Metastable Phase Equilibria of the Reciprocal Quaternary System Containing Sodium, Potassium, Chloride, and Borate Ions at 308.15 K

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The metastable solubility of the reciprocal quaternary system containing sodium, potassium, chloride, and borate ions and the physicochemical properties corresponding to density, viscosity, pH value, and refractive index at 308.15 K have been studied with the isothermal evaporation method. According to the experimental data, the metastable equilibrium phase diagrams of dry salt and the water phase diagram of the system were plotted. In the dry-salt phase diagram, there are two invariant points, five univariant curves, and four crystallizing regions corresponding to sodium chloride, potassium chloride, borax ($Na_2B_4O_7 \cdot 10H_2O$), and potassium tetraborate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$). The crystallized region of borax is the largest, while the phase region of NaCl is the smallest with the highest concentration and a strong salting-out effect to borax. There are neither double salts nor solid solutions formed in the metastable system. When compared with the stable phase diagram at 298.15 K of the system, the areas of both metastable phase regions of borax and potassium chloride are enlarged, while other metastable phase regions are decreased. The calculated values of densities and refractive index in the metastable quaternary system with the empirical equations are in good agreement with the experimental values.

1. Introduction

Brines with high concentrations of potassium and boron resources are widely distributed both in the oilfields of the Nanyishan Section of Chaidamu Basin, on the Qinghai-Tibet Plateau, and in the underground brines in the Sichuan Basin of Southwest China. The components of the brines are sodium, potassium, lithium, chloride, borate, as well as sulfate, and the rare alkaline elements rubidium and cesium.[1,2] The brines mostly belong to the complex six-component system of ($Li + Na + K + Cl + SO_4 + B_4O_7 + H_2O$). The climatic conditions in the region of Caidamu Basin is windy, is arid, has little rainfall, and has great evaporating capacity.[1] To economically exploit the brine and mineral resources, it is of great importance to adopt the local natural resources such as the energy of wind and sun for a solar pond technique. Therefore, metastable phase equilibrium research is essential to predict the crystallized path of the evaporation of the brines.

The reciprocal quaternary system ($Na + K + Cl + B_4O_7 + H_2O$) is a subsystem of the six-component system. Although the stable phase equilibrium of the quaternary system at 298.15 K and the metastable solubilities of its ternary subsystem at 308.15 K have been reported in our previous research,[3,4] the metastable phase equilibrium of the reciprocal quaternary system is not reported in the literature to describe the metastable behavior to separate and purify the mixture salts of borax and halo-sylvite. In this paper, the metastable solubilities and the physicochemical properties of the reciprocal quaternary system of ($Na + K + Cl + B_4O_7 + H_2O$) at 308.15 K are presented.

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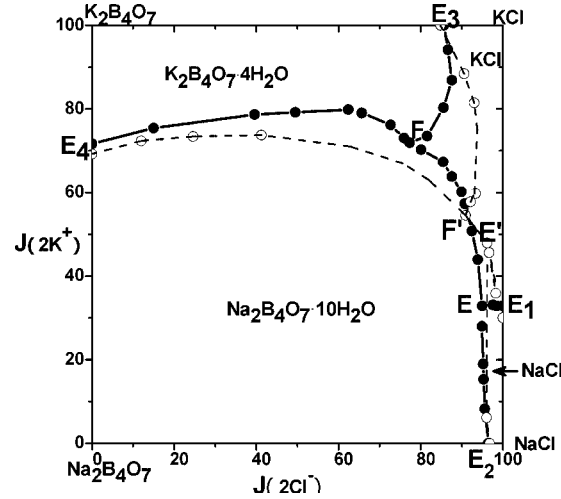

Figure 1. Metastable phase diagram at 308.15 K (solid line) and the stable phase diagram at 298.15 K (dashed line) of the quaternary system ($Na + K + Cl + B_4O_7 + H_2O$).

