J. Chem. Eng. Data **2010,** *55,* 4211–4215

Metastable Phase Equilibria of the Reciprocal Quaternary System Containing Lithium, Sodium, Chloride, and Sulfate Ions at 273.15 K[†]

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Experimental studies on the metastable solubilities and the physicochemical properties including density, refractive index, conductivity, and pH values in the reciprocal quaternary system containing lithium, sodium, chloride, and sulfate at 273.15 K were determined with the method of isothermal evaporation. According to the experimental results, the dry-salt phase diagram, the water phase diagram, and the physicochemical properties versus composition were plotted. In the dry-salt phase diagram, there are three invariant points, seven solubility isotherm curves, and five crystallization fields corresponding to sodium chloride, mirabilite, lithium chloride dehydrate ($LiCl \cdot 2H_2O$), lithium sulfate monohydrate, and a double salt ($Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$). There were no solid solutions formed in the reciprocal quaternary system. The crystallizing region of mirabilite is the largest, while the region of $LiCl \cdot 2H_2O$ is the smallest with the highest concentration and a strong salting-out effect to NaCl and $Li_2SO_4 \cdot H_2O$. When compared with the stable phase diagram at 273.15 K, the area of the phase region of mirabilite is enlarged significantly, while the areas of the phase regions of NaCl, $Li_2SO_4 \cdot H_2O$, and $Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$ are decreased. The calculated values of densities and refractive index in the quaternary system with empirical equations are in good agreement with the experimental values.

Introduction

A salt lake is a naturally occurring complex body of water and salt interaction. It is well-known that salt-water phase equilibria play an important role in exploiting brine resources and describing the geochemical behavior of brine minerals. There are more than 1000 salt lakes in China. The Salt Lake of Qaidam Basin consists of a series of lakes including the Dong-Xi-tai lake, Da-xiao-caidan lake, and Yiliping lake, and is one of the subtypes of magnesium sulfate brines famous for its abundance of lithium, potassium, magnesium, and boron resources.[1] The main components are Li^+, Na^+, K^+, Mg^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-} (HCO_3^-), and borate. To economically exploit the brine and mineral resources, it is important to adequately adopt the local natural resources such as the energy of the wind and solar pond techniques. Therefore, the simulative experimental studies on metastable phase equilibria are essential to predict the actual evaporation path of mineral crystallization for the effective separation and purification of the lithium-containing mixture of salts.

As a part of the complex component system, we have been studying some subsystems of the Salt Lake of Qaidam Basin at different temperatures.[2−6] However, the quaternary system containing lithium, sodium, chloride, and sulfate is not reported in the literature that describes the metastable behavior. The average temperature of the Qaidam Basin in winter is about 273.15 K, so the metastable phase equilibria study of this quaternary system at 273.15 K will be of great value for recovering lithium from the brines. In this paper, the metastable solubilities and the physicochemical properties of the quaternary system ($Li + Na + Cl + SO_4 + H_2O$) at 273.15 K are presented.

Experimental Section

Apparatus and Reagents. The isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermal insulated box (70 cm long, 65 cm wide, 60 cm high) with a refrigerating compressor and an apparatus to control the temperature was installed. The temperature-controlling apparatus is made up of an electric relay, an electrical contact thermometer, and heating lamps. When the solution temperature in the container was below (273.15 ± 0.2) K, the apparatus for controlling the temperature formed a circuit, and the heating lamp began to heat. Conversely, the circuit was interrupted, and the heating lamp stopped working when the temperature exceeded 273.15 K. Therefore, the temperature in the box could always be kept at (273.15 ± 0.2) K. An electric fan installed in the box always worked to accelerate the rate of evaporation of water from the solutions. The solid phase minerals were identified with a XP-300 Digital Polarizing Microscope (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, obtained from either the Tianjin Kermel Chemical Reagent Ltd. or the Shanghai-Lithium Industrial Co. Ltd., sodium chloride (NaCl, 99.5 % (by mass)), sodium sulfate (Na_2SO_4, 99.0 % (by mass)), lithium chloride (LiCl, 99.0 % (by mass)), and lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$, 99.0 % (by mass)), and were recrystallized before use. Doubly deionized water (DDW) with

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[†] Part of the "Sir John S. Rowlinson Festschrift".

