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(Liquid + Solid) Phase Equilibria in the Quinary System $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K

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An experimental study on phase equilibria at 288 K in the quinary system $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ was done by the isothermal solution saturation method. Equilibrium solubilities and properties such as the density, electrical conductivity, and pH of the equilibrium solution were determined experimentally. According to the experimental data, the equilibrium phase diagram saturated with Li_2CO_3 was constructed. The phase diagram of the quinary system has four invariant points, nine univariant curves, and six crystallization fields ($K_2CO_3 \cdot {}^3/_2H_2O$, $K_2B_4O_7 \cdot 4H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, $NaKCO_3 \cdot 6H_2O$, and $Li_2B_4O_7 \cdot 3H_2O$). Potassium carbonate ($K_2CO_3 \cdot 3/2H_2O$) has the smallest crystallization field. The borates ($K_2B_4O_7 \cdot 4H_2O$, $Li_2B_4O_7 \cdot 3H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$) have larger crystallization fields than the others. The double salt $NaKCO_3 \cdot 6H_2O$ was found in the quinary system.

Introduction

Salt lakes are naturally occurring complex bodies of water and salt. It is well known that liquid−solid phase equilibrium plays an important role in exploiting salt lake brine resources and describing the geochemical evolution of brine minerals.

Of all of the salt lakes in China, the Zhabuye salt lake has characteristics that are distinct from others: it has an area of 240 km^2 and is famous for its high concentrations of lithium, boron, and potassium. The main components are Li^+, K^+, Na^+, Rb^+, Cs^+, $B_4O_7^{2-}$, CO_3^{2-}, Cl^-, SO_4^{2-}, and H_2O.[1,2] The salt lake brines have high concentrations of potassium and sodium and low concentrations of calcium and magnesium, with abundant lithium and boron. Low concentrations of calcium and magnesium are advantageous for recovering lithium from brines.

Measurements of the solubilities and properties of the complex multicomponent brines are needed. This quinary system is a subsystem of Zhabuye salt lake brines. Some studies have been done on the solubility of quaternary subsystems $Li^+ + Na^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$, $Li^+ + Na^+ + K^+ + B_4O_7^{2-} + H_2O$, and $Na_2CO_3 + K_2B_4O_7 + K_2CO_3 + Na_2B_4O_7 + H_2O$ at 288 K.[3−5] The present article is a continuation of a previously undertaken project. The research of phase equilibria at different temperature for the Zhabuye salt lake, however, is the basis of the exploitation of brine resources. So far, no report has been found on the phase equilibria of the quinary system at 288 K. To exploit salt lake brines fully, the phase equilibrium of the quinary system $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K was studied because the average temperature of Tibet in the summer is about 288 K.

The objectives of this paper are to (1) measure the solubilities and physicochemical properties such as the pH, density, and electrical conductivity in the equilibrium solution for the quinary system $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K, (2) identify the equilibrium solid phase, and (3) construct the phase diagram for the quinary system on the basis of experimental results.

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Experimental Section

Reagents. All chemicals used were of analytical purity grade and were obtained from the following suppliers: Li_2CO_3 (99.5 mass %), K_2CO_3 (99.5 mass %), Na_2CO_3 (99.5 mass %), $Na_2B_4O_7 \cdot 10H_2O$ (99.8 mass %) − ChengDu KeLun Chemical Reagent manufactory, China; $Li_2B_4O_7$ (99.5 mass %), $K_2B_4O_7 \cdot 5H_2O$ (99.5 mass %) − BeiJing XingHua Chemical Reagent Manufactory, China. The electrical conductivity of distilled water is less than 1×10^{-4} S·m^{-1} at pH 6.6.

Instruments. An HZS-H type thermostated vibrator with the temperature controlled to (288.0 ± 0.1) K was used for the equilibrium measurement.

A PHS-3C type digital acidometer with an uncertainty of 0.01 was used to measure pH values of the equilibrium solution. The pH meter was calibrated with a standard buffer solution of either phosphate dihydrogen phosphate (pH 6.863) or Borax (pH 9.183).

A DDZ-11A type conductometer with an uncertainty of 0.1 S·m^{-1} was used to measure 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 quinary system were compounded by adding the fourth component gradually on the basis of the quaternary subsystem salt saturation points at 288 K. The mixed brines were put into a sealed tube and placed in the thermostated vibrator (HZS-H) whose temperature was controlled to (288.0 ± 0.1) K. The sealed tubes with solution were stirred for over 2 weeks. The time of clarification was about 10 days. The solutions were taken out periodically for chemical analysis. When the concentrations of solution did not change, equilibria were attained. After equilibrium, the liquid phase were taken out and quantitatively analyzed. The solid phase was separated from the solution at the corresponding temperature. After the wet residue mixture was filtered out, one part of the solid phase was dissolved into water and analyzed by a chemical method. The other part was dried at room temperature, ground into a powder, and then analyzed by X-ray diffraction.

