(Liquid + Solid) Phase Equilibria in the Quaternary System Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3 + $Na_2B_4O_7$ + H_2O at 288 K

Shi-hua Sang,* Hui-an Yin, Ming-lin Tang, and Ying Zeng

Department of Applied Chemistry, Chengdu University of Technology, Chengdu 610059, PRC

An experimental study on phase equilibria at 288 K in the quaternary system Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3+$Na_2B_4O_7$ + H_2O was done by an isothermal solution saturation method. Equilibrium solubilities and properties such as the density, electrical conductivity, and pH of the solution were determined experimentally. According to the experimental data, the equilibrium phase diagram was constructed in which there were three invariant points, seven univariant curves, and five crystallization fields (K_2CO_3·3/2H_2O, $K_2B_4O_7$·4H_2O, $Na_2B_4O_7$·10H_2O, Na_2CO_3·10H_2O, $NaKCO_3$·6H_2O). The experimental results were discussed briefly.

Introduction

It is well known that phase equilibrium and phase diagram studies are necessary to exploit salt lake brine resources (e.g., Searles salt lake, San Bernadino County, CA). Only after a stable and metastable phase equilibrium study of it at several temperatures were the resources of the salt lake able to be exploited fully.[1]

There are many salt lakes in China, especially on the Qinghai-Tibet plateau. More than 200 salt lakes, which are spread out over 1 km^2, have been found in Tibet. Of all of the salt lakes in Tibet, the Zhabuye salt lake is famous for the highest concentrations of lithium, boron, and potassium in the world. The main components are Li^+, K^+, Na^+, Rb^+, Cs^+, $B_4O_7^{2-}$, CO_3^{2-}, Cl^-, SO_4^{2-}, and H_2O. It has the distinct characteristics of high concentrations of potassium and sodium and low concentrations of calcium and magnesium with abundant lithium and boron.[2−4]

This quaternary system is a subsystem of the Zhabuye salt lake brines. The corresponding phase equilibria study on ternary subsystems K_2CO_3 + $K_2B_4O_7$ + H_2O, $Na_2B_4O_7$ + Na_2CO_3 + H_2O, $K_2B_4O_7$ + $Na_2B_4O_7$ + H_2O, and K_2CO_3 + Na_2CO_3 + H_2O at 288 K have been published.[5−8] The respective single-salt solubility data on the quaternary system were presented.[9] The research on phase equilibria of this quaternary system at 298 K have also been reported.[10] The study of phase equilibria at different temperatures for the Zhabuye salt lake, however, is the basis of the exploitation of brine resources. So far, no report has been found concerning phase equilibria of the quaternary system at 288 K. To exploit salt lake brines fully, the phase equilibrium of the quaternary system Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3 + $Na_2B_4O_7$ + H_2O at 288 K was studied because the average temperature of Tibet in summer is about 288 K.

Experimental Section

Reagents. All chemicals used were of analytical purity grade, that is, $K_2B_4O_7$·5H_2O, K_2CO_3, $Na_2B_4O_7$·10H_2O, and Na_2CO_3. The electrical conductivity of distilled water is less than 1×10^{-4} S·m^{-1} at pH 6.6.

* To whom correspondence should be addressed. E-mail: sangsh@cdut.edu.cn.

Instruments. An HZS-H type thermostated vibrator (Harbin Donglian Electronic and Technology Development Co. LTD of China) with an uncertainty of 0.1 K was used for the equilibria measurement.

A PHS-3C digital acidometer with an uncertainty of 0.01 (Shanghai Kangyi instrument plant of China) was used to measure the pH values of the equilibrium solution.

A DDZ-11A type conductometer with an uncertainty of 0.1 S·m^{-1}(Shanghai Kangyi instrument plant of China) was used for the conductivity values of the equilibrium solution.