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10.1021/je1003669

Table 1. Metastable Equilibrium Solubilities of the Quaternary System ($LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O$) at 273.15 K[a]

	composition of liquid phase w_b/% (by mass)				Jänecke index/[mol/100 mol dry salt]			
no.	Li^+	Na^+	Cl^-	SO_4^{2-}	$2Li^+$	SO_4^{2-}	H_2O	equilibrium solid phase[a]
1,A	0.00	10.48	15.57	0.80	0.00	3.67	1781.55	NaCl + Mir
2	0.29	9.55	15.53	0.90	9.06	4.12	1791.93	NaCl + Mir
3	0.54	8.86	15.52	1.25	16.88	5.60	1767.26	NaCl + Mir
4	0.73	8.36	15.58	1.41	22.44	6.27	1750.45	NaCl + Mir
5	0.98	7.60	15.54	1.62	29.99	7.15	1746.42	NaCl + Mir
6	1.11	7.20	15.45	1.83	33.90	8.03	1743.17	NaCl + Mir
7	1.29	6.82	15.42	2.28	37.64	10.01	1707.32	NaCl + Mir
8	1.48	6.26	15.44	2.36	43.86	10.15	1705.65	NaCl + Mir
9,E	1.54	6.17	15.42	2.62	45.19	11.14	1683.99	NaCl+Mir+Db1
10	1.68	5.76	15.77	2.30	49.69	9.84	1678.42	NaCl + Db1
11	1.93	5.03	15.87	2.36	56.08	9.90	1672.05	NaCl + Db1
12	2.29	4.21	16.18	2.72	64.31	11.04	1614.36	NaCl + Db1
13	2.90	2.89	16.96	3.10	76.85	11.89	1516.21	NaCl + Db1
14,F	2.94	2.72	17.06	3.13	78.34	11.91	1506.65	NaCl+Db1+Ls
15	3.08	2.45	17.78	2.31	80.65	8.75	1502.43	NaCl + Ls
16	3.40	1.57	18.76	1.36	87.55	5.60	1491.79	NaCl + Ls
17	3.47	1.39	19.11	1.02	89.24	3.78	1486.33	NaCl+ Ls
18	3.77	0.58	19.72	0.60	95.57	2.19	1470.46	Mir + Ls
19	3.97	0.32	20.50	0.35	97.60	1.24	1419.37	Mir + Ls
20,G	6.65	0.039	33.98	0.035	99.82	0.076	686.29	Mir + Ls
21,B	3.41	1.79	0.00	27.55	86.29	100.0	1301.62	Mir+Ls+Lc
22	2.89	2.34	2.75	21.15	80.33	85.02	1519.15	Mir + Db1
23	2.45	2.89	6.02	14.86	73.80	64.58	1709.32	Mir + Db1
24	2.27	3.53	9.18	10.68	68.06	46.21	1714.76	Mir + Db1
25	2.06	4.13	10.39	8.82	62.34	38.51	1737.34	Mir + Db1
26	1.85	4.90	13.02	5.38	55.58	23.38	1733.84	Mir + Db1
27	1.76	5.29	14.67	3.34	52.36	14.39	1721.31	Mir + Db1
28	1.56	6.05	15.27	2.76	46.07	11.77	1691.03	Mir + Db1
29,C	3.48	1.65	0.00	27.52	87.47	100.0	1304.98	Ls + Db1
30	3.21	1.67	2.98	21.70	86.43	84.32	1459.38	Ls + Db1
31	3.22	1.69	3.32	21.28	86.33	82.56	1458.38	Ls + Db1
32	3.12	1.69	3.56	20.3	85.97	80.80	1458.11	Ls + Db1
33	3.14	1.69	8.08	14.28	86.04	56.60	1513.95	Ls + Db1
34	3.07	1.68	8.87	12.70	85.81	51.38	1539.01	Ls + Db1
35	2.91	1.71	9.71	10.57	84.93	44.56	1589.52	Ls + Db1
36	2.90	1.93	11.79	8.15	83.28	33.78	1687.89	Ls + Db1
37	2.91	2.24	15.02	4.48	81.15	18.05	1662.92	Ls + Db1
38,D	6.63	0.047	33.88	0.00	99.98	0.00	690.55	NaCl + Lc
39,H	6.65	0.00	33.91	0.052	100.0	0.11	688.52	Ls + Lc

[a] Mir, $Na_2SO_4 \cdot 10H_2O$; Db1, $Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot 2H_2O$.

a conductivity less than $1 \cdot 10^{-4}$ S·m^{-1} was used to prepare the series of artificially synthesized brines and for chemical analysis.

