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Phase Equilibria for the Aqueous System Containing Sodium, Potassium, Carbonate, and Sulfate Ions at 273.15 K

Ying Zeng*,[†] and Zhiyuan Zheng[†,‡]

College of Materials and Chemical Engineering & Chemistry, Chengdu University of Technology, 610059 P. R. China, and College of Chemistry and Environmental Engineering, Yangtze University, 434023 P. R. China

The phase equilibria in the quaternary system $Na_2SO_4 + K_2SO_4 + Na_2CO_3 + K_2CO_3 + H_2O$ were studied at 273.15 K using an isothermal evaporation method. The solubilities and densities of the equilibrated solution were determined experimentally. The crystalloid forms of the solid phase were determined using chemical analysis and an X-ray diffraction method. On the basis of the experimental data, the isothermal equilibrium phase diagram, water content diagram, and density composition diagram of the quaternary system were plotted. The phase diagram consists of four invariant points, nine univariant curves, and six crystallization fields corresponding to sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), potassium sulfate, sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), potassium carbonate hydrate ($K_2CO_3 \cdot {}^3/_2H_2O$), potassium and sodium carbonate double salt ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$), and sulfate and carbonate double salt of sodium ($2Na_2SO_4 \cdot Na_2CO_3$). This quaternary system is of a complex type. Two kinds of double salts are formed. $Na_2CO_3 \cdot 10H_2O$ is the only crystalloid form of sodium carbonate in the given system at 273.15 K. $Na_2CO_3 \cdot 7H_2O$ and $Na_2CO_3 \cdot H_2O$ are not formed.

Introduction

Alkaline lakes, such as the Searles Salt Lake, the Zabuye Salt Lake, and so on, are widely distributed in the world. Zabuye Salt Lake is located in Tibet and is famous for its high concentrations of sodium, potassium, lithium, and borate.[1] The evaluated economic value of Zabuye Salt Lake is more than 200 billion Chinese yuan.[1] In recent years, the government and researchers gathered together to discuss the exploiting of this salt lake. Phase diagrams can give us information about the solubility and the crystallization condition of the salts; therefore, studies on the phase equilibria of salt aqueous systems are indispensable for comprehensive utilization of the saline brine resource.

It is commonly thought that in the evaporation process of seawater or saline brine, the equilibria among the salts are always metastable. Metastable phase equilibria can give us information about the evaporating crystallization process, salt separating sequence, and crystallization field of salts in aqueous solution, so much work has been done on the metastable phase equilibria. The seawater systems have been studied at (298, 323, and (343 to 373)) K by van't Hoff,[2] Lepeshko,[3] and Autenrienth,[4] respectively. The six-component system Na^+, $K^+//Cl^-$, CO_3^{2-}, SO_4^{2-}, $B_4O_7^{2-}-H_2O$ system was studied at 293 K by Teeple,[5] and also the phase equilibria of the system Na^+, K^+, $Mg^{2+}//Cl^-$, $SO_4^{2-}-H_2O$ were studied at (288,[6,7] 298,[8] and 308) K[9] using an isothermal evaporating method. The research results have shown great use in the industrial process of salt production, such as comprehensive exploiting of Searles Salt Lake and extracting schoenite ($MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$) or potassium sulfate from

the Chaidamu Saline Lake in China. However, most of the effort has focused on temperatures above 288 K, including our earlier work aimed at the Zabuye Salt Lake.[10,11] The Zabuye Salt Lake region is dry with high daily evaporation; its average temperature is about 273 K.[1] Therefore, studies on the phase equilibria at 273 K will be more closely related to reality and have great use in exploiting of the brine.

In this article, the metastable phase equilibrium of the aqueous system $Na_2SO_4 + K_2SO_4 + Na_2CO_3 + K_2CO_3 + H_2O$ has been studied at 273.15 K. The solubility and density of the equilibria solution of this system were measured. This system is a subsystem of the composition of the Zabuye brine. So far, no report has been found about its phase equilibrium at 273.15 K.