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Table 1. Solubilities w, Janecke Index Y, Density ρ, and Electrical Conductivity κ of the Solution in the Quinary System $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K

composition of solution $100w$(b)					Janecke index Y $2K^+ + 2Na^+ + B_4O_7^{2-} = 100$ mol								
$w(Li^+)$	$w(Na^+)$	$w(K^+)$	$w(CO_3^{2-})$	$w(B_4O_7^{2-})$	$Y(2Na^+)$	$Y(2K^+)$	$Y(B_4O_7^{2-})$	$Y(2Li^+)$	$Y(H_2O)$	equilibrium solid phase[a]	ρ/g·cm^{-3}	pH	κ/S·m^{-1}
0.30	0.00	4.30	2.27	6.05	0.00	58.55	41.45	23.02	5134.79	lb + kb + lc	1.156	9.95	4.4
0.27	0.77	3.66	2.54	6.33	16.06	44.88	39.06	18.60	4592.19	lb + kb + lc	1.161	9.78	4.5
0.24	1.34	3.09	2.93	5.75	27.45	37.47	35.08	16.35	4553.01	lb + kb + lc	1.166	9.15	4.6
0.23	1.54	2.83	2.84	6.06	30.77	33.32	35.91	15.28	4413.34	lb + kb + lc	1.170	8.70	4.6
0.33	2.21	2.54	3.65	6.74	38.75	26.23	35.02	19.03	3781.93	lb + kb + nb + lc	1.171	8.72	4.8
0.19	1.20	0.00	1.60	2.00	67.15	0.00	32.85	33.69	13727.15	nb + lb + lc	1.056	10.31	3.0
0.27	1.51	0.14	2.13	2.88	61.71	3.37	34.92	36.56	9717.44	nb + lb + lc	1.061	10.01	2.8
0.37	1.46	0.61	2.47	3.89	49.13	12.09	38.79	41.20	7830.45	nb + lb + lc	1.067	8.98	3.0
0.34	1.47	0.81	2.4	4.18	46.15	14.97	38.88	35.42	7271.73	nb + lb + lc	1.085	8.89	3.1
0.31	1.74	1.28	2.66	5.04	43.64	18.90	37.45	25.98	5693.07	nb + lb + lc	1.092	8.79	3.2
0.28	2.03	1.50	2.73	5.92	43.50	18.92	37.58	19.92	4784.49	nb + lb + lc	1.108	8.68	3.3
0.16	1.94	1.85	2.48	5.56	41.49	23.29	35.22	11.04	4801.32	nb + lb + lc	1.158	8.71	3.4
0.23	2.12	1.80	2.78	6.12	42.42	21.24	36.34	15.32	4445.56	nb + lb + lc	1.167	8.69	3.4
0.15	2.69	2.57	3.74	6.17	44.58	25.10	30.32	8.12	3583.41	nb + kb + lc	1.185	8.89	4.8
0.16	3.07	2.67	4.53	5.74	48.37	24.80	26.83	8.35	3373.83	nb + kb + lc	1.191	9.77	4.8
0.17	3.85	2.66	5.71	5.24	55.65	21.84	22.50	8.34	3049.48	nb + kb + lc	1.211	9.85	4.9
0.19	4.52	2.84	6.85	5.31	58.17	21.55	20.28	8.15	2640.58	nb + kb + lc	1.236	10.02	5.1
0.15	5.63	3.03	8.15	5.61	61.99	19.68	18.33	5.47	2179.04	nb + kb + lc	1.245	10.12	5.2
0.05	7.86	0.00	9.86	1.54	94.50	0.00	5.50	1.99	2482.42	nb + nc + lc	1.199	10.96	5.0
0.09	7.26	0.60	9.45	2.24	87.69	4.28	8.03	3.60	2481.43	nb + nc + lc	1.203	10.23	5.1
0.18	6.37	1.95	8.98	4.13	72.83	13.15	14.02	6.79	2291.49	nb + nc + lc	1.229	10.26	5.2
