JOURNAL OF CHEMICAL & ENGINEERING DATA

Article

pubs.acs.org/jced

Solid−Liquid Equilibria in the Quinary System Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O at 323 K

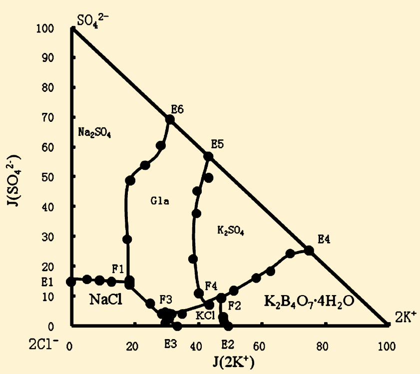
Sang Shi-Hua,*[†,‡] Zhang Xiao,[†,§] and Zhang Jun-Jie[†,‡]

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

[‡]Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, P. R. China

[§]Engineering Test Center, China Railway Eryuan Engineering Group Co., Ltd., Chengdu 610031, P. R. China

ABSTRACT: The solid−liquid equilibria in the quinary system Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O at 323 K has been studied experimentally using the method of isothermal solution saturation. Solubilities and densities of the solution of the quinary system were measured. On the basis of the solubility data and corresponding equilibrium solids, the dry-salt phase diagram and water content diagram of the quinary system were plotted, respectively. In the dry-salt solubility diagram, there are four invariant points, nine univariant curves, and six fields of crystallization saturated with $Na_2B_4O_7·10H_2O$, where the solids are Na_2SO_4, $Na_2SO_4·3K_2SO_4$(Gla), K_2SO_4, $K_2B_4O_7·4H_2O$, NaCl, and KCl, respectively. The experimental results show that Na_2SO_4, $Na_2SO_4·3K_2SO_4$(Gla), K_2SO_4, and $K_2B_4O_7·4H_2O$ have bigger fields of crystallization than other salts in the quinary system Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O at 323 K.



1. INTRODUCTION

Many salt lake brines on the Qinghai-Tibet Plateau in China are well-known for high concentration lithium, potassium, and boron.[1] Furthermore, a huge amount of underground gasfield brines was discovered recently, in Sichuan Western Basin.[2] Sodium chloride, potassium, boron, bromine, and sulfate are the major chemical components of the underground brines, and they also accompany lithium, strontium, and iodine. Particularly, the potassium ion concentration of the underground brines is up to 53.27 $g·L^{-1}$, and the boron concentration is up to 4.994 $g·L^{-1}$.[2] The proved reserves of the underground brines are up to $2.06·10^{12}$ m^3.[2] Therefore, the underground brines largely consist of the complex six-component system Na−K−Cl−B_4O_7−SO_4−Br−H_2O.

It is well-known that phase diagrams and phase equilibria play an important role in exploiting brine resources.[3] Although the underground brine resources are very valuable, nothing has been reported on their potential utilization because of the lack of data on phase equilibria and phase diagrams of the underground brine systems at different temperatures. To exploit the underground brines economically, the phase equilibria and phase diagrams of the underground brine systems at different temperatures are urgent.

The quinary system Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O is a subsystem of the six-component system. Some ternary subsystems and quaternary subsystems for the underground gasfield brines have been determined in our earlier work: $Na_2B_4O_7$−NaBr−H_2O at 298 K,[4] $K_2B_4O_7$−KBr−H_2O at 298 K,[5] K_2SO_4−$K_2B_4O_7$−KCl−H_2O at 298 K,[6] $Na_2B_4O_7$−Na_2SO_4−NaCl−H_2O[7] at 323 K, and Na_2SO_4−NaBr−H_2O[8] at 323 K. So far, no report has been found in the literature concerning the equilibrium solubility measurement of this quinary system Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O at 323 K. Accordingly, in this paper, the solid−liquid stable equilibria of the quinary system are presented in detail at 323 K.