Experimental Section

Reagents and Apparatus. The chemicals used in this work were of analytical purity grade and from either the Shanghai Chemical Reagent Plant or the Chengdu Chemical Reagent Plant. They were sodium sulfate (Na_2SO_4, 99.0 wt %), potassium sulfate (K_2SO_4, 99.5 wt %), sodium carbonate (Na_2CO_3, 99.0 wt %), and potassium carbonate (K_2CO_3, 99.0 wt %). Doubly deionized water was obtained from a Millipore water system with an electrical conductivity of less than $1 \cdot 10^{-4}$ S·m^{-1} and pH 6.6. For each experiment, the required amounts of reagents were dissolved in enough deionized water to produce the experimental solutions. The quantity of dissolved carbon dioxide from the atmosphere in the deionized water can be neglected during the analysis.

A SHH-250 type thermostatic evaporator made by the Chongqing INBORN Instrument Corporation, China, was used for the metastable phase equilibrium experiments. The temperature controlling precision was ± 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 were 35 kV and 25 mA.

* Corresponding author. E-mail: zengyster@gmail.com. Tel: 86-28-84079016. Fax: 86-28-84079074.
[†] Chengdu University of Technology.
[‡] Yangtze University.

Table 1. Solubilities and Densities of Solutions in the Quaternary System K$^+$, Na$^+$//CO$_3^{2-}$, SO$_4^{2-}$−H$_2$O at 273.15 K^a