2. Experimental Section

2.1. Apparatus and Reagents. The isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermal insulation material box (70 cm long, 65 cm wide, 60 cm high) with an apparatus to control the temperature was installed. The temperature controlling apparatus is made up of an electric relay, an electrical contact thermograph, and heating lamps. When the solution temperature in the container was under (308.15 ± 0.3) K, the apparatus for controlling the temperature formed a circuit and the heating lamp began to heat. Conversely, the circuit was broken, and the heating lamp stopped working when the temperature exceeded 308.15 K. Therefore, the

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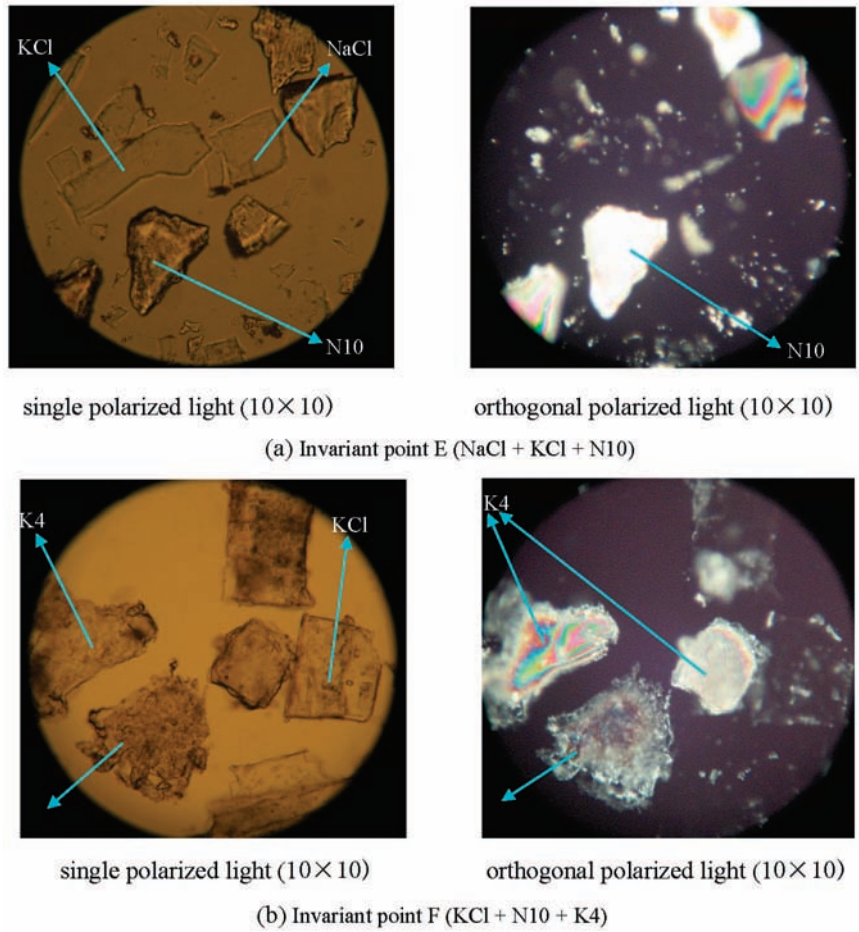


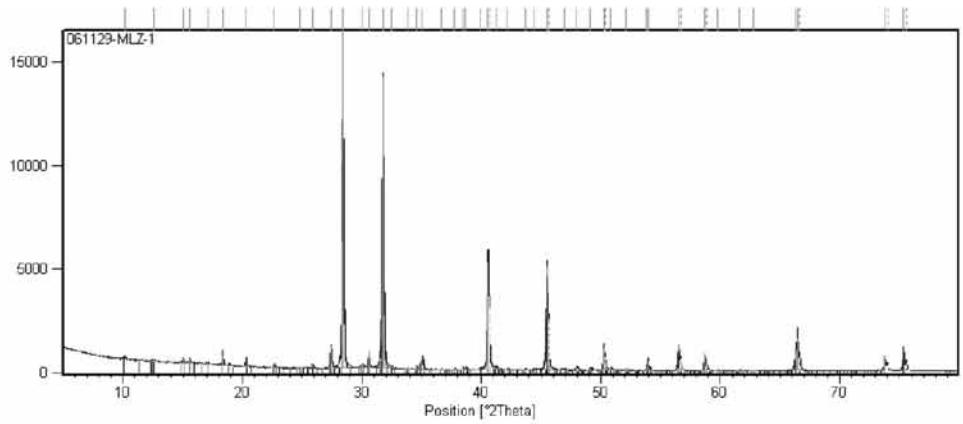
Figure 2. Identification of the invariant points for the solid phase in the reciprocal system with polarized microscopy using an oil immersion method. (a) The invariant point E (NaCl + KCl + $Na_2B_4O_7 \cdot 10H_2O$). (b) The invariant point F ($Na_2B_4O_7 \cdot 10H_2O$ + $K_2B_4O_7 \cdot 4H_2O$ + KCl).