0.17	6.22	3.19	8.91	6.19	62.60	18.92	18.48	5.67	1936.05	nb + nc + lc + kb	1.250	10.25	5.3
0.13	5.91	8.07	15.40	0.00	55.39	44.61	0.00	4.04	1688.42	nk + nc + lc	1.389	12.30	6.1
0.12	5.96	8.51	14.59	0.65	53.36	44.92	1.73	3.56	1604.81	nk + nc + lc	1.401	12.42	6.1
0.11	5.62	9.61	14.82	0.98	48.54	48.95	2.51	3.15	1519.75	nk + nc + lc	1.416	12.48	6.3
0.12	5.44	10.23	14.52	2.48	44.54	49.43	6.03	3.26	1407.19	nk + nc + lc	1.439	12.56	6.2
0.10	6.36	12.05	16.88	2.88	44.40	49.63	5.97	2.31	1101.72	nk + nc + lc	1.457	12.62	6.0
0.04	1.28	29.13	24.04	0.00	6.93	93.07	0.00	0.72	630.06	nk + kc + lc	1.542	13.14	5.5
0.06	1.26	28.70	23.94	0.75	6.84	91.95	1.21	1.08	628.75	nk + kc + lc	1.545	13.20	5.2
0.08	1.27	28.44	23.28	1.48	6.85	90.77	2.38	1.35	628.71	nk + kc + lc	1.549	13.02	4.8
0.08	1.26	28.41	23.19	1.71	6.80	90.46	2.74	1.47	625.68	nk + kc + lc	1.546	12.93	4.5
0.07	1.25	28.37	22.82	2.42	6.70	89.46	3.84	1.22	615.79	nk + kc + lc	1.547	12.94	4.8
0.03	0.00	29.96	22.45	1.88	0.00	96.94	3.06	0.49	640.52	kc + kb + lc	1.533	13.14	5.9
0.05	0.48	29.38	22.85	1.54	2.64	94.85	2.50	0.91	639.31	kc + kb + lc	1.541	13.23	4.9
0.08	0.64	29.18	23.07	1.38	3.48	94.27	2.24	1.38	639.20	kc + kb + lc	1.542	13.12	5.0
0.08	0.94	28.87	23.29	1.27	5.13	92.81	2.05	1.45	634.54	kc + kb + lc	1.546	13.18	5.0
0.07	1.29	28.51	23.3	1.60	6.92	90.52	2.56	1.28	622.32	kc + kb + lc	1.548	13.19	5.0
0.20	6.35	4.85	11.17	4.38	60.42	27.21	12.37	6.21	1776.22	kb + nc + lc	1.251	10.22	5.4
0.19	5.75	8.85	13.64	3.81	47.53	43.13	9.34	5.09	1430.87	kb + nc + lc	1.286	10.60	5.5
0.15	5.92	11.10	15.84	2.73	44.61	49.29	6.10	3.64	1236.54	kb + nc + lc	1.335	10.82	5.5
0.13	6.29	12.31	17.3	2.45	44.06	50.85	5.09	3.09	1101.16	kb + nc + lc	1.376	11.32	5.6
0.08	6.48	13.01	17.69	2.93	43.14	51.07	5.79	1.85	1017.34	kb + nc + lc + nk	1.469	12.60	5.9
0.07	5.34	16.49	19.15	2.06	34.05	62.05	3.90	1.48	927.72	kb + nk + lc	1.488	12.77	6.2
0.07	3.60	20.53	19.95	2.18	22.02	74.02	3.96	1.42	838.48	kb + nk + lc	1.505	12.90	5.8
0.06	2.23	24.78	21.36	2.23	12.71	83.50	3.78	1.14	720.56	kb + nk + lc	1.522	13.05	5.7
0.07	1.49	27.18	22.24	2.37	8.19	87.95	3.86	1.27	654.08	kb + nk + lc	1.540	13.10	5.5
0.07	1.21	28.56	23.03	2.15	6.47	90.12	3.41	1.29	614.98	kb + kc + lc + nk	1.549	13.13	5.5

