JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Solid−Liquid Stable Equilibria for the Quaternary $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ System at 288 K

Shi Hu Sang,* Heng Li, Ming-Liang Sun, and Jiang Peng

College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, ChengDu 610059, P. R. China

ABSTRACT: The solubilities and densities of the solution in the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K were investigated using the method of isothermal dissolution equilibrium. The solid−liquid stable equilibria in the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K were studied experimentally. On the basis of experimental data, the stable phase diagram of the quaternary system was plotted. In the solubility diagram of the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K, there are three invariant points, seven solubility isotherm curves, and five crystallization regions, which correspond to borax ($Na_2B_4O_7\cdot10H_2O$), potassium tetraborate ($K_2B_4O_7\cdot4H_2O$), mirabilite ($Na_2SO_4\cdot10H_2O$), arcanite (K_2SO_4), and glaserite ($Na_2SO_4\cdot3K_2SO_4$). It can be found from the experimental results that sulfates have bigger solubilities than borates in the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K.

INTRODUCTION

There are many salt lakes on the Qingzang plateau of China.[1,2] Furthermore, a huge amount of underground gasfield brine was discovered west of the Sichuan basin. Sodium chloride, potassium, boron, bromine, and sulfate are the major salts or ions in the oilfield brine. They are also accompanied by lithium, strontium, and iodine. Therefore, the underground gasfield brine largely consists of the complex six-component system $Na-K-Cl-B_4O_7-Br-SO_4-H_2O$.[3] The proved reserves of the gasfield brines are up to $2.06\cdot10^{12}$ m^3.[3] Although the gasfield brine resources are very valuable, there is no report on their potential utilization because of lack of data on the relevant solubilities or phase equilibrium data of the brine−mineral system. For exploiting the underground brines economically, the measurement of salt mineral solubilities at different temperatures is required.[4]

Aiming at understanding the behavior of the underground gasfield brine, some solid−liquid phase equilibrium systems at different temperatures have been reported in our earlier work: $Na_2B_4O_7-NaBr-H_2O$,[5] $K_2B_4O_7-KBr-H_2O$,[6] and $K_2SO_4-K_2B_4O_7-KCl-H_2O$[7] at 298 K and $Na_2B_4O_7-Na_2SO_4-NaCl-H_2O$[8] at 323 K.

The quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ is a subsystem of the six-component system. The solid−liquid equilibria of its ternary subsystems $Na_2B_4O_7-Na_2SO_4-H_2O$,[9] $Na_2B_4O_7-K_2B_4O_7-H_2O$,[10] and $K_2B_4O_7-K_2SO_4-H_2O$[11] at 288 K has already been reported by us in detail. The ternary system $Na_2SO_4-K_2SO_4-H_2O$ at 288 K has also been reported.[12,13] So far, no report has been found on stable equilibrium solubility measurements of this quaternary system ($Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$) at 288 K. Accordingly, in this paper, the solid−liquid equilibrium of the quaternary system at 288 K is presented in detail.

EXPERIMENTS

Reagents and Instruments. Distilled water with a conductivity less than 10^{-4} $S\cdot m^{-1}$ and pH = 6.6 was used to prepare the experimental samples and for chemical analysis. The reagents used were of analytical reagent grade: Na_2SO_4, K_2SO_4, $Na_2B_4O_7\cdot10H_2O$ (ChengDu KeLun Chemical Reagent factory, China), and $K_2B_4O_7\cdot4H_2O$ (BeiJing YiLi Chemical Reagent factory, China).

An HZS-H type thermostatted vibrator with a precision ± 0.1 K was used for the solid−liquid equilibrium measurements.

