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Metastable Phase Equilibrium in the Quaternary System $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ at 273 K

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The metastable phase equilibrium in the quaternary system $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ was studied at 273 K using an isothermal evaporation method. The solubility and the density of the equilibrated solution were determined. On the basis of the solubility data, the metastable phase diagram and the water diagram were plotted. The phase diagram consists of three invariant points, seven univariant curves, and five metastable crystallization fields. Among the three invariant points, points E_1 and E_3 are a commensurate invariant point type, while point E_2 is a incommensurate invariant point type. The three cosaturated salts for points E_1, E_2, and E_3 are $NaCl + KCl + Na_2CO_3 \cdot 10H_2O$, $KCl + Na_2CO_3 \cdot 10H_2O + KNaCO_3 \cdot 6H_2O$, and $KCl + K_2CO_3 \cdot 3/2H_2O + KNaCO_3 \cdot 6H_2O$, respectively. The five metastable crystallization fields correspond to the single salts potassium chloride (KCl), sodium chloride (NaCl), sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), potassium carbonate sesquihydrate ($K_2CO_3 \cdot 3/2H_2O$), and a hexahydrate double salt of potassium and sodium carbonate ($KNaCO_3 \cdot 6H_2O$). Sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) is the only crystallization form of sodium carbonate at 273 K in this system; the monohydrate ($Na_2CO_3 \cdot H_2O$) and heptahydrate ($Na_2CO_3 \cdot 7H_2O$) are not formed.

Introduction

Salt lakes are widely distributed in the west of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau. Salt lakes of the Qinghai-Xizang Plateau are of a carbonate brine type or sulfate brine type. Zabuye Salt Lake, located in Tibet, is a typical carbonate brine type famous for its abundance of lithium, potassium, and boron resources and also with a scarce magnesium resource.[1] The lowest concentration ratio of magnesium to lithium makes the comprehensive utilization technology of Zabuye Lake quite different from other salt lakes in the Qinghai-Xizang Plateau, such as Dongtai Lake, Xitai Lake, and so forth.

The composition of Zabuye Salt Lake brine falls under the complex system which includes lithium, sodium, potassium, carbonate, sulfate, chloride, and borate. The climate conditions in the region of Zabuye Lake are generally windy and arid, with an average temperature of about 273 K.[1] To economically exploit the brines and mineral resources, it is important to adequately adopt local wind and sun energy; thus a technique like solar ponds is widely used. Earlier researchers found that in the evaporation process of brine, the equilibria among the salts are always metastable;[2,3] therefore, metastable phase equilibrium research is essential to predict the crystallization path of evaporation of the salt lake brine. Although a number of papers describing the metastable equilibrium of the seawater system $Na + K + Mg + Cl + SO_4 + H_2O$ have been reported,[4−7] little work has been done on the carbonate brine type, and data for the quaternary system $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ at 273 K are not reported in the literature yet.

The quaternary system $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ is one of the most important and basic subsystems of carbonate type brines. In this paper, the metastable equilibria of the quaternary system $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ at 273 K are presented. The solubilities and densities of the equilibrium solution of this system were measured.

Experimental Section

Apparatus and Reagents. A SHH-250 type thermostatic evaporator made by the Chongqing Inborn Instrument Corporation, China, was used for the metastable phase equilibrium experiments. The equipment has a temperature-controlling apparatus with a blower accessory to control the temperature and the evaporation quantity of the evaporating system. The evaporation rate is (4.0 to 5.5) $mm \cdot d^{-1}$, and the temperature precision is ± 0.1 K.

A Siemens D500 X-ray diffractometer with Ni-filtered Cu Kα radiation was used to analyze the crystalloid form of the solid phases. The operating conditions are 35 kV and 25 mA. An atomic absorption spectrometer (type WYD-YΠ, Beijing Geology Instrument Corporation) was employed for the determination of the sodium ion concentration in solution.