Experimental Method. The experiments for phase equilibria have been done by the method of isothermal solution saturation. The system points for the quaternary system were compounded by adding the third component gradually on the basis of the ternary subsystem salt saturation points at 288 K. Then the mixed brines were poured into a sealed tube and placed in the thermostated vibrator (HZS-H). The sealed tubes with solution were stirred for 1 week. The time of clarification was about 8 days. The solutions were taken out periodically for chemical analysis. When the concentration of the solution did not change, the equilibria were finished. After equilibrium, the liquid phases were taken out and analyzed quantitatively.

The pH values and electrical conductivity values of the equilibrium solution were measured with the corresponding listed instruments. The densities of the solution were determined with a pycnometer with an uncertainty of 0.002 g·cm^{-3}.

Identification of the Solid Phase. When the equilibria were finished, the solid phases were separated from the solution at the corresponding temperatures. After the wet residue mixture was filtered out, wet crystals were separated from each other according to crystal shapes as much as possible. Then the solids were approximately evaluated by chemical analysis for wet residues; further identification would be done by X-ray diffraction.

A Rigaku D/max-3C X- ray diffraction analyzer (Japan) was used for solid-phase X-ray diffraction analysis. The X-ray analyses of the solid phase were based on the distribution curves of the dispersed radiation intensity $I = f(\theta)$. For the quantitative analysis, each of the diffraction patterns was inspected for the series of interplanar

10.1021/je0497956 CCC: $27.50
Published on Web 10/21/2004

Table 1. Solubilities w, Janecke Index Y, Density ρ, and Electrical Conductivity κ of Solution in Quaternary System $Na_2CO_3(1) + K_2B_4O_7(2) + K_2CO_3(3) + Na_2B_4O_7(4) + H_2O(5)$ at 288 K[a]