2. EXPERIMENT

2.1. Reagents and Instruments. Distilled water with a conductivity less than 10^{-4} $S·m^{-1}$ and pH of 6.6 was used for solubility experiments and chemical analysis. The reagents used were of analytical purity grade and obtained from the following suppliers: Na_2SO_4, K_2SO_4, $Na_2B_4O_7·10H_2O$, NaCl, and KCl (Chengdu KeLun Chemical Reagent Factory, China) and $K_2B_4O_7·4H_2O$ (Beijing YiLi Chemical Reagent Factory, China).

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

2.2. Experimental Method. The experiments of phase equilibria have been done by the method of isothermal solution saturation. The system points for the quinary system were compounded by adding the fourth component gradually on the basis of the quaternary invariant points at 323 K. Then the samples were poured into a sealed tube and placed in the thermostatted vibrator (HZS-H). The sealed tubes with solution were stirred for over two weeks. The time of clarification was about 10 days. The solutions were taken out periodically for chemical analysis. When composition of a solution does not change, the system should reach equilibrium state. After equilibrium, the compositions of solution were determined by chemical analysis.

Received: October 31, 2011
Accepted: February 9, 2012
Published: February 16, 2012

Table 1. Solubilities and Densities of the Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O System at 323 K

	composition of solution 100w(b)					Janecke index J (mol/100 mol), $2K^+ + 2Cl^- + SO_4^{2-}$ = 100 mol					density ρ
no.	K^+	Na^+	SO_4^{2-}	$B_4O_7^{2-}$	Cl^-	$2K^+$	$2Cl^-$	SO_4^{2-}	H_2O	solid phase[a]	$g\cdot cm^{-3}$
1(E1)	0.00	10.85	3.14	2.01	13.51	0.00	85.34	14.66	1741.10	NS+NL+NB	1.2444
2	0.89	10.69	3.65	2.10	13.66	4.72	79.58	15.70	1586.25	NS+NL+NB	1.2436
3	1.78	10.31	3.71	2.20	13.78	8.91	75.98	15.11	1483.64	NS+NL+NB	1.2523
4	2.63	9.96	3.78	2.25	13.94	12.47	72.91	14.62	1390.88	NS+NL+NB	1.2564
5(F1)	4.20	9.24	3.88	2.38	14.13	18.34	67.87	13.79	1254.18	NS+NL+NB +Gla	1.2707
6(E2)	12.86	2.06	0.00	6.25	12.02	49.28	50.73	0.00	1002.00	KL+KB+NB	1.2635
7	12.40	3.45	0.43	9.62	11.87	48.02	50.61	1.36	1046.85	KL+KB+NB	1.3017
8	12.40	3.47	0.64	9.44	11.82	47.80	50.20	2.01	1042.60	KL+KB+NB	1.3056
9	12.45	3.53	0.90	9.45	11.77	47.62	49.57	2.81	1028.79	KL+KB+NB	1.3073
10	12.46	3.47	0.89	9.44	11.69	47.81	49.39	2.79	1034.28	KL+KB+NB	1.3085
11(E3)	8.88	6.25	0.00	3.41	16.16	33.28	66.72	0.00	1063.44	NL+KL+NB	1.2545
12	7.80	7.12	0.38	2.90	16.75	29.38	69.46	1.16	1064.20	NL+KL+NB	1.2664
13	8.15	6.91	0.78	3.10	16.08	30.76	66.84	2.40	1065.23	NL+KL+NB	1.2759
14(F3)	7.41	7.62	1.30	3.84	15.77	28.68	67.23	4.10	1077.14	NL+KL+NB +Gla	1.2901
15	5.89	7.87	2.16	2.64	14.70	24.71	67.90	7.39	1216.24	NL+NB+Gla	1.2577
16	7.21	7.73	1.25	4.11	15.68	28.28	67.73	3.99	1090.23	NL+NB+Gla	1.2973
17(E4)	9.56	1.53	3.94	17.78	0.00	74.88	0.00	25.12	2285.33	KS+KB+NB	1.3191
18	9.28	1.90	4.04	16.47	0.84	68.79	6.82	24.40	2172.50	KS+KB+NB	1.3008
19	9.23	2.89	3.34	17.08	2.55	62.52	19.05	18.44	1909.89	KS+KB+NB	1.3236
20	8.94	3.25	3.05	15.93	3.60	58.10	25.79	16.11	1842.08	KS+KB+NB	1.3164
21	8.99	3.48	2.53	12.42	5.98	50.97	37.36	11.67	1640.24	KS+KB+NB	1.2910
22(F2)	8.89	3.62	2.13	9.32	7.44	47.24	43.53	9.22	1562.94	KS+KB+NB +KL	1.3088
23(F4)	8.85	3.84	1.74	7.47	9.26	43.24	49.84	6.92	1461.28	KS+Gla+NB +KL	1.2662
24	8.83	5.71	1.28	3.91	14.09	34.77	61.13	4.11	1132.15	Gla+NB+KL	1.2601
25	7.77	6.40	1.23	3.73	14.33	31.65	64.26	4.09	1177.51	Gla+NB+KL	1.2879
26	7.96	7.07	1.26	4.21	15.29	30.82	65.21	3.97	1080.46	Gla+NB+KL	1.2970
27	7.65	7.46	1.40	3.95	15.63	29.43	66.19	4.38	1068.01	Gla+NB+KL	1.2966
28(E6)	4.74	5.25	13.01	6.10	0.00	30.90	0.00	69.10	2010.31	Gla+NB+NS	1.2672
29	4.80	5.96	12.67	5.40	1.73	28.22	11.17	60.61	1773.14	Gla+NB+NS	1.2662
30	4.14	7.00	11.79	4.76	3.68	23.28	22.79	53.93	1675.29	Gla+NB+NS	1.2778
31	3.60	8.29	11.58	3.77	5.79	18.56	32.87	48.57	1498.36	Gla+NB+NS	1.2776
32	3.71	9.00	7.65	2.75	10.36	17.39	53.44	29.17	1353.07	Gla+NB+NS	1.2669
33	4.39	9.60	4.43	2.37	14.46	18.36	66.56	15.08	1175.62	Gla+NB+NS	1.2677
34(E5)	8.93	2.89	14.45	4.12	0.00	43.14	0.00	56.86	1461.50	Gla+NB+KS	1.3576
35	9.90	3.01	13.98	3.89	1.53	43.12	7.32	49.56	1280.12	Gla+NB+KS	1.3345
36	10.06	4.27	14.21	3.66	3.55	39.40	15.31	45.29	1092.95	Gla+NB+KS	1.3136
37	10.27	4.33	12.18	3.38	5.46	39.21	22.96	37.83	1067.34	Gla+NB+KS	1.2940
38	10.63	4.72	7.70	2.83	9.96	38.15	39.35	22.50	1000.21	Gla+NB+KS	1.2655
39	13.10	4.78	4.32	2.47	14.54	40.15	49.08	10.77	812.85	Gla+NB+KS	1.2687