The chemicals used in this work were of analytical purity grade and obtained from the Chengdu Chemical Reagent Ltd. or the Shanghai Chemical Reagent Ltd. They were sodium chloride (NaCl, 99.5 % (by mass)), potassium chloride (KCl, 99.5 % (by mass)), potassium carbonate (K_2CO_3, 99.0 % (by mass)), and sodium carbonate (Na_2CO_3, 99.0 % (by mass)). Potassium carbonate and sodium carbonate were heated at 553 K to eliminate bicarbonate before use. Doubly deionized water was obtained from a Millipore water system with an electrical conductivity less than $1 \cdot 10^{-4}$ $S \cdot m^{-1}$ and pH = 6.6. For each experiment, the required amounts of reagents were dissolved into enough deionized water to produce the experimental solutions.

Experimental Method. The isothermal evaporation method was employed in this study. According to the phase equilibrium composition, the appropriate quantity of salts were mixed

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Table 1. Experimental Solubility and Density Values of Equilibrated Solutions in the Quaternary System $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ at 273 K

	composition of liquid phase, $w(B)^a \cdot 100$				Janëcke index of the dry salt, $J(B)$/[mol/100 mol dry salt]			density	
no.	$w(CO_3^{2-})$	$w(Cl^-)$	$w(K^+)$	$w(Na^+)$	$J(CO_3^{2-})$	$J(K^{+)}$	$J(H_2O)$	$g \cdot cm^{-3}$	equilibria solid phase
1, C	19.17	0.00	17.05	4.63	100.0	68.47	812.3	1.4223	$Na_2CO_3 \cdot 10H_2O + KNaCO_3 \cdot 6H_2O$
2	21.72	0.86	20.07	5.40	96.76	68.62	770.9	1.4388	$Na_2CO_3 \cdot 10H_2O + KNaCO_3 \cdot 6H_2O$
3	21.94	0.86	20.74	5.18	96.77	70.19	753.4	1.4018	$Na_2CO_3 \cdot 10H_2O + KNaCO_3 \cdot 6H_2O$
4	19.77	0.89	19.98	3.98	96.31	74.69	898.5	1.4192	$Na_2CO_3 \cdot 10H_2O + KNaCO_3 \cdot 6H_2O$
5, E_2	11.36	0.44	12.99	1.33	96.83	85.15	2097	1.3393	$KCl + Na_2CO_3 \cdot 10H_2O + KNaCO_3 \cdot 6H_2O$
6	55.36	13.00	12.12	8.30	87.36	46.26	2897	1.3480	$KCl + Na_2CO_3 \cdot 10H_2O$
7	57.57	13.80	7.40	8.80	83.16	33.16	2789	1.3500	$KCl + Na_2CO_3 \cdot 10H_2O$
8	21.03	13.30	1.28	10.9	65.16	6.45	2795	1.2330	$KCl + Na_2CO_3 \cdot 10H_2O$
