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Solid-liquid Equilibria in the Quaternary System Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K

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Abstract According to the compositions of the underground gasfield brines in the west of Sichuan Basin, the solubilities and densities of the solid-liquid equilibria in the quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K were determined by the method of isothermal solution saturation. From the experimental data, the phase diagram, water content diagram and density-composition diagram were obtained. This quaternary system is of simple eutectic type, without double salt and solid solution. There are two invariant points, five univariant curves, four fields of crystallization in the system. The equilibrium solid phases are $Na_2B_4O_7\cdot10H_2O$, $K_2B_4O_7\cdot4H_2O$, $NaBr\cdot2H_2O$ and KBr. $Na_2B_4O_7\cdot10H_2O$ has a larger crystallization field, and $NaBr\cdot2H_2O$ has a smaller crystallization field. It is also found that bromide has the salting-out effect on borate in the quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K.

Keywords Underground brine; Phase equilibrium; Solubility; Potassium salt; Borate; Bromide

1 Introduction

The underground brine resources are rare liquid mineral resource in the world, which are distributed widely in Sichuan Basin. People have paid more and more attention to them due to their unusual element abundance and excellent quality and because of the solid mineral resource exhausting. The brine recently found in the west of Sichuan Basin has high potassium, boron contents and high concentrations of minerals. Besides NaCl, it also contains many other useful elements, which all meet or exceed their corresponding industrial grades. Especially, the potassium and boron contents of the brines are unusually high, up to 53.3 g/L and 4994 mg/L, respectively. These rare liquid mineral resources have very good exploitation and utilization prospects[1—3].

In view of the abundant borate resources, a series of studies has been conducted on the K^+-bearing and $B_4O_7^{2-}$-bearing metastable and stable phase equilibria in underground brines, salt lake brines and seawater system, such as the phase equilibria in the ternary systems $Mg_2B_4O_7$-Mg_2SO_4-H_2O at 298 K and K_2SO_4-$K_2B_4O_7$-H_2O at 288 K[4,5], quinary systems K-Mg-Cl-SO_4-NO_3-H_2O at 298 K[6], Li-Na-K-CO_3-B_4O_7-H_2O at 288 and 298 K[7,8], and the metastable phase equilibria in the quaternary systems Na_2CO_3-Na_2SO_4-$Na_2B_4O_7$-H_2O and Na-K-CO_3-B_4O_7-H_2O at 273.15 K[9,10], Li_2SO_4+K_2SO_4+Li_2CO_3+K_2CO_3+H_2O and Li_2SO_4-Li_2CO_3-$Li_2B_4O_7$-H_2O at 288 K[11,12].

Recently, a systematic study on the underground brine in Western Sichuan Basin has been carried out by our research group, such as the measurement and calculation of the phase equilibria of the quaternary system KCl-K_2SO_4-$K_2B_4O_7$-H_2O at 298 K[13,14], the measurement of the solid-liquid equilibria in the quinary system Na-K-Cl-SO_4-B_4O_7-H_2O at 298 and 323 K[15,16], as well as the quaternary systems $Na_2B_4O_7$-NaBr-Na_2SO_4-H_2O and NaCl-NaBr-$Na_2B_4O_7$-H_2O at 348 K[17,18]. And the mean activity coefficients of KCl in the KCl-$K_2B_4O_7$-H_2O ternary system at 308.15 K have also been studied[19] in the different ranges of the concentrations.

The main components in the underground brines in Western Sichuan Basin can be approximately described with the Na-K-Cl-Br-SO_4-B_4O_7-H_2O system. The quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O is a subsystem of the brine. There has been no research report about the phase equilibria of this quaternary subsystem at 298 K, which is just the object of this work. Two ternary subsystems KBr-$K_2B_4O_7$-H_2O and NaBr-$Na_2B_4O_7$-H_2O at 298 K have already been reported in our previous researches[20,21], and it will be useful to provide the foundation for this work.

2 Experimental

2.1 Reagents and Instruments

The chemicals used in this work were all analytically pure(Chengdu Kekong Chemical Reagent Factory). They were NaBr(99.0%), KBr(99.0%), $Na_2B_4O_7\cdot10H_2O$(99.0%) and

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$K_2B_4O_7·5H_2O$(99.0%). Distilled water, with a conductivity of less than $1.2×10^{-4}$ S/m and a pH value of 6.60 at 298.15 K, was used for preparing synthesized brines and chemical analysis.

A standard analytical balance with a capacity of 110 g and a resolution of 0.0001 g(AL104, the Mettler Toledo Instruments Co., Ltd.) was used to determine the solution densities.