no.	density/g·cm^{-3}	composition of equilibrium solution, $w(B)\cdot10^2$				Janëcke index of dry salt, $J(B)$				equilibrium solid phase
		$w(Na^+)$	$w(K^+)$	$w(SO_4^{2-})$	$w(CO_3^{2-})$	$J(Na_2^{2+})$	$J(K_2^{2+})$	$J(SO_4^{2-})$	$J(CO_3^{2-})$	
1	1.1316	3.73	3.69	6.43	1.24	46.20	53.80	76.37	23.63	ns + ks
2	1.1313	4.01	3.93	6.47	1.59	46.46	53.54	71.75	28.25	ns + ks
3	1.1307	4.21	3.88	6.24	1.82	48.02	51.98	68.22	31.78	ns + ks
4	1.1363	4.53	4.07	6.30	2.13	48.62	51.38	64.87	35.13	ns + ks
5	1.1408	4.39	4.13	6.00	2.28	47.45	52.55	62.17	37.83	ns + ks
6	1.1462	4.94	4.24	5.94	2.76	49.79	50.21	57.41	42.59	ns + ks
7	1.1573	5.43	4.41	5.54	3.46	51.15	48.85	50.00	50.00	ns + ks
8	1.1529	5.29	4.16	5.77	3.04	51.79	48.21	38.17	61.83	ns + nsc + ks
9	1.3297	1.16	16.32	0.78	12.80	5.70	94.30	3.65	96.35	kc + ks
10	1.4080	1.12	20.68	0.75	16.13	4.40	95.60	2.81	97.19	kc + ks
11	1.3754	1.27	18.17	0.71	14.33	5.61	94.39	2.99	97.01	kc + ks
12	1.3656	1.65	17.54	0.77	14.06	7.42	92.58	3.31	96.69	kc + ks
13	1.3721	1.29	17.66	0.89	13.83	5.84	94.16	3.88	96.12	kc + ks
14	1.3846	2.02	17.67	0.69	14.44	8.86	91.14	2.89	97.11	kc + ks
15	1.3836	0.93	17.68	0.32	13.97	4.27	95.73	1.43	98.57	kc + ks
16	1.3707	1.39	18.23	0.34	14.68	6.10	93.90	1.43	98.57	kc + ks
17	1.3856	1.82	17.77	0.24	14.67	8.03	91.97	1.01	98.99	kc + ks
18	1.3869	5.76	20.58	4.93	16.46	20.03	79.97	13.39	86.61	nc + knc
19	1.3711	3.15	29.70	5.98	21.10	17.09	82.91	8.64	91.36	nc + knc
20	1.3518	2.94	25.90	1.56	21.42	8.90	91.10	4.11	95.89	ks + knc + kc
21	1.0887	5.64	0.00	1.59	2.68	100.0	0.00	27.11	72.89	ns + nsc
22	1.0966	6.61	0.67	1.88	3.65	89.30	10.70	24.30	75.70	ns + nsc
23	1.0949	6.26	0.63	1.67	3.52	89.36	10.64	22.91	77.09	ns + nsc
24	1.0204	6.38	0.73	1.86	3.55	88.13	11.87	24.69	75.31	ns + nsc
25	1.0945	6.05	0.85	1.90	3.41	85.80	14.20	25.79	74.21	ns + nsc
26	1.1202	6.42	1.32	2.17	3.84	80.54	19.46	26.10	73.90	ns + nsc
27	1.1110	6.07	1.43	2.12	3.73	78.32	21.68	26.21	73.79	ns + nsc
28	1.1140	6.15	1.52	2.17	3.81	77.50	22.50	26.27	73.73	ns + nsc
29	1.1278	6.81	1.66	2.50	4.15	77.73	22.27	27.39	72.61	ns + nsc
30	1.3123	5.09	0.85	1.67	2.90	50.46	49.54	32.63	67.37	ks + knc
31	1.3189	6.35	0.95	1.82	3.08	49.58	50.42	28.71	71.29	ks + knc
32	1.3086	5.69	4.13	5.24	3.60	52.07	47.93	18.66	81.34	nc + nsc + ks
33	1.0861	5.37	0.00	1.95	2.28	100.0	0.00	34.79	65.21	ns + nsc
34	1.0839	5.71	0.56	2.05	2.87	89.74	10.26	30.86	69.14	ns + nsc
35	1.0939	5.88	0.58	1.80	3.16	89.54	10.46	26.28	73.72	ns + nsc
36	1.1011	6.44	0.75	1.80	3.65	87.96	12.04	23.52	76.48	ns + nsc
37	1.1123	6.03	1.19	1.85	3.69	81.15	18.85	23.87	76.13	ns + nsc
38	1.1206	6.16	1.48	2.20	3.78	77.98	22.02	26.64	73.36	ns + nsc
39	1.1250	6.74	1.61	2.49	4.07	78.10	21.90	27.68	72.32	ns + nsc
40	1.1187	6.05	1.76	2.25	3.89	74.46	25.54	26.56	73.44	ns + nsc
41	1.1203	6.14	1.97	2.40	4.02	72.62	27.38	27.19	72.81	ns + nsc
42	1.1324	6.51	2.17	2.60	4.29	71.80	28.20	27.49	72.51	ns + nsc
43	1.3761	6.16	20.35	4.33	16.92	20.46	79.54	13.79	86.21	nc + knc
44	1.3836	5.79	21.37	5.01	17.04	18.71	81.29	15.51	84.49	nc + knc
45	1.3953	9.55	19.77	7.13	16.94	29.11	70.89	20.82	79.18	nc + knc
46	1.3587	4.52	0.78	1.42	2.65	38.65	61.35	19.08	80.92	nc + ks
47	1.3789	8.44	20.61	6.93	16.98	25.83	74.17	20.33	79.67	nc + knc + ks
48	1.3604	4.00	20.45	4.07	15.76	14.27	85.73	13.89	86.11	nc + knc
49	1.4112	11.05	20.03	6.31	18.63	31.92	68.08	17.46	82.54	nc + knc
50	1.3802	5.33	20.05	6.03	15.09	18.44	81.56	19.98	80.02	nc + knc
51	1.3507	0.17	1.68	0.00	1.40	8.11	91.89	0.00	100.0	ks + knc
52	1.3765	0.26	1.86	0.15	1.51	10.76	89.24	5.68	94.32	ks + knc
53	1.4015	0.30	1.83	0.12	1.52	12.36	87.64	4.78	95.22	ks + knc

^{a} nc-Na$_2$CO$_3$·10H$_2$O; ns-Na$_2$SO$_4$·10H$_2$O; kc-K$_2$CO$_3$·$^3/_2$H$_2$O; ks-K$_2$SO$_4$; knc-K$_2$CO$_3$·Na$_2$CO$_3$·12H$_2$O; nsc-2Na$_2$SO$_4$·Na$_2$CO$_3$.

A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, supplied by Mettler Toledo Instruments) was employed in the determination of the solution density.

An atomic absorption spectrometer (type WYD-YII) was employed in the determination of the sodium ion concentration in solution.