Experimental Method. The isothermal dissolution equilibrium method was used for the solid−liquid equilibrium experiments. The quaternary system points were compounded by adding the third component gradually on the basis of the ternary saturation points at 288 K. For example, for the points in the univariant curve E1−F1, excess sodium sulfate and sodium borate were dissolved in distilled water, and then the respective solution−solid phase mixtures were added into the third salt K_2SO_4 with different quantity. The respective mixtures were placed in a bottle with 100 mL for the solubility experiments. Then all the prepared bottles were put into a water- bath thermostatted vibrator (HZS-H). The solutions in the bottles were stirred for one week to promote the establishment of the equilibrium. Experimental results showed that the equilibria were attained in (3 to 7) days with stirring, and the time of clarification was about (3 to 4) days. The solutions were taken out periodically for chemical analysis. When the solution composition did not change, the system had attained its equilibrium state. After equilibrium, the compositions of the solution were determined by the method of chemical analysis.

The compositions of the solid phases were identified by a Rigaku D/max-3C X-ray diffraction analyzer (Japan). Wet crystals were separated from the liquid phase by vacuum filtration using a sintered glass crucible and dried for X-ray diffraction. The densities of the solution were measured using a pycnometer with an uncertainty of 0.0002 $g\cdot cm^{-3}$.

Analytical Methods[14]**.** The K^+ concentration was measured by a sodium tetraphenylborate-hexadecyl trimethyl ammonium bromide titration (with an uncertainty of 0.5 %). The $B_4O_7^{2-}$ concentration was evaluated by a basic titration with mannitol

Received: September 25, 2010
Accepted: February 25, 2011
Published: March 15, 2011

Table 1. Phase Equilibrium Data of the $Na_2B_4O_7$−Na_2SO_4−$K_2B_4O_7$−K_2SO_4−H_2O Quaternary System at 288 K[a]

	composition of solution $100w$(b)				Jänecke index J J/[mol·100 mol^{-1}] (2Na$^+$ + 2K$^+$ = 100 mol)				density
no.	Na^+	K^+	SO_4^{2-}	$B_4O_7^{2-}$	$J(2K^+)$	$J(B_4O_7^{2-})$	$J(H_2O)$	equilibrium solids	g·cm^{-3}
1(E1)	3.83	0.00	7.54	0.74	0.00	5.72	5864.43	S_{10} + NB	1.1026
2	3.54	0.40	7.51	0.59	6.25	4.64	5952.54	S_{10} + NB	1.1186
3	3.50	0.81	7.93	0.60	12.00	4.46	5600.79	S_{10} + NB	1.1279
4	3.33	1.94	8.93	0.64	25.62	4.27	4867.15	S_{10} + NB	1.1479
5	3.59	2.62	10.30	0.67	30.12	3.84	4123.68	S_{10} + NB	1.1578
6	3.65	3.20	11.12	0.69	34.06	3.70	3755.09	Gla + NB	1.1832
7	3.54	3.39	11.14	0.69	36.07	3.71	3743.44	Gla + NB	1.1857
8(E5)	0.40	3.74	0.00	8.77	84.74	100.00	8551.50	KB + NB	1.0931
9	0.30	3.93	0.47	8.07	88.46	91.40	8507.63	KB + NB	1.1036
10	0.31	4.10	0.90	7.73	88.72	84.18	8154.58	KB + NB	1.1047
11	0.30	4.59	2.20	6.58	90.12	64.91	7338.09	KB + NB	1.1195
12	0.26	4.90	2.75	6.17	91.83	58.11	6974.85	KB + NB	1.1203
13	0.31	5.19	3.40	5.88	90.80	51.67	6457.75	KB + NB	1.1350
14	0.35	5.20	3.70	5.57	89.66	48.25	6361.86	KB + NB	1.1389
15(E4)	0.00	4.92	3.24	4.56	100.00	46.55	7683.80	KB + KS	1.1089
16	0.21	4.99	3.69	4.67	93.45	43.92	7011.28	KB + KS	1.1189
17	0.07	5.36	3.58	5.08	97.96	46.72	6810.02	KB + KS	1.1210
18	0.15	5.50	3.82	5.27	95.55	46.05	6421.26	KB + KS	1.1289
19	0.44	5.59	4.33	5.62	88.15	44.54	5735.95	KB + KS	1.1336
20(F3)	0.49	5.63	4.45	5.64	87.19	43.94	5623.40	KB + KS + NB	1.1334
21	0.57	5.60	5.05	4.89	85.31	37.45	5537.51	NB + KS	1.1269
22(E2)	3.95	3.41	12.44	0.00	33.74	0.00	3438.26	Gla + S_{10}	1.1800
23	3.88	3.06	11.66	0.35	31.72	1.82	3640.68	Gla + S_{10}	1.1878
24	3.92	2.96	11.40	0.69	30.78	3.58	3653.36	Gla + S_{10}	1.1897
25	3.94	2.94	11.35	0.78	30.53	4.07	3651.01	Gla + S_{10}	1.1857
26	4.00	3.01	11.55	0.80	30.70	4.13	3568.94	Gla + S_{10}	1.1899
27	3.92	2.96	11.33	0.81	30.76	4.23	3651.07	Gla + S_{10}	1.1829
28(F1)	3.89	3.09	11.40	0.85	31.87	4.41	3611.43	NB + Gla + S_{10}	1.1895
29(E3)	1.85	4.35	9.21	0.00	58.10	0.00	4895.94	KS + Gla	1.1276
30	1.59	4.26	8.36	0.31	61.32	2.26	5330.03	KS + Gla	1.1334
31	1.62	4.23	8.22	0.61	60.56	4.37	5295.26	KS + Gla	1.1385
32	1.65	4.40	8.23	1.00	61.11	6.99	5103.80	KS + Gla	1.1357
33(F2)	1.71	4.41	8.24	1.22	60.34	8.36	5007.12	Gla + KS + NB	1.1403
34	1.56	4.51	8.06	1.23	63.01	8.60	5121.61	KS + NB	1.1430
35	3.37	1.09	8.00	0.58	16.00	4.29	5546.90	S_{10} + NB	1.1383
36	3.19	2.20	8.98	0.62	28.97	4.11	4841.98	S_{10} + NB	1.1552
37	3.87	3.11	11.49	0.67	32.19	3.48	3622.61	S_{10} + NB	1.1697