An HZS-H type of thermostated vibrator made by Harbin Donglian Electronic Technology Co., Ltd. with an uncertainty of 0.1 K after secondary calibration by precise thermometer was used for the equilibria experiments.

2.2 Experimental Methods

The solid-liquid equilibrium experiments for quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K in this work were investigated by the isothermal dissolution equilibrium method. The system samples of the quaternary system were prepared by adding the third salt component to the invariant samples of relevant ternary subsystems at 298 K. The prepared mixtures were respectively put in sealed glass bottles that were placed in the thermostated vibrator(HZS-H). The sample temperature was maintained at (298.2±0.1) K. The solutions were taken out periodically for chemical analysis. The criterion for judging the equilibrium state of the system was the unchanging concentration of the solution. After equilibrium, the solution and wet crystals can be taken out for physicochemical analysis. The liquid phases were analyzed quantitatively by chemical methods, while the wet crystals were analyzed by X-ray diffraction to ascertain their crystalloid form[22]. The densities of the saturated solutions were determined *via* the pycnometer method (with a precision of 0.0002 g/cm^3).

2.3 Analytical Methods

Potassium ion(K^+) concentration was determined with sodium tetraphenyl borate-hexadecyltrimethyl ammonium bromide titration(with a precision of 0.5%, mass fraction). Bromide ion(Br^-) concentrations were determined by Mohr's method *via* a silver nitrate standard solution(with a precision of 0.3%, mass fraction). Borate ion($B_4O_7^{2-}$) was determined by basic titration in the presence of mannitol with phenolphthalein solution as indicator(with a precision of 0.3%, mass fraction). Sodium ion(Na^+) concentration was evaluated according to the ion charge balance.

3 Results and Discussion

The measured values of salt solubilities and solution densities of quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K are presented in Table 1, where ion concentrations are expressed in mass fraction *w*, *J* is the Jäneacke index, with $J(2Na^+) + J(2K^+)$=100 mol, and ρ is the density in g/cm^3. Based on the data in Table 1, a stable equilibrium phase diagram of the system at 298 K is given in Fig.1.

Table 1 Solubilities and densities of solution in the quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K

No.[a]	Composition of solution, *w*(%)				Jänecke index, *J*(mol/100 mol) $J(2Na^+)+J(2K^+)$=100 mol			Equilibrium solid[b]	Solution density, ρ/(g·cm^{-3})
	Na^+	K^+	Br^-	$B_4O_7^{2-}$	$J(2K^+)$	$J(2Br^-)$	$J(H_2O)$		
1(A)	9.78	2.52	39.14	0.00	13.15	100.00	1100.02	NBr + KBr	1.5795
2	9.84	2.47	39.05	0.18	12.87	99.52	1094.99	NBr + KBr	1.5801
3	9.78	2.47	38.70	0.33	12.92	99.14	1106.59	NBr + KBr	1.5818
4	9.91	2.48	38.99	0.50	12.82	98.69	1080.37	NBr + KBr	1.5843
5	9.93	2.49	39.00	0.59	12.85	98.47	1074.39	NBr + KBr	1.5864
6	9.95	2.50	39.10	0.57	12.86	98.52	1069.85	NBr + KBr	1.5874
7(B)	1.00	4.40	0.00	12.13	72.05	0.00	5854.34	NB + KB	1.1674
8	1.00	4.59	2.54	10.03	72.95	19.74	5641.59	NB + KB	1.1736
9	1.03	5.23	6.61	7.46	74.85	46.25	4943.25	NB + KB	1.1793
10	1.09	5.55	7.73	7.18	75.00	51.10	4600.59	NB + KB	1.1907
11	1.19	6.34	11.94	5.00	75.77	69.89	3920.13	NB + KB	1.2263
12	1.32	7.70	16.34	3.87	77.42	80.40	3088.64	NB + KB	1.2782
13	1.43	9.68	21.73	2.91	79.95	87.87	2303.36	NB + KB	1.3433
14	1.44	11.00	25.12	2.30	81.78	91.40	1940.30	NB + KB	1.3925
15(E)	1.29	12.03	27.19	1.81	84.63	93.58	1760.23	NB+KB+KBr	1.4215
16(C)	11.18	0.00	38.27	0.56	0.00	98.52	1141.49	NB + NBr	1.5497
17	10.62	0.76	37.89	0.55	4.03	98.53	1156.99	NB + NBr	1.5557
18	10.24	1.50	38.08	0.55	7.92	98.53	1139.01	NB + NBr	1.5701
19	9.88	2.51	38.88	0.55	12.99	98.56	1083.27	NB + NBr	1.5843
20	9.85	2.54	38.87	0.54	13.17	98.59	1084.29	NB + NBr	1.5869
21	9.88	2.56	39.02	0.55	13.23	98.58	1074.86	NB + NBr	1.5871
22(F)	9.93	2.52	39.11	0.55	13.00	98.58	1070.29	NB+NBr+KBr	1.5875
23	9.04	3.02	36.89	0.69	16.41	98.11	1187.97	NB + KBr	1.5674
24	8.23	3.81	35.55	0.81	21.42	97.72	1258.11	NB + KBr	1.5407
25	7.19	4.53	33.28	0.93	27.03	97.22	1401.08	NB + KBr	1.5121
26	5.38	6.90	31.55	1.22	42.98	96.16	1485.14	NB + KBr	1.4829
27	3.73	8.54	28.92	1.44	57.39	95.12	1673.71	NB + KBr	1.4549
28	2.28	10.25	27.23	1.59	72.53	94.32	1801.11	NB + KBr	1.4321