Experimental Method. The isothermal evaporation method was employed in this study. The required amounts of reagent, calculated according to the solubility of the salt at 273.15 K (Na$_2$SO$_4$ 4.76 wt %, K$_2$SO$_4$ 6.85 wt %, Na$_2$CO$_3$ 6.63 wt %, K$_2$CO$_3$ 54.65 wt %) and the solubility data of the invariant point in the ternary subsystem were dissolved in 1000 mL of deionized water to produce the initial evaporating solutions. A series of prepared experimental solutions of the quaternary system were loaded in clean opened polyethylene bottles. The bottles were

placed in a thermostatic evaporator. The temperature of the solution inside the evaporator was controlled to (273.15 ± 0.1) K and measured by a J thermocouple with an operating range of (258.15 to 373.15) K and a system precision of ± 0.1 K. When enough new solid appeared in the evaporating bottles, the liquid and solid phases were separated by filtration. The obtained wet crystals in the solid phase were separated from each other according to crystal shapes as much as possible. Each kind of solid sample was divided into two parts. One was analyzed by a chemical method to obtain the composition of the salt. The other was dried at 273.15 K, pestled into a powder, and then analyzed by X-ray diffraction to determine the crystalloid form of the solid phase. At the same time, 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 concentration of liquid-phase components. Another 5.0 mL sample of the clarified solution was taken to determine the density. The remainder of the solution was loaded back in the polyethylene bottles, placed in the thermostatic evaporator, and continued to be evaporated to reach the next measuring point. This same procedure was repeated until the solution was fully evaporated.

The densities of solution were determined in this study and used for the mass fraction calculation of liquid components. The specific gravity bottle method with correction of air floating force was used. The precision of the density measure was 0.0001 g·cm⁻³. The sample was obtained at 273.15 K and measured at room temperature. We calibrated the excursion caused by the temperature difference by using a multipoint temperature revision method.[12]

Analytical Methods. The potassium ion concentration was measured by sodium tetraphenylborate−hexadecyl trimethyl ammonium bromide titration (precision: ± 0.5 %). The sodium ion concentration was determined by atomic absorption spectrometry (precision: ± 0.06 mass %, type WYD-YII). The carbonate ion concentration was determined by acid−base neutralization titration. The mean determination uncertainty was less than 0.5 %.[13] The sulfate ion concentration was determined by titration with a standard solution of EDTA in the presence of an excess Ba−Mg mixture solution. First, the excess Ba−Mg mixture solution (contents 0.01 mol·L⁻¹ BaCl₂ and 0.005 mol·L⁻¹ MgCl₂) was added quantitatively to give a BaSO₄ precipitate. An excess of BaCl₂ solution was titrated with EDTA standard solution in the presence of mixed K−B (acid chrome blue K−naphthol green B) indicator. The precision of the measurements was better than 1 %. The ion concentration measurement was repeated up to three times to estimate the reproducibility.

Results and Discussion

Phase Diagram at 273.15 K. The experimental results of solubilities and densities for the quaternary system Na_2SO_4 + K_2SO_4 + Na_2CO_3 + K_2CO_3 + H_2O at 273.15 K were measured and are tabulated in Table 1. In Table 1, $w(B)$ is the mass fraction of B, and $J(B)$ is the Janĕcke index values of B, with $J(Na_2^{2+}) + J(K_2^{2+}) = J(CO_3^{2-}) + J(SO_4^{2-}) = 100$ mol. With the data of the Janĕcke index, $J(B)$, the experimental solubility isothermal metastable phase diagram of the system at 273.15 K was plotted, as shown in Figure 1.

The phase diagram of the quaternary system consists of six crystallization fields, four invariant points (marked as point M_1, M_2, M_3, and M_4) and nine univariant curves. The six crystallization fields correspond to the single salt potassium sulfate, the salt hydrates sodium sulfate decahydrate, sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$), hydrated potassium carbonate ($K_2CO_3 \cdot 3/2H_2O$), the double salts sodium sulfate and carbonate ($2Na_2SO_4 \cdot Na_2CO_3$), and dodecahydrated potassium and sodium carbonate double salt ($K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$). The salts potassium sulfate and sodium sulfate have lower solubility and larger crystallization areas than the other salts in the given system. The salt K_2CO_3 has the largest solubility and the smallest crystallization area. The salt Na_2SO_4 causes a salting out effect on the salt Na_2CO_3.