9	7.59	14.50	0.66	12.10	38.24	3.10	2210	1.2301	$KCl + Na_2CO_3 \cdot 10H_2O$
10	4.36	15.10	0.62	12.80	25.47	2.79	1857	1.2248	$KCl + Na_2CO_3 \cdot 10H_2O$
11	3.46	15.80	0.64	12.30	20.57	2.96	1785	1.2241	$KCl + Na_2CO_3 \cdot 10H_2O$
14	2.44	14.83	0.42	11.23	16.29	2.18	1582	1.2253	$KCl + Na_2CO_3 \cdot 10H_2O$
13	2.26	15.02	0.40	11.23	15.11	2.06	1585	1.2153	$KCl + Na_2CO_3 \cdot 10H_2O$
12	2.00	15.10	0.39	11.08	13.55	2.04	1613	1.2186	$KCl + Na_2CO_3 \cdot 10H_2O$
15, A	1.94	14.95	0.00	11.17	13.32	0.00	1646	1.2153	$NaCl + Na_2CO_3 \cdot 10H_2O$
16	1.79	14.08	0.32	10.31	13.08	1.82	1791	1.2053	$NaCl + Na_2CO_3 \cdot 10H_2O$
17	1.95	15.18	0.37	11.11	13.20	1.91	1611	1.2184	$NaCl + Na_2CO_3 \cdot 10H_2O$
18, E_1	1.93	15.21	0.44	11.08	13.06	2.27	1609	1.2231	$NaCl + Na_2CO_3 \cdot 10H_2O + KCl$
19	12.04	14.10	0.74	11.83	50.27	3.56	2523	1.2323	$NaCl + Na_2CO_3 \cdot 10H_2O$
20, B	0.00	15.64	3.68	7.96	0.00	21.42	1758	1.2173	$NaCl + KCl$
21	0.16	17.22	4.19	8.81	1.09	21.90	1577	1.2159	$NaCl + KCl$
22	0.17	17.43	4.10	9.00	1.14	21.17	1550	1.2233	$NaCl + KCl$
23	0.73	23.5	2.47	8.10	3.56	15.25	1555	1.2261	$NaCl + KCl$
24	1.11	21.12	2.15	8.00	5.87	13.68	1563	1.2302	$NaCl + KCl$
25	1.41	19.55	1.51	7.81	7.89	10.21	1576	1.2354	$NaCl + KCl$
26	1.66	18.56	0.74	7.55	9.59	5.47	1586	1.2360	$NaCl + KCl$
27, D	22.47	0.00	26.34	1.39	100.0	91.79	592.4	1.5361	$K_2CO_3 \cdot 3/2H_2O + KNaCO_3 \cdot 6H_2O$
28	24.87	0.32	28.73	1.98	98.93	89.72	575.6	1.4804	$K_2CO_3 \cdot 3/2H_2O + KNaCO_3 \cdot 6H_2O$
29	24.50	0.30	28.91	2.08	98.96	89.06	597.4	1.5015	$K_2CO_3 \cdot 3/2H_2O + KNaCO_3 \cdot 6H_2O$
30, E_3	24.96	0.30	28.58	2.11	99.00	89.09	573.1	1.5072	$K_2CO_3 \cdot 3/2H_2O + KNaCO_3 \cdot 6H_2O + KCl$
31	24.69	0.31	28.18	2.32	98.94	87.88	588.6	1.4962	$KCl + KNaCO_3 \cdot 6H_2O$
32	24.59	0.33	26.54	2.48	98.86	86.97	594.7	1.5040	$KCl + KNaCO_3 \cdot 6H_2O$
33, F	20.60	0.39	27.21	0.00	98.32	100.0	712.1	1.5199	$KCl + K_2CO_3 \cdot 3/2H_2O$
34	22.18	0.40	27.54	1.02	98.80	94.09	723.1	1.4941	$KCl + K_2CO_3 \cdot 3/2H_2O$
35	22.40	0.38	26.82	1.60	98.59	90.82	716.2	1.5198	$KCl + K_2CO_3 \cdot 3/2H_2O$