temperature in the box could always be kept to (308.15 ± 0.3) K. An electric fan installed on the box always worked to accelerate the evaporation of water from the solutions. The solid phase minerals were identified with a XP-300 Digital Polarizing Microscopy (Shanghai Caikon Optical Instrument Co., Ltd., China) and an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands).

The chemicals used were of analytical grade, except borax which was a guaranteed reagent (GR), and were obtained from either the Tianjin Kermel Chemical Reagent, Ltd., or the Shanghai Guoyao Chemical Reagent Co., Ltd.: sodium chloride (NaCl, ≥ 99.5 mass %), potassium chloride (KCl, ≥ 99.5 mass %), borax ($Na_2B_4O_7 \cdot 10H_2O$, ≥ 99.5 mass %), potassium borate tetrahydrate ($K_2B_4O_7 \cdot 4H_2O$, ≥ 99.5 mass %). They were recrystallized before use. Doubly deionized water (DDW) with conductivity less than $1.2 \cdot 10^{-4}$ $S \cdot m^{-1}$ and pH 6.60 was used to prepare the series of the artificial synthesized brines and chemical analysis.

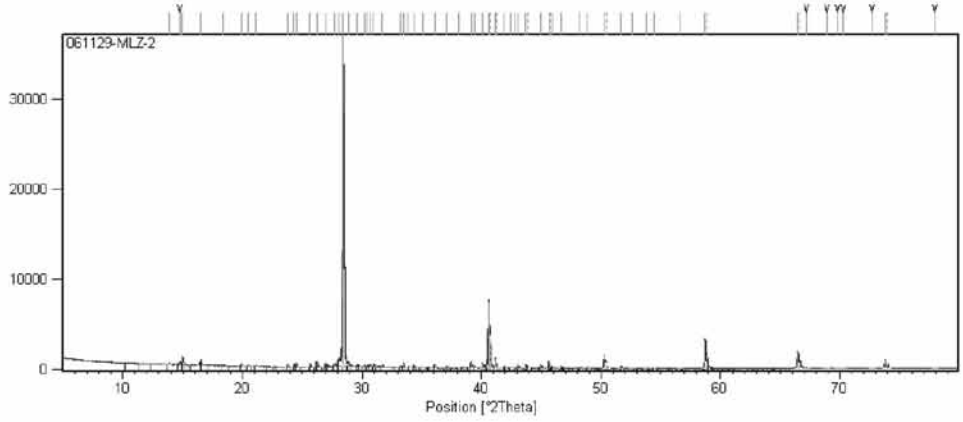
2.2. Experimental Method. The isothermal evaporation method was used in this study. According to phase equilibrium composition, the appropriate quantity of salts and DDW calculated was mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high). Then, the containers were put into the box for the isothermal evaporation at (308.15 ± 0.3) K. The experimental conditions with air flowing velocity of (3.5 to 4.0) $m \cdot s^{-1}$, relative humidity of (20 to 30) %, and evaporation rate of (4 to 6) $mm \cdot d^{-1}$ are presented, just like the climate of the Caidamu Basin. For metastable evaporation, the solutions were not stirred, and the crystal behavior of the solid phase was observed periodically. When enough new solid phase appeared, the wet residue mixtures were taken from the solution. The solids were then approximately evaluated by the combined chemical analysis, of XP-300D Digital Polarizing Microscopy using an oil immersion, and further identified with X-ray diffraction. Meanwhile, a 5.0 mL sample of the clarified solution was taken from the liquid phase of each polyethylene container through a filter pipet and then diluted to a 250.0 mL final volume in a volumetric flask filled with DDW for the quantitative analysis of the compositions of the liquid phase. Some other filtrates were used to measure the relative physicochemical properties individually according to the analytical method. The remainder of the solution continued to be evaporated and reached a new metastable equilibrium.