The saturated salts and the mass fraction composition for invariant points in this system are: (1) M_1 saturated with salts $Na_2SO_4 \cdot 10H_2O$ + K_2SO_4 + $2Na_2SO_4 \cdot Na_2CO_3$. The mass fraction composition of the liquid phase is $w(Na^+)$ 5.29 %, $w(K^+)$ 4.16 %, $w(SO_4^{2-})$ 5.77 %, $w(CO_3^{2-})$ 3.04 %. (2) M_2 saturated with salts $Na_2CO_3 \cdot 10H_2O$ + K_2SO_4 + $2Na_2SO_4 \cdot$
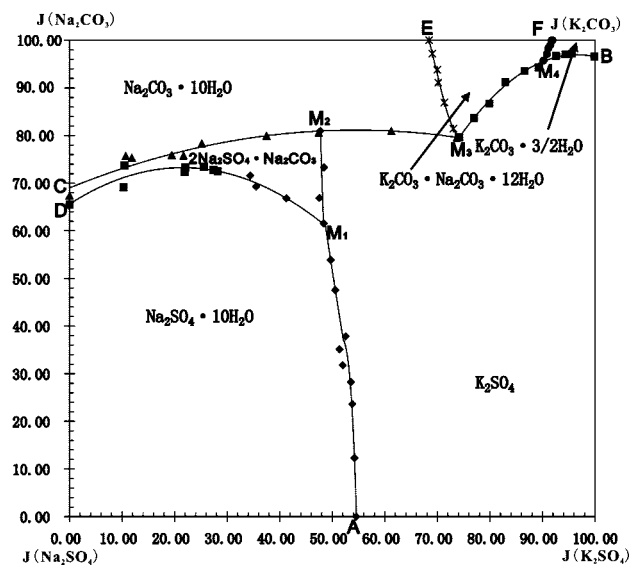
Figure 1. Isothermal evaporation diagram of the quaternary system K^+, $Na^+//CO_3^{2-}$, $SO_4^{2-}-H_2O$ at 273.15 K.
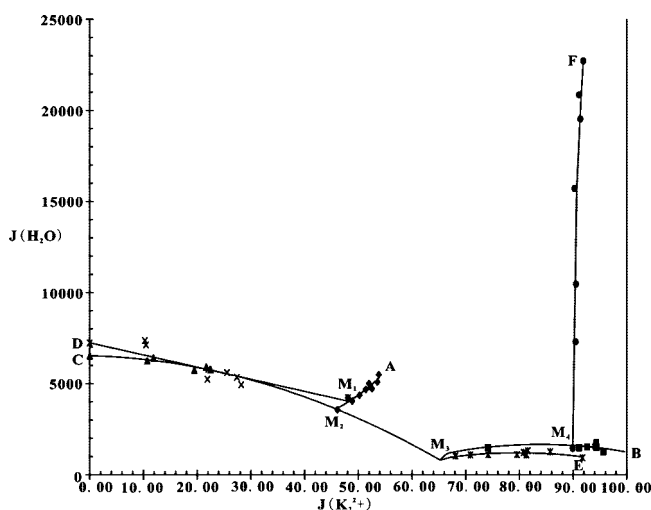
Figure 2. Water content diagram of the quaternary system K^+, $Na^+//CO_3^{2-}$, $SO_4^{2-}-H_2O$ at 273.15 K.

N_2CO_3. The mass fraction composition of the liquid phase is $w(Na^+)$ 5.69 %, $w(K^+)$ 4.13 %, $w(SO_4^{2-})$ 5.24 %, $w(CO_3^{2-})$ 3.60 %. (3) M_3 saturated with salts $Na_2CO_3 \cdot 10H_2O$ + K_2SO_4 + $K_2CO_3 \cdot N_2CO_3 \cdot 12H_2O$. The mass fraction composition of the liquid phase is $w(Na^+)$ 8.44 %, $w(K^+)$ 20.61 %, $w(SO_4^{2-})$ 6.93 %, $w(CO_3^{2-})$ 16.98 %. (4) M_4 saturated with salts $K_2CO_3 \cdot 3/2$-H_2O + K_2SO_4 + $K_2CO_3 \cdot N_2CO_3 \cdot 12H_2O$. The mass fraction composition of the liquid phase is $w(Na^+)$ 2.94 %, $w(K^+)$ 25.90 %, $w(SO_4^{2-})$ 1.56 %, $w(CO_3^{2-})$ 21.42 %.