100w				Janecke index Y ($2Na^+ + 2K^+ = 100$ mol)						
CO_3^{2-}	$B_4O_7^{2-}$	K	Na^+	$Y(B_4O_7^{2-})$	$Y(2Na^+)$	$Y(H_2O)$	solid phase	ρ/(g·cm^{-3})	pH	κ/(S·m^{-1})
9.50	2.11	0.00	7.91	7.92	100.00	2600.31	nc + nb	1.180	11.25	4.6
9.31	2.53	1.05	7.27	9.52	92.15	2586.52	nc + nb	1.192	11.05	4.6
9.70	2.64	2.03	7.02	9.53	85.44	2443.81	nc + nb	1.205	10.95	4.7
9.84	2.70	2.29	6.99	9.60	83.82	2393.94	nc + nb	1.210	10.63	4.8
10.02	2.93	4.15	6.10	10.17	71.38	2294.98	nc + nb	1.224	10.60	4.9
10.19	3.03	4.44	6.09	10.32	69.94	2236.72	nc + nb + kb	1.236	10.50	5.0
11.45	2.89	6.57	5.76	8.90	59.79	1944.74	nc + kb	1.266	10.45	5.3
12.77	2.61	8.29	5.68	7.33	53.72	1709.06	nc + kb	1.300	10.52	5.4
13.50	2.32	9.04	5.71	6.24	51.70	1607.46	nc + kb	1.323	10.60	5.5
14.14	2.26	10.48	5.33	5.83	46.31	1504.94	nc + kb + nk	1.336	10.72	5.6
16.78	2.22	14.11	5.20	4.87	38.47	1165.72	nk + kb	1.349	11.15	5.8
16.86	2.15	15.78	4.26	4.70	31.39	1148.38	nk + kb	1.385	11.26	6.1
17.50	2.06	18.12	3.34	4.36	23.82	1074.43	nk + kb	1.396	11.40	6.4
17.92	1.68	18.76	3.17	3.50	22.29	1049.46	nk + kb	1.440	11.67	6.5
18.82	1.54	20.31	2.91	3.07	19.54	968.64	nk + kb	1.461	11.89	6.3
21.51	1.48	26.68	1.20	2.59	7.06	741.66	nk + kb	1.531	12.46	6.1
11.85	0.00	6.24	5.41	0.00	59.49	2152.04	nk + nc	1.211	12.43	5.8
12.01	0.55	7.09	5.19	1.74	55.38	2049.71	nk + nc	1.223	12.35	5.8
12.82	0.89	8.13	5.30	2.62	52.49	1844.90	nk + nc	1.259	12.40	6.0
13.28	1.05	9.11	5.12	2.97	48.80	1739.91	nk + nc	1.311	12.44	6.1
13.99	1.96	10.25	5.26	5.14	46.54	1549.01	nk + nc	1.330	12.40	6.4
23.00	0.00	28.15	1.03	0.00	5.85	693.04	nk + kc	1.527	13.77	6.9
22.89	1.04	28.29	1.17	1.73	6.57	666.97	nk + kc	1.532	13.73	6.1
22.81	1.36	28.25	1.23	2.26	6.88	662.04	nk + kc	1.536	13.63	5.9
22.69	1.59	28.29	1.18	2.64	6.62	661.45	nk + kc	1.537	13.42	5.8
22.66	1.65	28.39	1.12	2.74	6.27	660.70	kc + kb + nk	1.540	13.50	5.9
22.62	1.69	28.29	1.16	2.81	6.50	662.25	kc + kb	1.538	13.51	5.9
22.30	1.62	28.50	0.77	2.74	4.38	680.57	kc + kb	1.536	13.40	5.9
22.24	1.51	28.86	0.48	2.56	2.74	685.10	kc + kb	1.529	13.53	5.8
22.05	1.24	28.81	0.28	2.13	1.64	704.51	kc + kb	1.522	13.30	6.0
21.59	1.07	28.61	0.00	1.88	0.00	738.23	kc + kb	1.514	13.01	6.8
0.00	9.89	3.86	0.66	100.00	22.44	7452.34	kb + nb	1.117	10.02	2.8
0.73	9.01	3.79	1.00	82.69	30.88	6754.92	kb + nb	1.128	10.15	2.9
1.02	8.71	3.35	1.39	76.77	41.32	6491.82	kb + nb	1.131	10.25	3.2
1.83	8.67	3.55	1.88	64.71	47.34	5403.36	kb + nb	1.151	10.26	3.4
2.73	8.17	3.56	2.42	53.67	53.53	4702.06	kb + nb	1.177	10.36	3.6
3.84	7.59	3.94	2.87	43.35	55.29	4020.67	kb + nb	1.193	10.40	3.7
5.19	5.49	4.02	3.24	29.05	57.73	3739.38	kb + nb	1.201	10.45	3.9
6.76	4.76	4.68	3.84	21.42	58.15	3098.48	kb + nb	1.221	10.55	4.0
9.33	3.75	5.02	5.31	13.46	64.18	2368.06	kb + nb	1.232	10.53	4.3

[a] Note: nc − $Na_2CO_3 \cdot 10H_2O$, kb − $K_2B_4O_7 \cdot 4H_2O$, nb − $Na_2B_4O_7 \cdot 10H_2O$, kc − $K_2CO_3 \cdot {}^3/_2H_2O$, nk − $NaKCO_3 \cdot 6H_2O$, w − mass fraction.

distances (d) and relative intensities (I) and then compared with the numeric data listed in the powder diffraction file.

Analytical Methods

The potassium ion concentration was measured by adding quantitative sodium tetraphenylboron−hexadecyl trimethylammonium bromide via titration (uncertainty of 0.5 mass %). The potassium ion and sodium tetraphenylboron can form potassium tetraphenylboron ($K[B(C_6H_5)_4]$) under basic conditions, and sodium tetraphenylboron was titrated by 0.35% hexadecyl trimethylammonium bromide using a thiazole yellow solution as the indicator. The carbonate ion concentration was determined by a method of acidic titration applying 0.1 M HCl using a methyl orange solution as the indicator (uncertainty of 0.18 mass %). The borate ion concentration was evaluated by using basic titration (0.05 M NaOH) with the existence of mannitol with a phenolphthalein solution as the indicator (uncertainty of 0.3 mass %). Na^+ was evaluated according to ion balance.