2.3. Analytical Method. The composition of the potassium ion in liquids and their corresponding wet solid phases was analyzed by gravimetric methods of sodium tetraphenyl borate with a precision of ≤ ± 0.05 mass %, both with a precision of ≤ ± 0.3 mass %. The concentrations of chloride and borate were determined by titration with mercury nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromphenol blue and by basic titration in the



No.	Visible	Ref. Code	Chemical Formula	Score	Scale Factor	SemiQuant/%
1	True	01-075-0296	KCl	49	0.369	22
2	True	01-075-0296	NaCl	45	0.732	57
3	True	01-075-0296	$B_4O_5(OH)_4(Na_2(H_2O)_8$	39	0.030	20
4	True	01-075-0296	$Na_2B4O_7(H_2O)_5$	13	0.007	1

(a), the X-ray diffraction photograph and the analytical data for the invariant points E



No.	Visible	Ref. Code	Chemical Formula	Score	Scale Factor	SemiQuant/%
1	True	01-072-1540	KCl	39	0.650	72
2	True	01-076-0753	$K_2(B_4O_5(OH)_4)(H_2O)_2$	37	0.011	22
3	True	01-074-0339	$B_4O_5(OH)_4(Na_2(H_2O)_8$	10	0.004	5

(b), the X-ray diffraction photograph and the analytical data for the invariant points F

Figure 3. X-ray diffraction data of the invariant points. (a) The invariant point E (NaCl + KCl + $Na_2B_4O_7 \cdot 10H_2O$). (b) The invariant point F ($Na_2B_4O_7 \cdot 10H_2O$ + $K_2B_4O_7 \cdot 4H_2O$ + KCl).

presence of mannitol, respectively.[5] The concentration of the sodium ion was calculated by subtraction via charge balance.

A PHS-3C precision pH meter supplied by the Shanghai Precision & Scientific Instrument Co. Ltd. was used to measure the pH of the equilibrium aqueous solutions (precision of ± 0.01). The pH meter was calibrated with standard buffer solutions of a mixed phosphate of potassium dihydrogen phosphate and sodium dihydrogen phosphate (pH 6.84) as well as borax (pH 9.18). The densities (ρ) were measured with a density bottle method with a precision of ± 0.2 mg. The viscosities (η) were determined using an Ubbelohde capillary viscometer, which was placed in a thermostat at (308.15 ± 0.1) K. No fewer than five flow times for each equilibrium liquid phase were measured with a stopwatch with a precision of 0.1 s to record the flowing time, and the results calculated were the average. An Abbe refractometer (model WZS-1) was used for measuring the refractive index (n_D) with an accuracy of ± 0.0001. Conductivities (κ) were measured with an Orion 145A+ Conductivity Meter (Thermo Electron Corporation, America) with a precision of ± 0.001 $S \cdot m^{-1}$. The physicochemical parameters of density, refractive index, and pH were also all placed in a thermostat that electronically controlled the set temperature at (308.15 ± 0.1) K.

3. Results and Discussion

For the mineral identification when enough new solid phase appeared, the wet residue mixtures were taken from the solution according to the experimental method. First, as for the minerals of $Na_2B_4O_7 \cdot 10H_2O$ and $K_2B_4O_7 \cdot 4H_2O$, the former belongs to a

Table 1. Solubilities of the Metastable Quaternary System (Na + K + Cl + B_4O_7 + H_2O) at 308.15 K