To be continued on the next page.

No.[a]	Composition of solution, w(%)				Jänecke index, J(mol/100 mol) $J(2Na^+)+J(2K^+)=100$ mol			Equilibrium solid[b]	Solution density, $\rho/(g\cdot cm^{-3})$
	Na^+	K^+	Br^-	$B_4O_7^{2-}$	$J(2K^+)$	$J(2Br^-)$	$J(H_2O)$		
29(D)	0.00	13.55	26.24	1.41	100.00	94.74	1882.62	KB + KBr	1.4072
30	0.19	13.33	26.42	1.43	97.64	94.71	1863.81	KB + KBr	1.4076
31	0.38	13.19	26.77	1.45	95.33	94.71	1826.40	KB + KBr	1.4063
32	0.47	13.07	26.82	1.49	94.23	94.59	1818.31	KB + KBr	1.4094
33	0.61	12.93	26.95	1.55	92.58	94.42	1800.64	KB + KBr	1.4114
34	0.84	12.56	26.89	1.64	89.83	94.08	1801.93	KB + KBr	1.4137
35	1.32	12.09	27.38	1.85	84.38	93.49	1737.00	KB + KBr	1.4159

a. Points A, B, C and D are the invariant points of the ternary subsystems $NaBr-KBr-H_2O$, $Na_2B_4O_7-K_2B_4O_7-H_2O$, $NaBr-Na_2B_4O_7-H_2O$ and $KBr-K_2B_4O_7-H_2O$ at 298 K; points E and F are two invariant points of this quaternary system at 298 K; *b*. NB: $Na_2B_4O_7\cdot 10H_2O$; KB: $K_2B_4O_7\cdot 4H_2O$; NBr: $NaBr\cdot 2H_2O$.

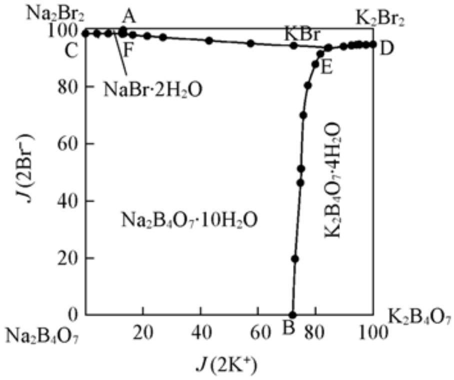

Fig.1 Dry-salt solubility diagram of quaternary system Na^+, $K^+//Br^-$, $B_4O_7^{2-}-H_2O$ at 298 K

Quaternary system Na^+, $K^+//Br^-$, $B_4O_7^{2-}-H_2O$ at 298 K has no complex salt and solid solution. There are two invariant points, five univariant curves and four regions of crystallization in this system. The four crystallization fields correspond to potassium borate tetrahydrate($K_2B_4O_7\cdot 4H_2O$), potassium bromide(KBr), sodium bromide dihydrate($NaBr\cdot 2H_2O$), and borax($Na_2B_4O_7\cdot 10H_2O$), respectively.

Five univariant curves are BE, DE, AF, CF and EF. The two invariant points of this quaternary system are respectively labeled as points E and F. Invariant point E is saturated with salts $KBr+K_2B_4O_7\cdot 4H_2O+Na_2B_4O_7\cdot 10H_2O$, and the X-ray diffraction pattern of the invariant point E in the quaternary system is given in Fig.2(A). The mass fraction composition of the corresponding liquid phase is $w(Na^+)=1.29\%$, $w(K^+)=12.03\%$, $w(Br^-)=27.19\%$, $w(B_4O_7^{2-})=1.81\%$. System $NaBr\cdot 2H_2O+KBr+Na_2B_4O_7\cdot 10H_2O$ is saturated at invariant point F, and the X-ray diffraction pattern of the quaternary system at invariant point F is given in Fig.2(B). The mass fraction composition of the corresponding liquid phase is $w(Na^+)=9.93\%$, $w(K^+)=2.52\%$, $w(Br^-)=39.11\%$, $w(B_4O_7^{2-})=0.55\%$.