[a]Note: KB, $K_2B_4O_7\cdot4H_2O$; NB, $Na_2B_4O_7\cdot10H_2O$; KS, K_2SO_4; NS, Na_2SO_4; NL, NaCl; KL, KCl; Gla, $Na_2SO_4\cdot3K_2SO_4$.

Wet crystals are separated from the liquid phase by vacuum filtration using a sintered glass crucible and dried for X-ray diffraction. A Rigaku D/max-3C X-ray diffraction analyzer (Japan) was used for solid phase X-ray diffraction analysis.

The densities of the solution were measured using a pycnometer with an uncertainty of 0.0002 $g\cdot cm^{-3}$.

2.3. Analytical Methods.[9] The concentration K^+ was measured by sodium tetraphenylborate–hexadecyl trimethyl ammonium bromide titration (uncertainty of 0.5 %). The concentration $B_4O_7^{2-}$ was evaluated by basic titration with the existence of mannitol (precision: ± 0.3 %). The concentration SO_4^{2-} was determined by a method of mixing barium chloride and magnesium chloride/ethylenediaminetetraacetic acid (EDTA) titration (uncertainty of 0.5 %). The concentration Cl^- was measured by titration with silver nitrate standard solution in the presence of potassium bichromate (uncertainty ± 0.3 %). The concentration Na^+ is evaluated according to the ion balance.