	comp. of the sol., W_B (%)				Jänecke index, J_B/[mol/100 mol($2Na^+ + 2K^+$)]			
no.	Na^+	K^+	Cl^-	$B_4O_7^{2-}$	$J(2Cl^-)$	$J(2K^+)$	$J(H_2O)$	solid phase[a]
A	1.30	0.00	0.00	4.40	0.00	0.00	2090.17	N10
B	10.47	14.87	16.15	0.00	100.00	0.00	1788.31	NaCl
C	0.00	3.87	13.49	0.00	100	100	18468.05	KCl
D	0.00	6.56	0.00	19.26	0.00	100	4311.59	K4
1(E_1)	7.85	6.54	18.06	0.00	100	32.94	1471.69	NaCl + KCl
2	7.84	6.60	17.76	0.58	98.54	32.89	1469.10	NaCl + KCl
3	7.85	6.56	17.66	0.95	97.6	33.09	1456.10	NaCl + KCl
4(E)	7.87	0.00	17.17	1.99	94.98	32.89	1445.77	NaCl + KCl + N10
5(E_2)	10.62	1.51	15.80	1.28	96.47	0.00	1736.76	NaCl + N10
6	9.88	2.87	15.89	1.59	95.63	8.25	1684.84	NaCl + N10
7	9.36	3.62	16.24	1.74	95.33	15.27	1612.49	NaCl + N10
8	9.10	5.38	16.50	1.81	95.22	18.97	1566.69	NaCl + N10
9	8.15	15.22	16.57	1.94	94.92	27.96	1532.30	NaCl + N10
10(E_3)	0.00	14.75	11.83	4.34	85.66	100	1955.76	KCl + K4
11	0.49	14.73	12.16	4.34	85.99	94.61	1899.70	KCl + K4
12	0.54	13.68	12.29	4.15	86.66	94.16	1894.74	KCl + K4
13	1.22	12.88	12.51	3.88	87.60	86.86	1893.49	KCl + K4
14	1.86	12.41	12.45	4.60	85.56	80.30	1844.98	KCl + K4
15	2.65	12.36	12.51	6.19	81.57	73.39	1699.85	KCl + K4
16(F)	2.84	8.65	12.06	7.74	77.34	71.90	1641.11	KCl + K4 + N10
17(E_4)	2.01	9.86	0.00	24.00	0.00	71.66	2346.01	N10 + K4
18	1.89	9.55	1.78	22.09	15.03	75.41	2134.79	N10 + K4
19	1.74	10.78	4.49	15.01	39.58	76.36	2000.89	N10 + K4
20	1.66	12.05	6.11	13.66	49.49	79.22	2160.56	N10 + K4
21	1.79	12.73	8.55	11.27	62.43	79.81	1906.21	N10 + K4
22	1.87	12.65	9.48	10.86	65.66	79.97	1773.28	N10 + K4
23	2.28	12.61	10.89	8.97	72.68	76.57	1712.53	N10 + K4
24	2.78	11.86	8.30	11.95	75.94	72.72	1838.60	N10 + K4
25	3.11	11.41	12.46	6.78	80.09	69.15	1664.48	N10 + KCl
26	3.26	10.91	13.13	4.90	85.45	67.31	1723.59	N10 + KCl
27	3.64	10.43	13.59	4.20	87.64	63.8	1717.14	N10 + KCl
28	4.06	10.17	14.15	3.45	89.98	60.17	1699.65	N10 + KCl
29	4.45	9.25	14.57	3.30	90.62	57.36	1652.70	N10 + KCl
30	5.27	8.23	15.16	2.97	91.80	50.79	1604.93	N10 + KCl
31	6.17		15.94	2.27	93.91	43.95	1562.35	N10 + KCl

[a] K4, $K_2B_4O_7 \cdot 4H_2O$; N10, $Na_2B_4O_7 \cdot 10H_2O$; W_B, in mass fraction.

monoclinic system and a dual optical negative crystal, i.e., $2v(-)$, whereas the later belongs to a trimetric system and the dual optical positive crystal, i.e., $2v(+)$. Second, the minerals NaCl and KCl can be identified through the property of refractive index. The refractive index of NaCl is higher than that of KCl. Observed with an XP-300D Digital Polarizing Microscopy using an oil immersion method, the crystal photos of single and orthogonal polarized light on representative solid phases in the invariant points E (NaCl + KCl + $Na_2B_4O_7 \cdot 10H_2O$) and F ($Na_2B_4O_7 \cdot 10H_2O$ + $K_2B_4O_7 \cdot 4H_2O$ + KCl) are presented in Figure 2. The metastable equilibria solid phases in the invariant points E and F are further confirmed with X-ray diffraction analysis and listed in Figure 3, except in the invariant points E in Figure 3 a which show that the minerals KCl, NaCl, $Na_2B_4O_7 \cdot 10H_2O$, and a minor $Na_2B_4O_7 \cdot 5H_2O$ exist. The minor of $Na_2B_4O_7 \cdot 5H_2O$ may be formed due to the dehydration of $Na_2B_4O_7 \cdot 10H_2O$ in the processes of transfer operation and/or grinding.