Point A is the invariant point for the ternary subsystem Na_2SO_4 + K_2SO_4 + H_2O. Point B is the invariant point for the ternary subsystem K_2CO_3 + K_2SO_4 + H_2O. Points C and D are two invariant points for the ternary subsystem Na_2CO_3 + Na_2SO_4 + H_2O. The double salt $2Na_2SO_4 \cdot Na_2CO_3$ is formed in this subsystem at 273.15 K. Points E and F are two invariant points for the ternary subsystem Na_2CO_3 + K_2CO_3 + H_2O. The double salt $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ is formed in this subsystem at the experimental temperature.

Figure 2 is the water content diagram of the quaternary system. At the invariant point M_3, the system has the lowest water content. Invariant point M_3 is a congruent eutonic point
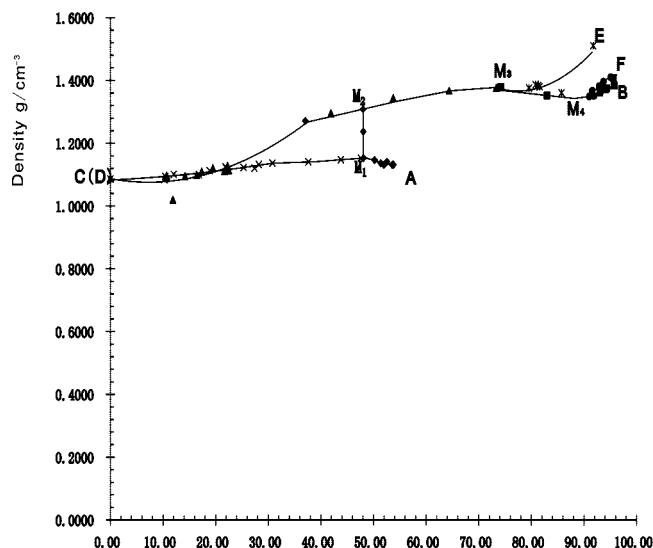
Figure 3. Density versus composition diagram of the equilibrium solutions in the quaternary system at 273.15 K.

and the evaporating end point of the whole system. At this point, the salts $Na_2CO_3 \cdot 10H_2O$, K_2SO_4, and $K_2CO_3 \cdot N_2CO_3 \cdot 12H_2O$ can be simultaneously salted out without any dissolving conversion action.

In the phase equilibrium of the quaternary system Na_2SO_4 + K_2SO_4 + Na_2CO_3 + K_2CO_3 + H_2O at 273.15 K, the crystalloid form of the salt sodium carbonate is $Na_2CO_3 \cdot 10H_2O$. As we know, there are three crystalloid forms of sodium carbonate, that is, $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 7H_2O$, and $Na_2CO_3 \cdot H_2O$. As previously reported, the crystalloid form of the sodium salt is $Na_2CO_3 \cdot 10H_2O$ in the metastable phase equilibrium[14] and stable phase equilibrium at 298 K.[15−17] A systematic investigation of how the crystalloid form of sodium carbonate changes with temperature was carried out by Li et al.[17,18] It was found that the crystalloid form of sodium carbonate is $Na_2CO_3 \cdot 10H_2O$ at (273 and 288) K, $Na_2CO_3 \cdot 7H_2O$ and $Na_2CO_3 \cdot 10H_2O$ coexist at (298 and 308) K, and $Na_2CO_3 \cdot H_2O$ at 318 K. It can be concluded that the species $Na_2CO_3 \cdot H_2O$ and $Na_2CO_3 \cdot 7H_2O$ mainly exist at 298 K or higher temperatures, and the species $Na_2CO_3 \cdot 10H_2O$ is the only crystalloid form of sodium carbonate at 273 K. Our studies in this article also support this standpoint.