Results and Discussion

The phase equilibrium experimental results of solubilities and properties for the quaternary system Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3 + $Na_2B_4O_7$ + H_2O at 288 K were measured and are listed in Table 1.

The ion concentration values in the equilibrium solution were expressed in mass fraction w(b). The solution density (ρ) was given in grams per cubic centimeter. To plot the quaternary system diagram, Janecke index values were necessary. According to the Janecke index, the phase equilibrium diagram was plotted in Figure 1.

It can be found from Table 1 and Figure 1 that the quaternary system has five crystallization fields ($K_2CO_3 \cdot {}^3/_2H_2O$(E4F3E3E4), $K_2B_4O_7 \cdot 4H_2O$(E2F1F2F3E3E2), $Na_2B_4O_7 \cdot 10H_2O$(E1F1E2E1), $Na_2CO_3 \cdot 10H_2O$(E1F1F2E5E1), $NaKCO_3 \cdot 6H_2O$(E5F2F3E4E5)), seven univariant curves (E1F1, E3F3, F1F2, E4F3, F2F3, E5F2, E2F1), and three invariant points (F1, F2, F3). Points E1, E2, E3, E4, and E5 represent the equilibrium points saturated with two solid phases.

The salt of $K_2CO_3 \cdot {}^3/_2H_2O$ has the smallest crystallization field, and we note, in particular, that it has the largest solubility in the quaternary system. We conclude that, by analyzing the data in Table 1 and Figure 1, the concentrations of $K_2B_4O_7$, $Na_2B_4O_7$, and Na_2CO_3 declined sharply because of the salting-out effect of K_2CO_3. The salts of $K_2B_4O_7 \cdot 4H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$ have larger crystallization fields than the others.

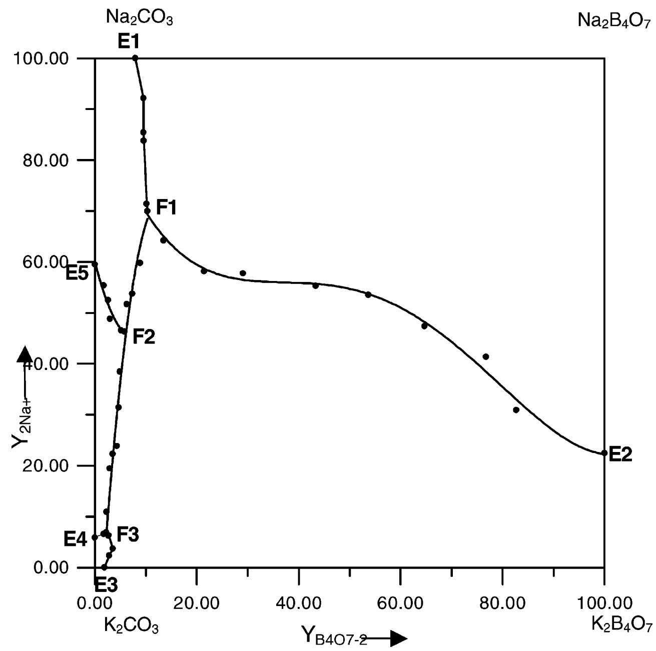

Figure 1. Phase diagram of the quaternary system Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3 + $Na_2B_4O_7$ + H_2O at 288 K.

Sodium carbonate septahydrate ($Na_2CO_3 \cdot 7H_2O$) was not found in the quaternary system, although $Na_2CO_3 \cdot 7H_2O$ exists in the system $Na_2CO_3-K_2CO_3-H_2O$ at 298 K.[11] Double salt $NaKCO_3 \cdot 6H_2O$ was found in the quaternary system at 288 K. Potassium carbonate (K_2CO_3) has the highest concentration and strong salting-out effects on other salts.

Comparison with the Equilibrium Phase Diagram for the System at 298 K

Some differences can be found by comparing the equilibrium phase diagram for the system at 298 K with that of the system at 288 K.

The crystallization fields of $Na_2CO_3 \cdot 10H_2O$ were obviously larger at 298 K than at 288 K for the quaternary system.