[a] Note: NB−$Na_2B_4O_7\cdot 10H_2O$, KB−$K_2B_4O_7\cdot 4H_2O$, S_{10}−$Na_2SO_4\cdot 10H_2O$, KS−K_2SO_4, Gla−$Na_2SO_4\cdot 3K_2SO_4$.

(with an uncertainty of 0.3 %). The SO_4^{2-} concentration was determined by a method of mixing barium chloride and magnesium chloride−EDTA titration (with an uncertainty of 0.5 %). The Na^+ concentration was evaluated according to ion balance.

RESULTS AND DISCUSSION

The equilibrium experimental solubilities of salts, densities of solutions, and equilibrium solids in the quaternary system $Na_2B_4O_7$−Na_2SO_4−$K_2B_4O_7$−K_2SO_4−H_2O at 288 K are tabulated in Table 1.

The ion concentration values of the equilibrium solution are expressed in mass fraction $w(b)$. The solution density (ρ) is given in grams per cubic centimeter. To plot the quaternary system diagram, Jänecke dry-salt index values are necessary. $J(2Na^+)$, $J(SO_4^{2-})$, $J(2K^+)$, $J(B_4O_7^{2-})$, and $J(H_2O)$ are respective ion and water Jänecke index values. The respective ion and water Jänecke index values are calculated according to defined correlations

$$w(Na^+) = 2M_{Na}\cdot[w(SO_4^{2-})/M_{SO4} + w(B_4O_7^{2-})/M_{B4O7} - w(K^+)/(2\cdot M_K)]\text{g}/100\text{ g of solution}$$

$$w(H_2O) = 100 - w(B_4O_7^{2-}) - w(SO_4^{2-}) - w(K^+) - w(Na^+)\text{g}/100\text{ g of solution}$$