The metastable phase equilibrium experimental results of solubilities and properties of the quaternary system (Na + K+ Cl + B_4O_7 + H_2O) at 308.15 K were determined and are listed in Tables 1 and 2, respectively. On the basis of the Jänecke index (J_B, J_B/[mol/100 mol($2Na^+ + 2K^+$)]) in Table 1, the metastable equilibrium phase diagram of the system at 308.15 K was plotted (Figure 1). In Figure 1, the metastable phase diagram consists of two invariant points of three solid phases cosaturated corresponding to (NaCl + KCl + $Na_2B_4O_7 \cdot 10H_2O$) and ($Na_2B_4O_7 \cdot 10H_2O$ + $K_2B_4O_7 \cdot 4H_2O$ + KCl), five univariant curves, and four crystallizing zones corresponding to NaCl, KCl, $Na_2B_4O_7 \cdot 10H_2O$, and $K_2B_4O_7 \cdot 4H_2O$. The crystallization area of $Na_2B_4O_7 \cdot 10H_2O$ is the largest, which indicates that borax

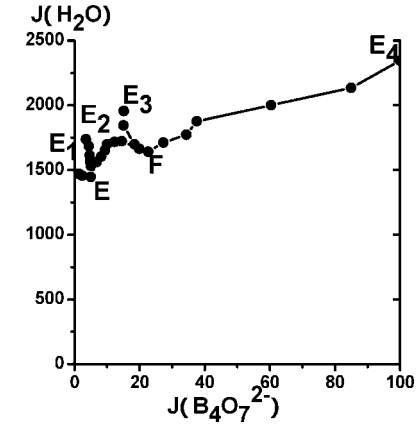


Figure 4. Water-phase diagram of the quaternary system (Na + K + Cl + B_4O_7 + H_2O) at 308.15 K.

is of low solubility, and the areas of the crystallization zones decrease in the order of $K_2B_4O_7 \cdot 4H_2O$, KCl, and NaCl. Due to the high solubilities of sodium chloride and potassium chloride, there is a strong salting-out effect on other salts of borate. Neither double salts nor solid solutions are formed in the reciprocal quaternary system. The water phase diagram of the quaternary system at 308.15 K is shown in Figure 4. It shows that the Jänecke index values of $J(H_2O)$ gradually change with increasing $J(B_4O_7^{2-})$. At the invariant point E, the Jänecke index of $J(H_2O)$ is the smallest, while at point E_4, the Jänecke index is the largest indicating that the solubility of borax is quite low.

Figure 5 shows diagrams of physicochemical properties vs composition. The physicochemical properties of the metastable

Table 2. Physicochemical Properties of the Metastable Reciprocal Quaternary System (Na + K + Cl + B_4O_7 + H_2O) at 308.15 K

no.	density $10^{-3}\rho$/(kg·m^{-3})	pH	refractive index	viscosity η/(mPa·s)[a]	no.	density $10^{-3}\rho$/(kg·m^{-3})	pH	refractive index	viscosity η/(mPa·s)[a]
A	1.0441	—	1.3405	—	15	1.2536	9.1	1.384	1.0876
B	1.1935	—	1.38	—	16(F)	1.27	9.3	1.3863	1.1963
C	1.1857	—	1.3742	—	17(E_4)	1.304	10.36	1.3868	2.8279
D	1.2003	—	1.3678	—	18	1.3206	10.12	1.3868	2.8032
1(E_1)	1.23	5.63	1.3869	1.1241	19	1.2533	9.94	1.3803	1.5661
2	1.2414	7.29	1.3872	1.1452	20	1.26	9.62	1.3823	1.4548
3	1.2433	7.72	1.388	1.193	21	1.2636	9.58	1.384	—
4(E)	1.2524	7.81	1.389	1.262	22	1.2764	9.53	—	1.39
5(E_2)	1.206	—	1.3802	—	23	1.2784	9.47	1.3856	—
6	1.2172	8.22	1.3836	1.3023	24	—	—	—	—
7	1.2274	8.66	1.386	1.2865	25	1.2555	9.08	1.3857	1.1682
8	1.2313	9.21	1.3862	1.2829	26	1.2484	9.51	1.3842	1.0812
9	1.2398	8.51	1.3879	1.2729	27	1.2409	9.48	1.3828	1.048
10(E_3)	1.227	9.55	1.3782	0.8499	28	1.2348	9.02	1.3827	1.0252
11	1.2347	9.43	1.3798	0.8443	29	1.2366	9.04	1.3835	1.0421
12	—	—	—	—	30	1.2404	8.65	1.3841	1.0809
13	—	—	1.3792	0.8844	31	1.2381	8.38	1.3849	1.013
14	1.2433	9.02	1.3814	1.0625					

