, and they were stored in a stoppered bottle. Then, 5 mL of each liquid was placed in the weighing bottles. The weighing bottles and the weighing bottles with liquids were weighted with a standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, supplied by Mettler Toledo Instruments Shanghai Co., Ltd.). All measurements were made at (288 ± 0.1) K.

The viscosities were measured using a capillary viscosimeter (size 75, supplied by Shanghai Grass Instrument Factory). The uncertainty in the viscosity was better than 2×10^{-3} mPa·s. The refractive indices were measured using a thermostatically controlled Abbe refractometer (supplied by Beijing Science Instrument Factory). A minimum of three independent readings were taken for each composition, and their average value was used in all calculations. The maximal variation of the measured refractive index was 2×10^4. The conductivities were measured using a DDS-11A conductimeter (supplied by the Second Analytical Instrument Factory, China). The cell constant was determined by using 0.01 N KCl solutions whose specific conductivity is known. The measured conductivity values were reproducible to within ±0.05%. All viscosity measurements were run three times, and the average value was reported.

Analytical Methods. The potassium ion concentration was measured by sodium tetraphenylborate-hexadecyl trimethylammonium bromide titration. The average relative deviation of the determination was less than 0.5%. The sodium ion concentration was determined by atomic absorption spectrometry (type WYD-YΠ). The mean determination uncertainty was less than 0.06%. The borate ion concentration was determined by neutralization titration with the existence of propanetriol. The mean determination uncertainty was less than 0.3%.[11] The sulfate ion concentration was determined by titration with a standard solution of EDTA in the presence of excess Ba−Mg mixture solution. First, excess Ba−Mg mixture solution (which contains 0.01 $mol{\cdot}L^{-1}$ $BaCl_2$ and 0.005 $mol{\cdot}L^{-1}$ $MgCl_2$) was added quantitatively to give a $BaSO_4$ precipitate. Excess

Table 2. Density ρ, Viscosity η, Refractive Index n_D, Conductivity κ, and pH Value for the Quaternary System $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at 288 K[a]

no.	$10^{-3}\rho$/kg·m^{-3}	pH	n_D	κ/S·m^{-1}	$10^{-3}\eta$/Pa·s
1, E_1	1.0988	9.13	1.3589	10.43	1.4802
2	1.1198	8.93	1.3610	7.10	1.4395
3	1.1262	8.91	1.3618	4.10	1.5919
4	1.1299	8.98	1.3621	3.55	1.6527
5	1.1511	8.72	1.3650	3.71	1.3106
6	1.1952	8.70	1.3708	3.70	1.5673
7	1.1851	8.58	1.3696	3.42	1.6638
8, E_2	1.0751	9.76	1.3555	4.53	1.5123
9	1.0813	9.62	1.3568	4.40	1.3723
10	1.0878	9.62	1.3570	2.92	1.3419
11	1.0838	9.57	1.3562	2.93	1.3242
12	1.0838	9.38	1.3567	2.84	1.2471
13	1.0869	9.22	1.3569	3.23	1.1852
14	1.1001	8.87	1.3570	3.19	1.2034
15	1.1147	8.98	1.3594	3.41	1.2234
16, E_3	1.1369	9.84	1.3620	12.67	1.2444
17	1.1503	9.52	1.3651	14.42	1.3494
18	1.1803	9.67	1.3670	11.69	1.4545
19	1.1833	9.47	1.3713	12.03	2.0523
20,	1.1203	9.32	1.3609	12.54	1.3545
21, E	1.1239	9.30	1.3610	10.82	1.3294
22	1.1470	9.13	1.3637	4.24	1.4320
23	1.1629	9.10	1.3651	4.53	1.5022
24	1.1619	9.17	1.3668	3.81	1.5162
25	1.1751	8.88	1.3679	3.86	1.5545
26	1.1874	8.69	1.3700	3.57	1.6492
27	1.1898	8.86	1.3711	3.41	1.6999
28, F	1.1963	8.89	1.3716	3.24	1.7221
29, E_4	1.1689	2.74	1.3665	14.54	1.5490
30	1.1847	8.31	1.3688	8.72	1.6917
31	1.1832	8.90	1.3690	5.12	1.6752
32	1.1881	8.77	1.3700	4.57	1.6677
33	1.1898	8.96	1.3708	3.91	1.6735
34	1.1935	8.85	1.3711	3.45	1.6455
35	1.1879	8.71	1.3708	3.50	1.5618
36	1.1831	8.63	1.3693	3.49	1.5143

[a] Numbers in this Table corresponding to Table 1.

$BaCl_2$ solution was titrated with EDTA standard solution in the presence of mixed K−B (acid chrome blue K + naphthol green B) indicator. The mean determination uncertainty was less than 1%.