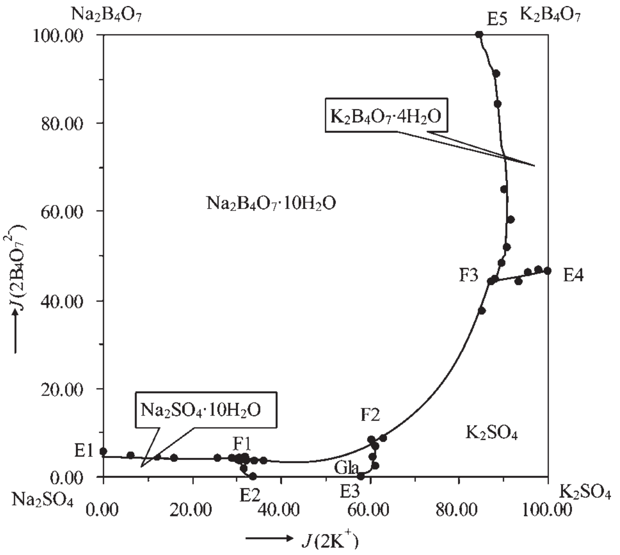

Figure 1. Stable equilibrium phase diagram of the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K: ●, experimental solubility data in this work; —, smoothed univariant curve.

$$\text{Letting } [b] = w(Na^+)/(2M_{Na}) + w(K^+)/(2M_K) \text{ mol}$$

then

$$J(2Na^+) = 100 \cdot w(Na^+)/(2M_{Na})/[b] \text{ mol/mol } (2K^+ + 2Na^+)$$

$$J(SO_4^{2-}) = 100 \cdot w(SO_4^{2-})/M_{SO4}/[b] \text{ mol/mol } (2K^+ + 2Na^+)$$

$$J(2K^+) = 100 \cdot w(K^+)/(2M_K)/[b] \text{ mol/mol } (2K^+ + 2Na^+)$$

$$J(B_4O_7^{2-}) = 100 \cdot w(B_4O_7^{2-})/M_{B4O7}/[b] \text{ mol/mol } (2K^+ + 2Na^+)$$

$$J(H_2O) = 100 \cdot w(H_2O)/M_{H2O}/[b] \text{ mol/mol}(K^+ + Na^+)$$

where $w(\text{ion})$ and $w(H_2O)$ are the mass of ion and water in grams per 100 g of solution. $J(\text{ion})$ and $J(H_2O)$ are the Jänecke index value of an ion and water, and M_{ion} is the molecular weight of the ion. Figure 1 is the isothermal solubility diagram plotted according to the Jänecke index values above. The quaternary solubility diagram consists of five crystallization fields corresponding to $Na_2B_4O_7 \cdot 10H_2O$ (E1F1F2F3E5 field), $K_2B_4O_7 \cdot 4H_2O$ (E5F3E4 field), K_2SO_4 (E3F2F3E4 field), $Na_2SO_4 \cdot 10H_2O$ (E1F1E2 field), and $Na_2SO_4 \cdot 3K_2SO_4$ (E2F1F2E3 field). The crystallization field of mirabilite ($Na_2SO_4 \cdot 10H_2O$) has the smallest crystallization area. Borax ($Na_2B_4O_7 \cdot 10H_2O$) has the biggest crystallization field in this quaternary system. The biggest crystallization region in the phase diagram indicates that borax ($Na_2B_4O_7 \cdot 10H_2O$) is of low solubility. Experimental results imply that natural borax ($Na_2B_4O_7 \cdot 10H_2O$) might form in the salt lake.