Different potassium and sodium double salts were formed in the quaternary system at 298 K. The double salt was $NaKCO_3 \cdot H_2O$ at 298 K for the quaternary system,[10] but X-ray diffraction showed that the potassium and sodium double salt was $NaKCO_3 \cdot 6H_2O$ at 288 K for the system Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3 + $Na_2B_4O_7$ + H_2O.

Conclusions

Phase equilibria of the quaternary system Na_2CO_3 + $K_2B_4O_7$ + K_2CO_3 + $Na_2B_4O_7$ + H_2O at 288 K were studied by an isothermal solution saturation method. Solubilities and properties were measured experimentally. According to the experimental data, phase diagrams were plotted. The experimental results show that the quaternary system has five solid phases: $K_2CO_3 \cdot {}^3/_2H_2O$, $K_2B_4O_7 \cdot 4H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, $NaKCO_3 \cdot 6H_2O$. Sodium carbonate septahydrate ($Na_2CO_3 \cdot 7H_2O$) was not found in the quaternary system.

Potassium carbonate (K_2CO_3) had the highest concentration and strongest salting-out effect on other salts. The potassium and sodium double salt is $NaKCO_3 \cdot 6H_2O$ in this system.

Literature Cited

(1) Song, P. S. Utilization of salt lake resources. *J. Salt Lake Sci.* **1993**, *1*, 68−80.
(2) Zheng, X. Y.; Zhang M. G.; Xu Y.; Li, B. X. *Salt Lakes of China*; Science Press: Beijing, 2002 (in Chinese).
(3) Zheng, M. P.; Xiang, J. *Salt Lakes of the Qinghai-Tibet Plateau*; Science and Technology Press: Beijing, 1989 (in Chinese).
(4) Zheng, X. Y.; Tang, Y.; Xu, Y. et al. Salt Lakes of Tibet, Science and Technology Press: Beijing, 1988 (in Chinese).
(5) Sang, S. H.; Tang, M. L.; Yin, H. A.; Zhang, Y. X. Study on Equilibrium Solubilities and Properties of Solutions in the Ternary System $Li^+(K^+)/CO_3^{2-}$, $B_4O_7^{2-}$ - H_2O. *Ind. Miner. Process.* **2002**, *31*, 7−9.
(6) Sang, S. H.; Tang M. L.; Yin H. A.; Zhang, Y. X. A Study on Phase Equilibria for the Ternary System Na_2CO_3-$Na_2B_4O_7$-H_2O at 288 K. *J. Mineral. Petrol.* **2002**, *22*, 91−94.
(7) Sang S. H.; Tang, M. L.; Yin, H. A.; Zhang, Y. X. A Study on Phase Equilibria for the Ternary System $K_2B_4O_7$-$Na_2B_4O_7$-H_2O at 288 K, *Sea-Lake Salt Chem. Ind.* **2002**, *31*, 16−18.
(8) Sang, S. H.; Tang, M. L.; Yin, H. A.; Zhang, Y. X. A Study on Phase Equilibria for the ternary system $K_2CO_3-Na_2CO_3-H_2O$ at 288K, *J. Inorg. Chem. Ind.* **2003**, *35*, 23−24.
(9) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1979; Vol. 1.
(10) Zeng, Y.; Yin, H. A.; Tang, M. L. A Study on Phase Equilibrium of the Quaternary System Na, K/CO_3^{2-}, $B_4O_7^{2-}-H_2O$ at 298 K. *Chin. J. Inorg. Chem.* **2001**, *17*, 665−668.
(11) Harvie, C. E.; Moller. N.; and Weare, J. H. Prediction of Mineral Solubilities in Nature Waters: Na-K-Mg-Ca-H-SO_4-Cl-OH-HCO_3-CO_3-CO_2-H_2O System to High Strength at 25 °C *Geochim. Cosmochim. Acta* **1984**, *48*, 723−751.

Received for review May 31, 2004. Accepted August 4, 2004. This work was supported by the National Nature Science Foundation of China (no. 40303010).

JE0497956