Results and Discussion

The phase equilibrium experimental results of solubilities and properties for quaternary system $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at 288 K were measured and are tabulated in Tables 1 and 2, respectively. In Table 1, w(B) is the mass fraction of B, and n(B) is the Janëcke index values of B, with $n(Na_2^{2+}) + n(K_2^{2-}) = 100$ mols. On the basis of Janëcke index n(B), the experimental solubility isothermal metastable phase diagram of the system at 288 K was plotted, as shown in Figure 1.

The phase diagram of the quaternary system in Figure 1 consists of four crystallization fields, two invariant points (points E and F), and five univariant curves. The four crystallization fields correspond to borax ($Na_2B_4O_7·10H_2O$), sodium sulfate, potassium sulfate, and potassium borate quahydrate ($K_2B_4O_7·4H_2O$), respectively. The crystallization area of potassium borate quahydrate is the largest, and the crystallization zone of sodium sulfate is the smallest. These results indicate that potassium borate is easy to saturate and crystallize from solution. Invariant point E saturated with salts $Na_2B_4O_7·10H_2O + K_2SO_4 + K_2B_4O_7·4H_2O$ and the mass fraction compositions of the corresponding liquid phase are $w(K^+) = 2.41\%$, $w(SO_4^{2-}) = 7.88\%$, $w(B_4O_7^{2-}) = 1.67\%$, and $w(Na^+) = 2.85\%$. Invariant point F saturated with salts $Na_2B_4O_7·10H_2O + K_2SO_4 + Na_2SO_4$ and the mass fraction compositions of the corresponding liquid phase are $w(K^+) = 1.76\%$, $w(SO_4^{2-}) = 12.78\%$, $w(B_4O_7^{2-}) = 0.86\%$, and $w(Na^+) = 5.34\%$.

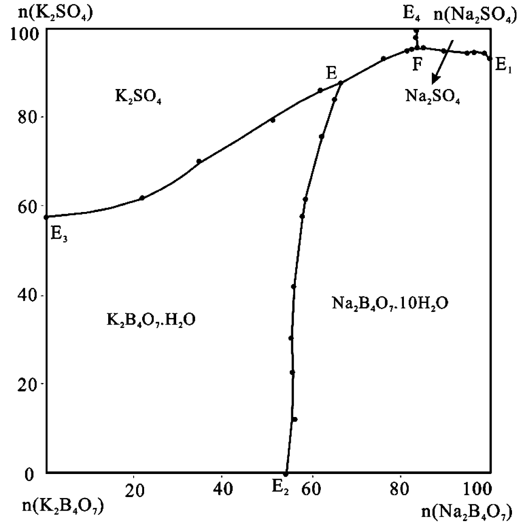

Figure 1. Isothermal phase diagram of the quaternary system $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at 288 K.

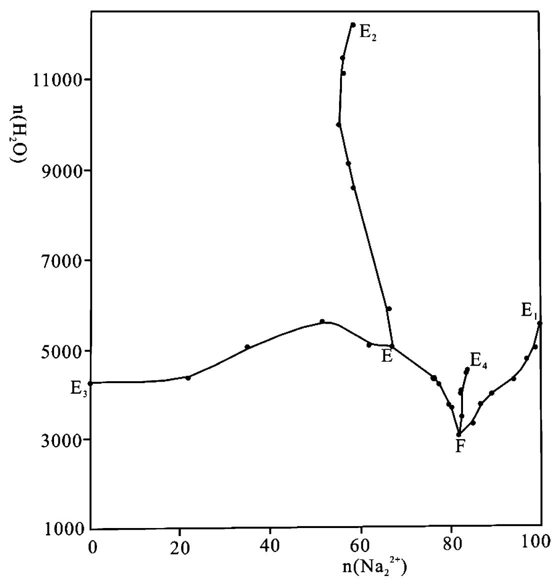

Figure 2. Water diagram of the quaternary system $Na_2SO_4 + K_2SO_4 + Na_2B_3O_7 + K_2B_4O_7 + H_2O$ at 288 K.

Figure 1 also shows that no solid solution or double salts are formed in the system. The easily formed double salt glasserit ($3K_2SO_4·Na_2SO_4$) from sodium and potassium sulfate salt at 298 K[7] or higher temperature[8] does not exist at 288 K.

Figure 2 is the relevant water diagram of the system at 288 K. Figure 2 shows that the Janëcke index values of water $n(H_2O)$ change with the Janëcke index values of Na^+ and reach the smallest value at invariant point F.

The physicochemical properties of the equilibrium solution change with the solution composition. Table 2 indicates that the densities, refractive indexes, and viscosities of the equilibrium solution gradually increase with increasing sodium ion concentration, whereas the change in the trend for the pH is reversed and the conductivities change irregularly.

Conclusions

The experimental solubility data and the relevant physicochemical properties data of the quaternary system $Na_2SO_4 + K_2SO_4 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at 288 K were investigated. According to the experimental data, the metastable isothermal phase diagram and water diagram of the system were plotted. The results show that this system comes from the simple quaternary system, without any solid solution or double salts formed.

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