[a] η_{H2O} = 0.7190 mPa·s in the Landard Chemical Handboook 5.141.

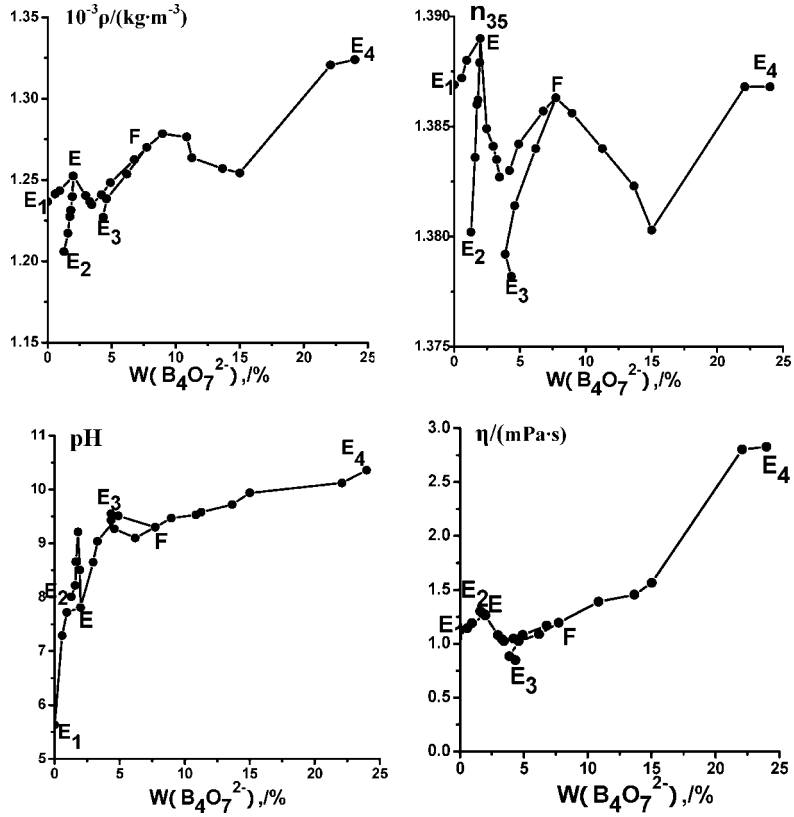


Figure 5. Diagram of physicochemical properties vs composition for the metastable quaternary system (Na + K + Cl + B_4O_7 + H_2O) at 308.15 K.

equilibrium solution vary regularly with the composition of borate mass fraction. The singular point on every curve of the composition vs property diagram corresponds to the same invariant point E and F on the metastable solubility. The density, pH, and viscosity values reach maximum values at point E_4. The refractive index has a maximum value at the invariant point E. The pH in the liquid phases, except curve E_1E which is cosaturated with NaCl and KCl, varies between 7.81 and 10.36 when borate salts exist in solid phases in the reciprocal quaternary system.

Comparison of the dry-salt diagrams of the metastable equilibrium at 308.15 K and the stable equilibrium at 298.15 K in the same system is also shown in Figure 1. The areas of the metastable crystallization regions of borax and potassium chloride are both enlarged, while the other minerals decrease in area.

