

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

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The phase equilibria in the quaternary system $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ 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 ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), potassium sulfate, sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), potassium carbonate hydrate ($\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O}$), potassium and sodium carbonate double salt ($\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$), and sulfate and carbonate double salt of sodium ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$). This quaternary system is of a complex type. Two kinds of double salts are formed. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is the only crystalloid form of sodium carbonate in the given system at 273.15 K. $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ 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 Autenrieth,⁴ respectively. The six-component system $\text{Na}^+, \text{K}^+//\text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{B}_4\text{O}_7^{2-}-\text{H}_2\text{O}$ system was studied at 293 K by Teeple,⁵ and also the phase equilibria of the system $\text{Na}^+, \text{K}^+, \text{Mg}^{2+}//\text{Cl}^-, \text{SO}_4^{2-}-\text{H}_2\text{O}$ were studied at (288,^{6,7} 298,⁸ and 308) K⁹ 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 ($\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) 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 $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ 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 $1 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$ 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 $\pm 0.1 \text{ K}$.

A Siemens D500 X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation was used to analyze the crystalloid form of the solid phases. The operating conditions were 35 kV and 25 mA.

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Table 1. Solubilities and Densities of Solutions in the Quaternary System K^+ , $Na^+//CO_3^{2-}$, $SO_4^{2-}-H_2O$ at 273.15 K^a

no.	density/g·cm ⁻³	composition of equilibrium solution, w(B)·10 ²				Janěcke 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-Na₂CO₃·10H₂O; ns-Na₂SO₄·10H₂O; kc-K₂CO₃·³/₂H₂O; ks-K₂SO₄; knc-K₂CO₃·Na₂CO₃·12H₂O; nsc-2Na₂SO₄·Na₂CO₃.

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 (Na₂SO₄ 4.76 wt %, K₂SO₄ 6.85 wt %, Na₂CO₃ 6.63 wt %, K₂CO₃ 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 $0.0001 \text{ g} \cdot \text{cm}^{-3}$. 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: $\pm 0.5 \%$). The sodium ion concentration was determined by atomic absorption spectrometry (precision: $\pm 0.06 \text{ mass } \%$, 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 $0.01 \text{ mol} \cdot \text{L}^{-1} \text{ BaCl}_2$ and $0.005 \text{ mol} \cdot \text{L}^{-1} \text{ MgCl}_2$) was added quantitatively to give a BaSO_4 precipitate. An excess of BaCl_2 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 $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ at 273.15 K were measured and are tabulated in Table 1. In Table 1, $w(\text{B})$ is the mass fraction of B, and $J(\text{B})$ is the Janěcke index values of B, with $J(\text{Na}_2^{2+}) + J(\text{K}_2^{2+}) = J(\text{CO}_3^{2-}) + J(\text{SO}_4^{2-}) = 100 \text{ mol}$. With the data of the Janěcke index, $J(\text{B})$, 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 ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), hydrated potassium carbonate ($\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O}$), the double salts sodium sulfate and carbonate ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), and dodecahydrated potassium and sodium carbonate double salt ($\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$). 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 $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. The mass fraction composition of the liquid phase is $w(\text{Na}^+) 5.29 \%$, $w(\text{K}^+) 4.16 \%$, $w(\text{SO}_4^{2-}) 5.77 \%$, $w(\text{CO}_3^{2-}) 3.04 \%$. (2) M_2 saturated with salts $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4 \cdot$

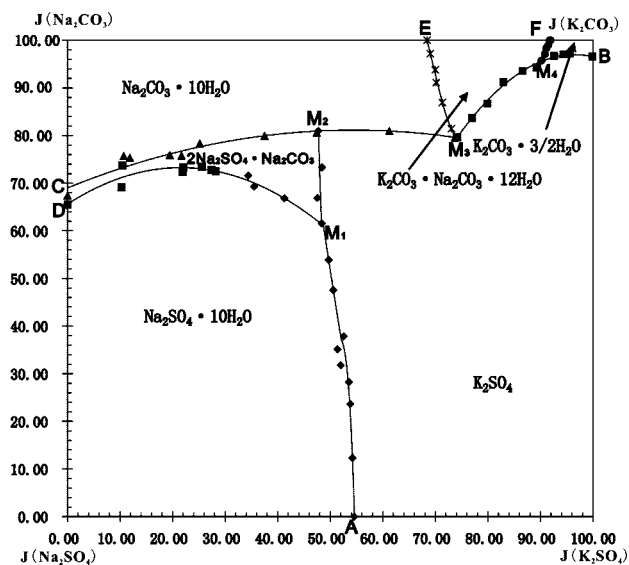


Figure 1. Isothermal evaporation diagram of the quaternary system K^+ , $\text{Na}^+/\text{CO}_3^{2-}$, $\text{SO}_4^{2-}-\text{H}_2\text{O}$ at 273.15 K.