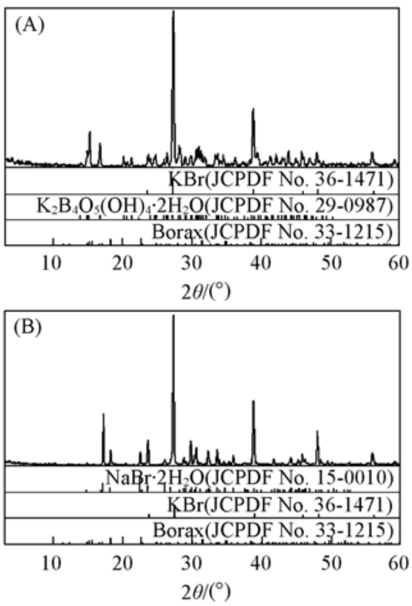

Fig.2 XRD patterns of quaternary system Na^+, $K^+//Br^-$, $B_4O_7^{2-}$- H_2O at 298 K at eutectic points E(A) and F(B)

Fig.3 is the water content diagram of quaternary system Na^+, $K^+//Br^-$, $B_4O_7^{2-}-H_2O$ at 298 K, and the abscissa is the Jänecke index of $J(2K^+)$. Fig.3 shows that the water content decreases at the uninvariant curves BE, and almost remains the same at the uninvariant curves DE, AF, CF and EF with the increase of the Jänecke index value of $J(2K^+)$. It reaches the biggest value at point B.

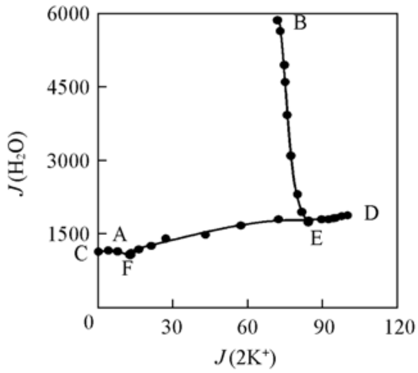

Fig.3 Water contents of saturated solutions in the quaternary system Na^+, $K^+//Br^-$, $B_4O_7^{2-}-H_2O$ at 298 K

Based on the data collected in Table 1, the density diagram of the system is constructed in Fig.4. Fig.4 shows that

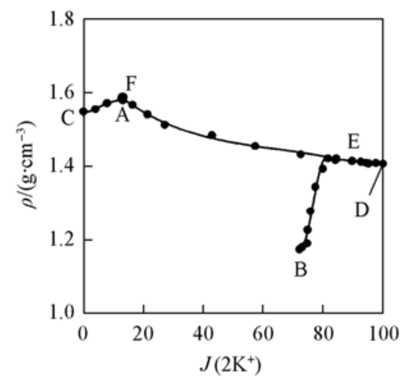

Fig.4 Density-composition relations of the solutions in the quaternary system Na^+, $K^+//Br^-$, $B_4O_7^{2-}-H_2O$ at 298 K

the density value of the system changes regularly at each of uninvariant curves, reaching a minimum value at point B(1.1942 g/cm^3).

The underground gas field brines in Western Sichuan Basin, China, are very rare liquid mineral resources in the world, and have high concentrations of potassium, boron, bromine. It could be found from Fig.1 that there are four crystallization regions in the quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K, *i.e.*, $NaBr{\cdot}2H_2O$, KBr, $K_2B_4O_7{\cdot}4H_2O$ and $Na_2B_4O_7{\cdot}10H_2O$. The crystallization regions of bromide are smaller, and the crystallization regions of borate are bigger. It is found that bromide has the salting-out effect on borate in the quaternary system at 298 K. The crystallization area of borax($Na_2B_4O_7{\cdot}10H_2O$) is larger than those of other salts. It indicates that borax has lower solubility than other salts in the quaternary system. Therefore, borax can be easily crystallized and extracted from the solution in a wide concentration range at 298 K.

4 Conclusions

The solid-liquid equilibria in the quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K was studied by the isothermal solution saturation method. Solubilities, densities and corresponding equilibrium solids were determined. The results show that this quaternary system belongs to the simple co-saturation type. The quaternary system Na^+, K^+//Br^-, $B_4O_7^{2-}$-H_2O at 298 K has two invariant points, five uninvariant curves and four crystallization regions, *i.e.*, $NaBr{\cdot}2H_2O$, KBr, $Na_2B_4O_7{\cdot}10H_2O$ and $K_2B_4O_7{\cdot}4H_2O$.

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