[a] $w(B)$ is the mass fraction of B.

together as a series of artificial synthesized brines and loaded into clean polyethylene containers (24 cm long, 14 cm wide, and 6 cm high), and then the containers were placed in a thermostatic evaporator for isothermal evaporation. The temperature of the solution inside the evaporator was controlled to (273 ± 0.1) K and measured by a J thermocouple with an operating range of (258.15 to 373.15) K. The crystal behavior of the solid phase was observed periodically. When enough new solids appeared in the evaporating bottles, the liquid and solid phases were separated by filtration. The obtained wet solids were divided into two parts. One was analyzed by chemical methods to obtain the composition of the salts. The other was dried at 273 K, pestled into a powder, and then identified with X-ray diffraction to determine the crystalloid form of the solid phase. Meanwhile, a 5.0 mL sample of the clarified solution was taken from the liquid phase and diluted to a 50 mL final volume in a volumetric flask filled with deionized water to analyze the liquid-phase components. Another 5.0 mL sample of the clarified solution was taken to measure the density. The remainder of the solution continued to be evaporated to reach the next measuring point. The same procedure was repeated until the solution was fully evaporated.

The densities of solution determined in this study were used for the mass fraction calculation of the liquid components. The specific gravity bottle method with a correction for the air floating force was used. The precision of the density measurements was 0.0001 $g \cdot cm^{-3}$. The sample was obtained at 273 K and measured at room temperature. The excursion caused by the temperature difference was calibrated by using a multipoint temperature-revision method.[8]

Analytical Method. The composition of K^+ in the liquids and their corresponding wet solid phases were analyzed by using a sodium tetraphenyborate (STPB)/hexadecyl trimethyl ammonium bromide (CTAB) back-titration method with the existence of propanetriol, with a precision within 0.5 % (by mass).[9] The sodium ion concentration was determined by atomic absorption spectrometry, with a precision of 0.06 % (by mass). The chlorine ion concentration was determined by titration with a mercury nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue with a precision of 0.3 % (by mass). The carbonate ion concentration was determined by an acid−base neutralization titration with a precision within 0.5 % (by mass).[9]

Results and Discussion

The determined values of solubilites and densities of the equilibrated solution in the quaternary system $NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O$ at 273 K are presented in Table 1. The ion concentration values in the equilibrated solution are expressed in mass fraction $w(B)$. The composition of dry salts are expressed in Janëcke index $J(B)$, with $J(Na_2^{2+}) + J(K_2^{2+}) = 100$ mol or $J(CO_3^{2-}) + J(SO_4^{2-}) = 100$ mol. On the basis of the experimental data in Table 1, the metastable equilibrium phase diagram of the system at 273 K is plotted in Figure 1.

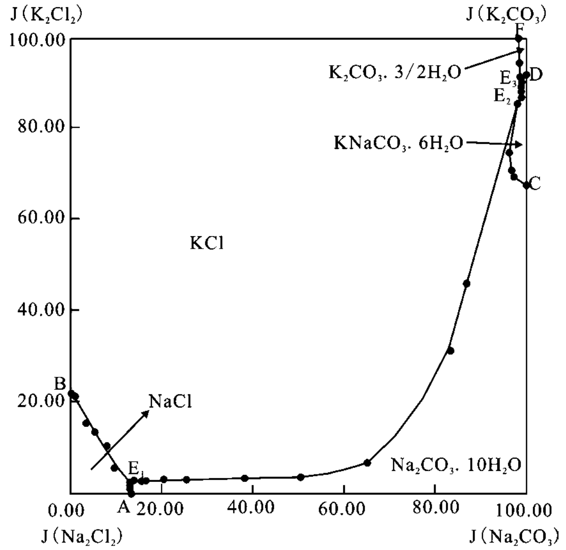

Figure 1. Metastable equilibrium phase diagram of the quaternary system NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O at 273 K.