[a] Note: kb, $K_2B_4O_7 \cdot 4H_2O$; lb, $Li_2B_4O_7 \cdot 3H_2O$; nb, $Na_4B_4O_7 \cdot 10H_2O$; kc, $K_2CO_3 \cdot {}^3/_2H_2O$; lc, Li_2CO_3; nc, $Na_2CO_3 \cdot 10H_2O$; nk, $NaKCO_3 \cdot 6H_2O$; w(b), mass fraction.

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

Analytical Methods. The potassium ion concentration was measured by adding quantitative sodium tetraphenylboron−hexadecyl trimethylammonium bromide by titration (uncertainty of 0.5 %). The potassium ion and sodium tetraphenylboron forms potassium tetraphenylboron ($K[B(C_6H_5)_4]$) under basic conditions, and the excess sodium tetraphenylboron was titrated by 0.35 % hexadecyl trimethylammonium bromide using thiazole yellow solution as the indicator. The carbonate ion concentration was determined by a method of acidic titration by applying 0.1 mol·dm^{-3} HCl (uncertainty of 0.18 %). The borate ion concentration was evaluated by using basic titration (0.05 mol·dm^{-3} NaOH) with the existence of mannitol with phenolphthalein solution as the indicator (uncertainty of 0.3 %). The lithium ion concentration was determined by atomic absorption spectrophotometery (AAS) (uncertainty of less than 0.5 %), and Na^+ was evaluated according to the ion balance.

Results and Discussion

The phase equilibrium experimental results of solubilities and properties for quinary system $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K were determined and are tabulated in Table 1.

The ion concentration values in the equilibrium solution were expressed in mass fraction w(b). To plot the quinary system diagram, Janecke index values were necessary. Janecke index values were the dry salt mole index.

According to Janecke index values, the phase diagram (saturated with Li_2CO_3) was plotted in Figure 1.

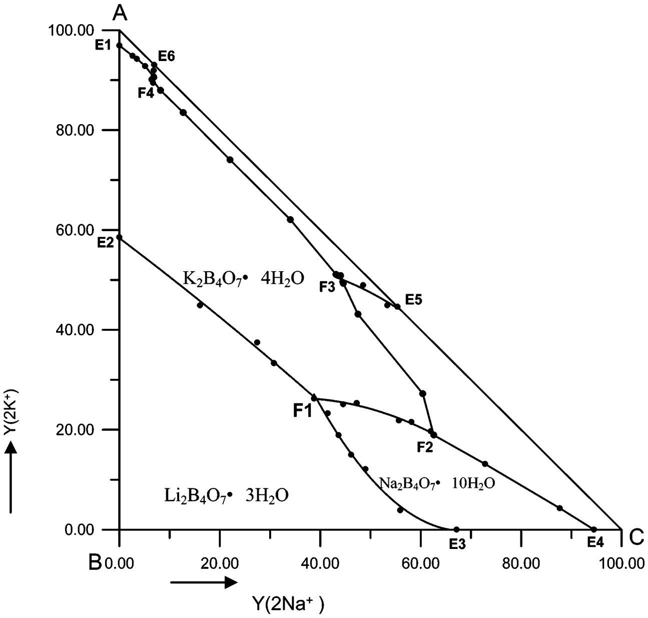

Figure 1. Phase diagram of the quinary system $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 288$ K (saturated with Li_2CO_3): ●, Experimental data point; lines, experimental phase diagram.

The phase diagram of the quinary system has six crystallization fields all saturated with Li_2CO_3 in Figure 1: ($K_2CO_3 \cdot {}^3/_2H_2O$(AE1F4E6A), $K_2B_4O_7 \cdot 4H_2O$(E1E2F1F2F3F4E1), $Li_2B_4O_7 \cdot 3H_2O$(E2BE3F1E2), $Na_2B_4O_7 \cdot 10H_2O$(E3F1F2E4E3), $Na_2CO_3 \cdot 10H_2O$(CE4F2F3E5C), and $NaKCO_3 \cdot 6H_2O$(E5F3F4E6E5)). Potassium carbonate ($K_2CO_3 \cdot {}^3/_2H_2O$) has the smallest crystallization field, which corresponds to the largest solubility in the quinary system. The borates ($K_2B_4O_7 \cdot 4H_2O$, $Li_2B_4O_7 \cdot 3H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$) have larger crystallization fields than others, which means that borates are very easily separated out from solution.

There are nine univariant curves (E2F1, E3F1, F1F2, E4F2, F2F3, E5F3, F3F4, E6F4, and E1F4) and four invariant points (F1, F2, F3, and F4).

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

Conclusions

Phase equilibria of the quinary system $Li^+ + Na^+ + K^+ + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 288 K were studied by the isothermal solution saturation method. Solubilities and properties such as the density, electrical conductivity, and pH were determined experimentally. According to the experimental results, the phase diagram was plotted. There are seven solid phases under the condition of phase equilibria for the quinary system: Li_2CO_3, $K_2CO_3 \cdot {}^3/_2H_2O$, $K_2B_4O_7 \cdot 4H_2O$, $Li_2B_4O_7 \cdot 3H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, and $NaKCO_3 \cdot 6H_2O$. The crystallization fields of borates were $K_2B_4O_7 \cdot 4H_2O$, $Li_2B_4O_7 \cdot 3H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$ in the equilibrium phase diagram at 288 K.

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