4. Theorized Calculation of the Densities and Refractive Index

Based on the following empirical equations of the density and refractive index in electrolyte solutions developed in the previous study,[6] the density and refractive index of the solution were also calculated.

$$\ln(d/d_0) = \sum A_i \cdot W_i$$

$$\ln(n/n_0) = \sum B_i \cdot W_i$$

where d_0 = 0.99406 g·mL^{-1}, the density of water at 308.15 K; n_0 = 1.3313076, the refractive index of water at 308.15 K, respectively. A_i and B_i are the constants of each possible component

Table 3. Comparison of the Experimental and the Calculated Values of Density and Refractive Index in the Quaternary System at 308.15 K

	density $10^{-3}\rho/(kg \cdot m^{-3})$			refractive index		
no.	experiments	calculation	absolute Err	experiments	calculation	absolute Err
1(E_1)	1.23	1.2347	0.0038	1.3869	1.3869	0.0000
2	1.2414	1.2384	−0.0024	1.3872	1.3872	0.0000
3	1.2433	1.2423	−0.0008	1.388	1.3877	−0.0002
4(E)	1.2524	1.2498	−0.0021	1.389	1.3885	−0.0004
5(E_2)	1.206	1.2059	−0.0001	1.3802	1.3817	0.0011
6	1.2172	1.2147	−0.0021	1.3836	1.3828	−0.0006
7	1.2274	1.2247	−0.0022	1.386	1.3845	−0.0011
8	1.2313	1.2309	−0.0003	1.3862	1.3855	−0.0005
9	1.2398	1.2378	−0.0016	1.3879	1.3863	−0.0012
10(E_3)	1.227	1.2282	0.001	1.3782	1.373	−0.0038
11	1.2347	1.2314	−0.0027	1.3798	1.3799	0.0001
12	—	1.2305		—	1.3799	
13	—	1.227		1.3792	1.3794	0.0001
14	1.2433	1.2343	−0.0008	1.3814	1.3806	−0.0005
15	1.2536	1.2562	0.0021	1.384	1.3842	0.0001
16(F)	1.27	1.2714	0.0011	1.3863	1.3861	−0.0001
17(E_4)	1.304	1.324	0.0154	1.3868	1.3868	0.0001
18	1.3206	1.3252	0	1.3868	1.3868	0.0000
19	1.2533	1.2607	0.0035	1.3903	1.3881	−0.0016
20	1.26	1.2675	0.006	1.3823	1.3819	−0.0003
21	1.2636	1.2712	0.006	1.384	1.3838	−0.0001
22	1.2764	1.2802	0.003	—	1.3858	
23	1.2784	1.273	−0.0042	1.3856	1.3855	−0.0001
24	—	1.2957		—	1.3874	
25	1.2555	1.2624	0.0055	1.3857	1.3852	−0.0004
26	1.2484	1.2447	−0.003	1.3842	1.3831	−0.0008
27	1.2409	1.2402	−0.0006	1.3828	1.3829	0.0001
28	1.2348	1.2366	0.0015	1.3827	1.383	0.0002
29	1.2366	1.2398	0.0026	1.3835	1.3839	0.0003
30	1.2404	1.2414	0.0008	1.3841	1.3848	0.0005
31	1.2381	1.2402	0.0017	1.3849	1.3856	0.0005

i in the system, and they can be obtained from the saturated solubility of the binary system at 308.15 K. W_i is the salt of i in the solution in mass fraction (mass %). Constants A_i and B_i of NaCl, KCl, $Na_2B_4O_7$, and $K_2B_4O_7$ for calculation of density and refractive index of solution are 0.006869, 0.006367, 0.008616, and 0.008153 and 0.001349, 0.001118, 0.001207, and 0.001169, respectively. The calculated results and experimental values are presented in Table 3 for comparison, and all the calculated results with the maximum relative deviations are less than 0.3 %.

5. Conclusions

The solubilities and physicochemical properties of the metastable equilibria of the reciprocal quaternary system (Na + K + Cl + B_4O_7 + H_2O) at 308.15 K were experimentally determined with the isothermal evaporation method. In the metastable salt diagram of the system at 308.15 K, there are two invariant points, five univariant curves, and four crystallizing regions corresponding to NaCl, KCl, $Na_2B_4O_7 \cdot 10H_2O$, and $K_2B_4O_7 \cdot 4H_2O$. When compared to the stable diagram, the areas of the crystallized regions of borax and potassium are larger, while those of sodium chloride and potassium tetraborate tetrahydrate are smaller in the metastable diagram. The calculated values of densities and refractive index in the metastable quaternary system with empirical equations are in good agreement with the experimental values.

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