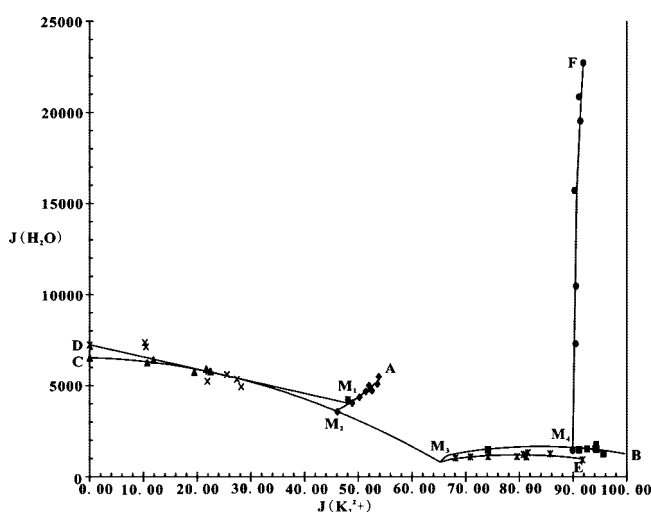


Figure 2. Water content diagram of the quaternary system K^+ , $\text{Na}^+/\text{CO}_3^{2-}$, $\text{SO}_4^{2-}-\text{H}_2\text{O}$ at 273.15 K.

N_2CO_3 . The mass fraction composition of the liquid phase is $w(\text{Na}^+) 5.69 \%$, $w(\text{K}^+) 4.13 \%$, $w(\text{SO}_4^{2-}) 5.24 \%$, $w(\text{CO}_3^{2-}) 3.60 \%$. (3) M_3 saturated with salts $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + \text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. The mass fraction composition of the liquid phase is $w(\text{Na}^+) 8.44 \%$, $w(\text{K}^+) 20.61 \%$, $w(\text{SO}_4^{2-}) 6.93 \%$, $w(\text{CO}_3^{2-}) 16.98 \%$. (4) M_4 saturated with salts $\text{K}_2\text{CO}_3 \cdot 3/2\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + \text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. The mass fraction composition of the liquid phase is $w(\text{Na}^+) 2.94 \%$, $w(\text{K}^+) 25.90 \%$, $w(\text{SO}_4^{2-}) 1.56 \%$, $w(\text{CO}_3^{2-}) 21.42 \%$.

Point A is the invariant point for the ternary subsystem $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$. Point B is the invariant point for the ternary subsystem $\text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$. Points C and D are two invariant points for the ternary subsystem $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$. The double salt $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ is formed in this subsystem at 273.15 K. Points E and F are two invariant points for the ternary subsystem $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$. The double salt $\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ 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

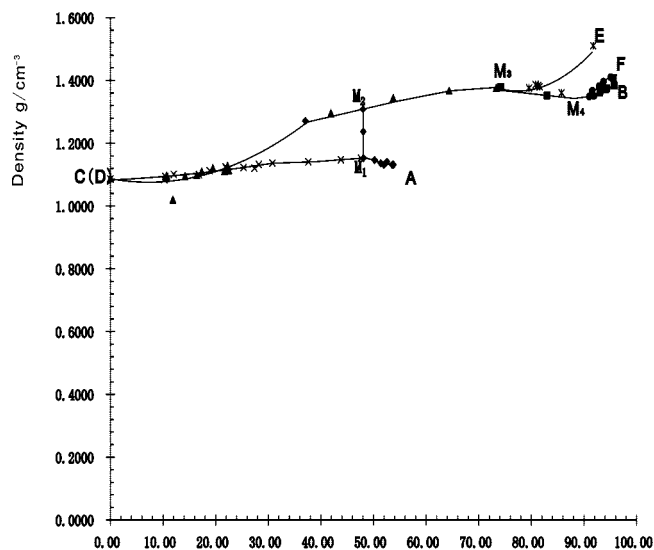


Figure 3. Density versus composition diagram of the equilibrium solutions in the quaternary system at 273.15 K.

and the evaporating end point of the whole system. At this point, the salts $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, K_2SO_4 , and $\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ can be simultaneously salted out without any dissolving conversion action.

In the phase equilibrium of the quaternary system $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ at 273.15 K, the crystalloid form of the salt sodium carbonate is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. As we know, there are three crystalloid forms of sodium carbonate, that is, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. As previously reported, the crystalloid form of the sodium salt is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in the metastable phase equilibrium¹⁴ 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 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ at (273 and 288) K, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ coexist at (298 and 308) K, and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ at 318 K. It can be concluded that the species $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ mainly exist at 298 K or higher temperatures, and the species $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is the only crystalloid form of sodium carbonate at 273 K. Our studies in this article also support this standpoint.

Teeples⁵ pointed out that in the system including potassium and sodium carbonate, the crystalloid form of the sodium and potassium carbonate double salt is anhydrous $\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3$, whereas in this study at 273 K, the double salt is separated as the dodecahydrate, that is, $\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ (or $\text{KNaCO}_3 \cdot 6\text{H}_2\text{O}$). This crystalloid form is also found at 288 K¹⁹ 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 $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ 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 $\text{K}_2\text{CO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ and $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, respectively; the crystalloid forms of the other single salts are $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{K}_2\text{CO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$, K_2SO_4 , and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, respectively. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is the only crystalloid form of sodium carbonate at 273.15 K; the crystallization fields of salts $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ 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.

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