3. RESULTS AND DISCUSSION

The equilibrium experimental results of solubilities, densities, and equilibrium solids for the quinary system Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 323 K are given in Table 1.

The ion concentration values of the equilibrium solutions are expressed in mass fractions w(b), where b represents the ion. 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 (SO_4^{2-}), J ($2K^+$), J ($2Cl^-$), and J (H_2O)

are respective ion and water Jänecke index values. The ion and water Jänecke index values are calculated as follows:

$$w(Na^+) = 22.99 \cdot 2[w(SO_4{}^{2-})/M_{SO_4} + w(B_4O_7{}^{2-})/M_{B_4O_7} + w(Cl^-)/2M_{Cl} - w(K^+)/(2M_K)] \text{ g/100 g solution}$$

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

$$\text{Let } [b] = w(SO_4{}^{2-})/M_{SO_4} + w(K^+)/(2M_K) \text{ mol} + w(Cl^-)/2M_{Cl}, \text{ then}$$

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

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

$$J(2Cl^-) = 100w(Cl^-)/2M_{Cl}/[b] \text{ mol/100 mol}$$

$$J(H_2O) = 100w(H_2O)/M_{H_2O}/[b] \text{ mol/100 mol}$$

W (ion) and w (H_2O) are the mass of ion and water in grams per 100 g of solution. J(ion) and $J(H_2O)$ are the Jänecke index values of ion and water, and M_{ion} is the molecular weight of the ion.

According to Jänecke index values of J ($SO_4{}^{2-}$), J ($2K^+$), J ($2Cl^-$), and $J(H_2O)$, the isothermal solubility diagram was plotted in Figure 1.

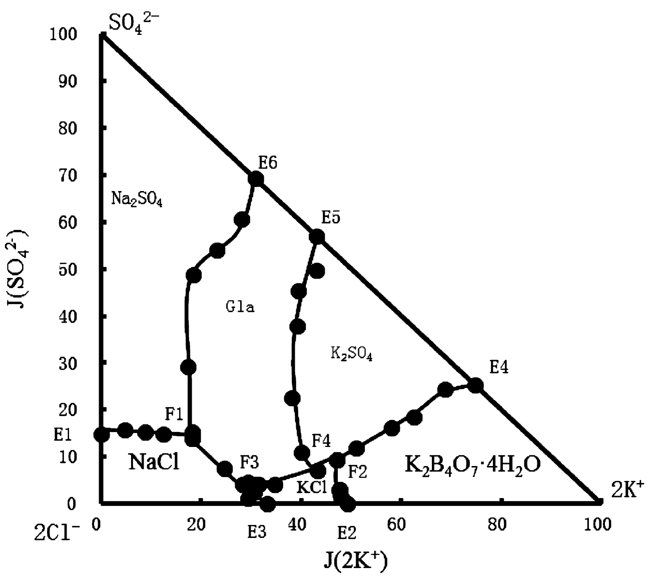


Figure 1. Dry-salt solubility diagram of the quinary system Na^+, K^+//Cl^-, $SO_4{}^{2-}$, $B_4O_7{}^{2-}$–H_2O at 323 K saturated with $Na_2B_4O_7 \cdot 10H_2O$.

The quinary phase diagram in Figure 1 has six crystallization fields saturated with $Na_2B_4O_7 \cdot 10H_2O$, where the corresponding solids are $K_2B_4O_7 \cdot 4H_2O$ (E2F2E4 field), K_2SO_4 (E4F2F4E5 field), Na_2SO_4 (E1F1E6 field), $Na_2SO_4 \cdot 3K_2SO_4$ (E5F4F3F1E6 field), NaCl (E1F1F3E3 field), and KCl (E3F3F4F2E2 field), respectively. The crystallization fields of NaCl and KCl are much smaller than those of the other salts (namely, Na_2SO_4, $K_2B_4O_7 \cdot 4H_2O$, $Na_2SO_4 \cdot 3K_2SO_4$, and K_2SO_4). This indicates NaCl and KCl have larger solubilities than other salts under the experimental conditions.