The metastable phase diagram of the system in Figure 1 consists of five crystallization fields corresponding to potassium chloride (KCl), sodium chloride (NaCl), sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), potassium carbonate sesquihydrate ($K_2CO_3 \cdot 3/2H_2O$), and a hexahydrate double salt of potassium and sodium carbonate ($KNaCO_3 \cdot 6H_2O$). There are three invariant points in this system, noted as E_1, E_2, and E_3, respectively. Point E_1 is a commensurate invariant point, which is saturated with three salts NaCl + $Na_2CO_3 \cdot 10H_2O$ + KCl, and the mass fraction composition of the corresponding liquid phase is $w(CO_3^{2-}) = 1.93$ %, $w(Cl^-) = 15.21$ %, $w(K^+) = 0.44$ %, and $w(Na^+) = 11.08$ %. Point E_2 is an incommensurate invariant point, which is saturated with three salts, $Na_2CO_3 \cdot 10H_2O$ + KCl + $KNaCO_3 \cdot 6H_2O$, and the mass fraction composition of the corresponding liquid phase is $w(CO_3^{2-}) = 11.36$ %, $w(Cl^-) = 0.44$ %, $w(K^+) = 12.99$ %, and $w(Na^+) = 1.33$ %. Point E_3 is also a commensurate invariant point. The cosaturated three salts for invariant point E_3 are KCl + $K_2CO_3 \cdot 3/2H_2O$ + $KNaCO_3 \cdot 6H_2O$, and the mass fraction composition of the corresponding liquid phase is $w(CO_3^{2-}) = 24.96$ %, $w(Cl^-) = 0.30$ %, $w(K^+) = 28.58$ %, and $w(Na^+) = 2.11$ %. There are seven isothermal evaporation curves corresponding to curves E_1A, BE_1, E_1E_2, E_2C, E_2E_3, E_3D, and E_3F, indicating the cosaturation of two salts. Points A, B, C, D, and F, cosaturated with two salts, are the invariant points of the ternary subsystems of the quaternary system NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O, respectively. The double salt $KNaCO_3 \cdot 6H_2O$ is formed in the ternary subsystem Na_2CO_3 + K_2CO_3 + H_2O and also formed in the quaternary system NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O at 273 K. The crystallization field of salt $K_2CO_3 \cdot 3/2H_2O$ is the smallest, while the crystallizing field of potassium chloride is the largest. These results indicate that potassium chloride is easy to saturate and crystallize from solution at 273 K.

Figure 2 is the relevant water-phase diagram of the system at 273 K. Figure 2 shows that the Janëcke indexes of water (mol/100 mol of dry salt) change with the Janëcke indexes of carbonate and reach the smallest value at the commensurate invariant point E_3.

There are three hydrated salts of sodium carbonate, that is, $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot 7H_2O$, and $Na_2CO_3 \cdot 10H_2O$. A lot of work has been done on the metastable or stable equilibria of the systems containing sodium carbonate from (273 to 318) K.[10−13] According to previous studies on the stable equilibria,[9−12] the crystallization forms of sodium carbonate are $Na_2CO_3 \cdot H_2O$ at 318 K, $Na_2CO_3 \cdot 7H_2O$ at 308 K, and $Na_2CO_3 \cdot 10H_2O$ at (273 to 298) K. However, Fang's study on the metastable equilibria at 298 K showed that the crystallization form of sodium carbonate is $Na_2CO_3 \cdot 7H_2O$ at 298 K.[14] The transition temperature of $Na_2CO_3 \cdot 7H_2O$ and $Na_2CO_3 \cdot 10H_2O$ is 298 K. The crystal water in the sodium carbonate decreases along with an increase of temperature. No matter whether in the stable equilibria or in the metastable equilibria, the crystallization form of sodium carbonate is $Na_2CO_3 \cdot 10H_2O$ at 273 K. Our research result also supports this conclusion.

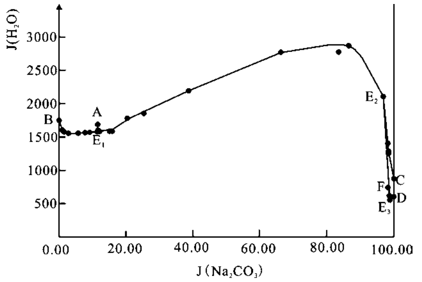

Figure 2. Water-phase diagram of the quaternary system NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O at 273 K.

Conclusions

Metastable equilibria of the quaternary system NaCl + KCl + Na_2CO_3 + K_2CO_3 + H_2O at 273 K were studied using an isothermal evaporation method. The solubilities and densities of the equilibrated solution were determined experimentally. According to the experimental data, the metastable equilibrium phase diagram and the water diagram of the system were plotted. The results show that there is a double salt of potassium and sodium carbonate ($KNaCO_3 \cdot 6H_2O$) formed in this quaternary system. $Na_2CO_3 \cdot 10H_2O$ is the only crystallization form of sodium carbonate at 273 K in this system.

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