Teeple[5] pointed out that in the system including potassium and sodium carbonate, the crystalloid form of the sodium and potassium carbonate double salt is anhydrous $K_2CO_3 \cdot Na_2CO_3$, whereas in this study at 273 K, the double salt is separated as the dodecahydrate, that is, $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ (or $KNaCO_3 \cdot 6H_2O$). This crystalloid form is also found at 288 K[19] and at 298 K.[20,21]

Density of the System. The density data are plotted in Figure 3. The density increases with the increase in potassium ion content at each univariant curve. The change in density with ion content agrees with Howard's empirical formula.[22] At the eutonic point M_3, the density is a maximum.

Conclusions

The phase diagram and density of solution of the system Na_2SO_4 + K_2SO_4 + Na_2CO_3 + K_2CO_3 + H_2O were studied at 273.15 K. The isothermal evaporation method was employed. This system is of a complex type. In this system

at 273.15 K, the double salt of sodium and potassium carbonate and the double salt of sodium sulfate and carbonate are formed with the form $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ and $2Na_2SO_4 \cdot Na_2CO_3$, respectively; the crystalloid forms of the other single salts are $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot {}^3/_2H_2O$, K_2SO_4, and $Na_2SO_4 \cdot 10H_2O$, respectively. $Na_2CO_3 \cdot 10H_2O$ is the only crystalloid form of sodium carbonate at 273.15 K; the crystallization fields of salts $Na_2CO_3 \cdot 7H_2O$ and $Na_2CO_3 \cdot H_2O$ are not found. The salt K_2CO_3 has the largest solubility and the smallest crystallization area. The salt Na_2SO_4 has a salting out effect on the salt Na_2CO_3.

The density of the solution changes regularly with the composition. At the congruent eutonic point of the system, the density reaches the maximum value.

Literature Cited

(1) Zheng, M. P.; Liu, W. G.; Xiang, J. *Qinghai-Xizhang Plateau Saline Lakes*; Beijing Science and Technology Press: Beijing, China, 1989; pp 192−270.

(2) van't Hoff; J. H. *Untersuchungen über die Bildungsverhältnisse der Ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagers*; H., Precht, E., Cohen, Eds.; Akademische Verlagsgesellschaft: Leipzig, Germany, 1912; 91−106.

(3) Lepeshko, I. N.; Romaschova, N. N. Solubility in system Li_2SO_4−Na_2SO_4−$MgSO_4$−H_2O at 298 K. *Russ. J. Inorg. Chem.* **1959**, *12*, 2812–2815.

(4) Autenrieth, H.; Braune, G. Ein neues salzmineral, seine eigenschaften, seine auftrenten und seine existenzbedingungen im system der salze ozeanischer salzablagerungen. *Naturwiss.* **1958**, *15*, 362–363.

(5) Teeple, J. E. *The Industrial Development of Searles Lake Brines: With Equilibrium Data*; American Chemical Society Monograph Series 49; The Chemical Catalog Company: New York, 1928.

(6) Shu, Y. G.; Li, J.; Jiang, C. F. Studies on the metastable phase equilibrium of Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}−H_2O quinary system at 288 K. *J. Chem. Ind. Eng. Chin.* **1992**, *43*, 549–555.

(7) Jin, Z. M.; Zhou, H. N.; Wang, L. S. Studies on the metastable phase equilibrium of Na^+, K^+, Mg^{2+}/Cl^-, SO_4^{2-}−H_2O quinary system at 288 K. *Chem. J. Chin. Univ.* **2002**, *23*, 690–694.

(8) Jin, Z. M.; Xiao, X. Z.; Liang, S. M. Study of the metastable equilibrium for pentanary system of (Na^+, K^+, Mg^{2+}), (Cl^-, SO_4^{2-}), H_2O. *Acta Chim. Sin.* **1980**, *38*, 313–321.

(9) Jin, Z. M.; Zhou, H. N.; Wang, L. S. Studies on the metastable phase equilibrium of (Na^+, K^+, Mg^{2+}), (Cl^-, SO_4^{2-}), H_2O quinary system at 308.15 K. *Chem. J. Chin. Univ.* **2001**, *22*, 634–638.