The bigger crystallization regions in the phase diagram indicate those are of low solubility. Experimental results imply the possible formation of potassium salts (K_2SO_4 and $Na_2SO_4 \cdot 3K_2SO_4$) crystal in gasfield brine.

There are nine double saturated curves: E1F1, E2F2, E3F3, E4F2, E5F4, E6F1, F1F3, F3F4, and F2F4. According to the modified Gibbs phase rule, there should be five coexisting phases at each quinary invariant point, where four are solids and one is solution. The solids at each invariant point are clearly shown in Figure 1. The corresponding water content diagram of the quinary system is plotted in Figure 2, where $J(2K^+)$ and $J(H_2O)$ are chosen as coordinate variables.

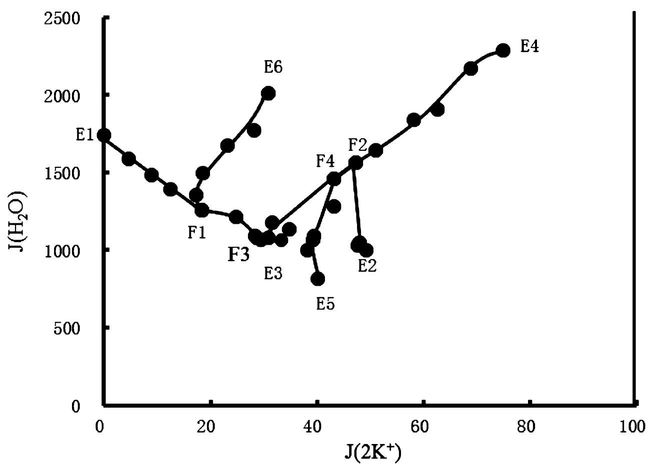


Figure 2. Water content diagram of the quinary system Na^+, K^+//Cl^-, $SO_4{}^{2-}$, $B_4O_7{}^{2-}$–H_2O at 323 K.

The point F1 represents the equilibrium of four solid phases ($Na_2B_4O_7 \cdot 10H_2O$, $Na_2SO_4 \cdot 3K_2SO_4$(Gla), Na_2SO_4, and NaCl).

The point F2 represents the equilibrium of four solid phases ($Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 4H_2O$, K_2SO_4, and KCl).

The point F3 represents the equilibrium of four solid phases ($Na_2B_4O_7 \cdot 10H_2O$, $Na_2SO_4 \cdot 3K_2SO_4$(Gla), KCl, and NaCl).

The point F4 represents the equilibrium of four solid phases ($Na_2B_4O_7 \cdot 10H_2O$, K_2SO_4, $Na_2SO_4 \cdot 3K_2SO_4$(Gla), and KCl).

To explain the water content in the phase diagram, the corresponding water content diagram of the quinary system Na^+, K^+//Cl^-, $SO_4{}^{2-}$, $B_4O_7{}^{2-}$–H_2O at 323 K is plotted in Figure 2 using the Jänecke index values of $J(2K^+)$ and $J(H_2O)$.

The solubility experimental data in Table 1 and Figure 2 show that water contents for the invariant points decrease apparently from E4–F2 and E6–F1. It also implies that NaCl and KCl have higher solubilities than other salts in the quinary system at 323 K.

There are no solid solutions formed in this quinary system at 323 K. Double salt glaserite ($Na_2SO_4 \cdot 3K_2SO_4$) formed in the equilibrium of the quinary system Na^+, K^+//Cl^-, $SO_4{}^{2-}$, $B_4O_7{}^{2-}$–H_2O at 323 K. The borate ions exist with the $B_4O_5(OH)_4{}^{2-}$ ion in saturated solution, and the chemical structure types of borates are $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ and $K_2[B_4O_5(OH)_4] \cdot 2H_2O$. On the basis of equilibrium data of the ternary system Na_2SO_4–K_2SO_4–H_2O at different temperatures,[10,11] the sodium sulfates can crystallize from saturation solution in the form of $Na_2SO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$, or Na_2SO_4. When the temperature attains 308 K, those sodium

dx.doi.org/10.1021/je201138z | J. Chem. Eng. Data 2012, 57, 907–910

sulfates only crystallize from saturation solution in the form of thenardite (Na_2SO_4). In this studied quinary system at 323 K, the crystallization fields of Gla and Na_2SO_4 exist simultaneously.