There are seven univariant curves each characterized by two solids and a solution: curve E1F1, corresponding to the coexistence of the salts $Na_2SO_4 \cdot 10H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$ with the saturated solution; curve E2F1, corresponding to the coexistence of the salts $Na_2SO_4 \cdot 10H_2O$ and $Na_2SO_4 \cdot 3K_2SO_4$ with the saturated solution; curve E3F2, corresponding to the coexistence of the salts $Na_2SO_4 \cdot 3K_2SO_4$ and K_2SO_4 with the saturated solution; curve E4F3, corresponding to the coexistence of the salts $K_2B_4O_7 \cdot 4H_2O$ and K_2SO_4 with the saturated solution; curve E5F3, corresponding to the coexistence of the salts $K_2B_4O_7 \cdot 4H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$ with the saturated solution; curve F1F2, corresponding to the coexistence of the salts $Na_2SO_4 \cdot 3K_2SO_4$ and $Na_2B_4O_7 \cdot 10H_2O$ with the saturated solution; curve F2F3, corresponding to the coexistence of the salts K_2SO_4 and $Na_2B_4O_7 \cdot 10H_2O$ with the saturated solution.

There are three isothermal invariant points F1, F2, and F3. The point F1 represents the equilibrium of three solid phases ($Na_2B_4O_7 \cdot 10H_2O$, $Na_2SO_4 \cdot 10H_2O$, and $Na_2SO_4 \cdot 3K_2SO_4$). The point F2 represents the equilibrium of three solid phases ($Na_2B_4O_7 \cdot 10H_2O$, K_2SO_4, and $Na_2SO_4 \cdot 3K_2SO_4$). The point F3 represents the equilibrium of three solid phases ($Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 4H_2O$, and K_2SO_4).

There are no solid solutions formed in the quaternary system at 288 K.

The double salt glaserite ($Na_2SO_4 \cdot 3K_2SO_4$) formed in the stable equilibrium of the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K. The borate ions exist with the $B_4O_5(OH)_4^{2-}$ ion in saturated solution, and the chemical structures of borates can be expressed as $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ and $K_2[B_4O_5(OH)_4] \cdot 2H_2O$.[15] The solubility data of the ternary system $Na_2SO_4-K_2SO_4-H_2O$ at different temperatures[12,13] suggest that the sodium sulfates can crystallize from saturated solution in the form of $Na_2SO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$, and Na_2SO_4. When the temperature reaches 35 °C, only thenardite (Na_2SO_4) can crystallize from the saturation solution. At 288 K, however, the sodium sulfate that can crystallize in the quaternary system is mirabilite ($Na_2SO_4 \cdot 10H_2O$).

Some differences can be found between Figure 1 and the metastable equilibrium diagram[16] for the quaternary system at 288 K. The crystallization field of $Na_2B_4O_7 \cdot 10H_2O$ becomes obviously smaller in the metastable solubility diagram than that in Figure 1; that is, the solubility of $Na_2B_4O_7 \cdot 10H_2O$ in the metastable equilibrium is supersaturated in the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K. There is no crystallization field of $Na_2SO_4 \cdot 3K_2SO_4$ in the metastable equilibrium diagram at 288 K.[16] Only thenardite (Na_2SO_4) in the quaternary system can crystallize from the saturated solution in the metastable equilibria at 288 K.[16]

■ CONCLUSIONS

The solubilities of salts, densities of solution, and coexisting equilibrium solids in the quaternary system $Na_2B_4O_7-Na_2SO_4-K_2B_4O_7-K_2SO_4-H_2O$ at 288 K were determined using an isothermal dissolution saturation method. In the phase diagram, there are three invariant points F1, F2, and F3, seven univariant curves E1−F1, E2−F1, E4−F3, E5−F3, E3−F2, F1−F2, and F2−F3, and five fields of crystallization, which correspond to $Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 4H_2O$, $Na_2SO_4 \cdot 10H_2O$, K_2SO_4, and $Na_2SO_4 \cdot 3K_2SO_4$. The experimental results show that borax has lower solubility and sulfates have higher solubilities.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sangshihua@sina.com.cn.

Funding Sources

This project was supported by the National Natural Science Foundation of China (No. 40973047), the New Century Excellent Talents in Universities of China (NCET-07-0125), and the Youth Science Foundation of Sichuan Province in China (08ZQ026-017).

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