(10) Zeng, Y.; Lin, X. F.; Ni, S. J.; Zhang, C. J. Study on the metastable equilibria of the salt lake brine system Li_2SO_4 + Na_2SO_4 + K_2SO_4 + $Li_2B_4O_7$ + $Na_2B_4O_7$ + $K_2B_4O_7$ + H_2O at 288 K. *J. Chem. Eng. Data* **2007**, *52*, 164–167.

(11) Zeng, Y.; Shao, M. Liquid−solid metastable equilibria in the quinary system Li^+ + K^+ + Cl^- + CO_3^{2-} + $B_4O_7^{2-}$ + H_2O at $T = 288$ K. *J. Chem. Eng. Data* **2006**, *51*, 219–222.

(12) Xu, G. L. The determination and application of the temperature correction coefficient for the density of vinyl acetate. *Fujian Anal. Test.* **1999**, *3*, 1104–1108.

(13) Institute of Qinghai Salt-Lake of Chinese Academy of Sciences. *Analytical Methods of Brines and Salts*, 2nd ed.; Chinese Science Press: Beijing, 1984; pp 75−80.

(14) Fang, C. H.; Niu, Z. D.; Liu, Z. Q.; Chen, J. Q. Studies on the metastable phase diagram of the quinary system Na^+, $K^+//Cl^-$, SO_4^{2-}, CO_3^{2-}−H_2O at 298 K. *Acta Chim. Sin.* **1991**, *49*, 1062–1070.

(15) Zeng, Y.; Yin, H. A.; Tang, M. L.; Feng, X. X. Studies on the phase equilibrium of the quinary system Li^+, Na^+, $K^+//CO_3^{2-}$, Cl^-−H_2O at 298.15 K. *Chem. J. Chin. Univ.* **2003**, *24*, 968–972.

(16) Yin, H. A.; Hao, L. F.; Zeng, Y.; Tang, M. L. Studies on the phase equilibrium and the physico-chemical properties of equilibria solution in the quinary system Li^+, $Na^+//CO_3^{2-}$, $B_4O_7^{2-}$, Cl^-−H_2O at 298 K. *J. Chem. Eng. Chin. Univ.* **2003**, *17*, 1–5.

(17) Li, J.; Yang, Q.; Zhang, F. X.; Li, H. X.; Wang, Z. J. The isothermal solubilities of the quaternary system $Na_2B_4O_7$−Na_2CO_3−$NaHCO_3$−$NaBO_2$−H_2O. *Acta Phys. Chim. Sin.* **2001**, *17*, 1045–1048.

(18) Li, J.; Yang, Q.; Zhang, F. X.; Li, H. X.; Wang, Z. J. Isothermal studies on the solubilities of the quaternary system $Na_2B_4O_7-Na_2CO_3-NaHCO_3-NaBO_2-H_2O$ at 273 and 288 K. *Chin. J. Inorg. Chem.* **2001**, *17*, 849–852.

(19) Sang, S. H.; Yin, H. A.; Tang, M. L.; Zhang, Y. X. (Liquid + solid) metastable equilibria in quinary system $Li_2CO_3 + Na_2CO_3 + K_2CO_3 + Li_2B_4O_7 + Na_2B_4O_7 + K_2B_4O_7 + H_2O$ at $T = 288$ K for Zabuye salt lake. *J. Chem. Thermodyn.* **2003**, *35*, 1513–1520.

(20) Harvie, C. E.; Móller, N.; Weare, J. H. The prediction of mineral solubilities in nature waters: $Na-K-Mg-Ca-H-SO_4-Cl-OH-HCO_3-CO_3-CO_2-H_2O$ system to high ionic strengths at 298 K. *Geochim. Cosmochim. Acta* **1984**, *48*, 723–751.

(21) Zeng, Y.; Yang, H. M.; Yin, H. A.; Tang, M. L. A study on phase equilibrium and solution properties of the quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K. *J. Chem. Eng. Data* **2004**, *49*, 1648–1651.

(22) Howard, L. S. In *Solubilities of Inorganic and Organic Componds*; Stephen, H., Stephen, T., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 3.