4. CONCLUSION

The solid−liquid equilibria in the quinary system Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O at 323 K were studied by isothermal solution saturation method. Solubilities, densities, and corresponding equilibrium solids were determined. On the basis of experimental data, the phase diagram is plotted. In the phase diagram, there are four invariant points; nine univariant curves, and six fields of crystallization saturated with $Na_2B_4O_7\cdot 10H_2O$ corresponding to Na_2SO_4, $Na_2SO_4\cdot 3K_2SO_4$(Gla), K_2SO_4, $K_2B_4O_7\cdot 4H_2O$, NaCl, and KCl.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail:sangsh@cdut.edu.cn; sangshihua@sina.com.cn.

Funding

This project was supported by the National Natural Science Foundation of China (No. 40973047) and the Young Science Foundation of Sichuan Province in China (08ZQ026-017).

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Zheng, X. Y.; Zhang, M. G.; Xu, Y.; Li, B. X. *Salt Lakes of China* (in Chinese); Science Press: Beijing, 2002.

(2) Lin, Y. T. Geochemical characteristics of gas field water in one field in west Sichuan and its development evaluation. *Nat. Gas Ind.* **2000**, *20* (5), 9−14 ; in Chinese.

(3) Song, P. S. Comprehensive Utilization of Salt Lake and Related Resources. *J. Salt Lake Res.* **2000**, *8* (2), 33−58 ; in Chinese.

(4) Sang, S. H.; Yin, H. A.; Ni, S. J.; Zhang, C. J. A study on equilibrium solubilities and properties of solutions in the ternary system $K_2B_4O_7$ - KBr - H_2 O at 298 K. *J. Chengdu Univ. Technol. (Sci. Technol. Ed.)* **2006**, *33* (4), 414−416 ; in Chinese.

(5) Sang, S. H.; Yu, H. Y. Study on the Phase Equilibrium of $Na_2B_4O_7$−NaBr−H_2O Ternary System at 298 K. *Sea-Lake Salt Chem. Ind.* **2006**, *35* (2), 4−6 ; in Chinese.

(6) Zhang, Z. L.; Sang, S. H; Li, M.; Hou, C. H. Study on Equilibrium of the Quaternary System $K_2B_4O_7$−K_2SO_4−KCl−H_2O at 298 K. *Chem. Eng.* **2009**, *37* (5), 46−48 ; in Chinese.

(7) Zhang, X.; Sang, S. H.; Lai, C. H.; Sun, M. L. Study on Equilibrium of the Quaternary System $Na_2B_4O_7$−Na_2SO_4−NaCl−H_2O at 323 K. *Chem. Eng.* **2009**, *37* (11), 44−46 ; in Chinese.

(8) Sun, M. L.; Sang, S. H.; Li, H.; Zhao, X. Y. Study on Equilibrium of the Ternary System Na_2SO_4−NaBr−H_2O at 323 K. *Chem. Eng.* **2010**, *38*, 67 ; in Chinese.

(9) Institute of Qinghai Salt-Lake, Chinese Academy of Sciences. *Analytical Methods of Brines and Salts* (in Chinese), 2nd ed.; Science Press: Beijing, 1988.

(10) Niu, Z. D.; Cheng, F. Q. *The Phase Diagram of Salt-Water Syatem and Its Application* (in Chinese); Tianjin University Press: Tianjin, 2002.

(11) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds, v. 2: Ternary and Multicomponent Systems*; Pergamon Press, Macmillan: Oxford, U.K., 1979.