Experimental Method. The isothermal evaporation method was used in this study. According to phase equilibrium composition, the appropriate quantity of salts and DDW was calculated. They were mixed together as a series of artificially synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high). The containers were put into the box for isothermal evaporation at (273.15 ± 0.3) K. The experimental conditions of air flow velocity of (3.5 to 4.0) m·s^{-1}, relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) mm·day^{-1} are similar to those of the climate of Qaidam Basin. The solutions were not stirred for metastable evaporation, 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 evaluated with combined chemical analysis, observation with XP-300D Digital Polarizing Microscopy, and further identification with X-ray diffraction. Meanwhile, a 5.0 mL sample of the clear solution was taken from the liquid phase of each polyethylene container through a filter pipet and then diluted with DDW to 250.0 mL final volume in a volumetric flask for the quantitative analysis of the composition 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.

Analytical Method. The composition of the SO_4^{2-} in the liquids was analyzed by the classical gravimetric method using barium chloride with a precision within ± 0.05 % (by mass). The Cl^- concentration was determined by titration with hydrargyrum nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue with a precision of ± 0.3 % (by mass). The Li^+ concentration was determined by ICP-AES.[7]

A PHS-3C precision pH meter supplied by the Shanghai Precision and 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 two standard buffer solutions of potassium dihydrogen phosphate and disodium hydrogen phosphate (pH 6.98) and borax (pH 9.46); the densities (ρ) were measured with a density bottle $V = 5.0$ mL with a precision of ± 0.2 mg. An Abbe refractometer (model WZS-1) was used for measuring the refractive index (n_D) with a precision of ± 0.0001. Conductivities (κ) were measured with an Orion 145A+ Conductivity Meter (Thermo Electron Corporation, America) with a precision of ± 0.001 S·m^{-1}. The physicochemical parameters, density, refractive index, conductivity, and pH, were also measured at the experimental temperature at (273.15 ± 0.1) K.

Results and Discussion

The experimental data on the metastable solubilites and the relevant physicochemical properties of the quaternary system

Table 2. Physicochemical Property Data of the Quaternary System ($LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O$) at 273.15 K

no.[a]	density[b] $10^{-3}\rho$ ($kg\cdot m^{-3}$)	conductivity κ ($S\cdot m^{-1}$)	n_D	pH
1,A	1.2146	1.160	1.3830	6.92
2	1.2096	1.140	1.3826	7.15
3	1.2062	1.134	1.3822	7.23
4	1.2039	1.105	1.3821	—
5	1.1988	1.071	1.3820	7.34
6	1.1950	1.051	—	—
7	—	1.028	1.3823	7.41
8	1.1927	—	1.3825	7.52
9,E	—	1.008	1.3831	7.66
10	1.1884	0.996	1.3824	—
11	1.1827	0.988	1.3832	8.00
12	1.1822	0.952	—	—
13	—	—	1.3847	8.43
14,F	1.1813	0.908	1.3855	8.52
15	1.1758	0.885	1.3867	8.22
16	1.1652	0.846	1.3871	—
17	1.1636	0.824	1.3875	—
18	—	0.725	1.3901	7.94
19	1.1603	0.645	1.3910	—
20,G	1.2645	0.408	1.4250	4.30
21,B	—	0.316	1.3858	9.46
22	—	0.400	—	9.42
23	1.2264	0.555	1.3821	9.21
24	1.2115	0.698	—	8.82
25	1.2048	0.846	1.3816	8.33
26	—	0.903	—	—
27	—	0.967	1.3820	7.81
28	1.1942	0.991	1.3828	7.86
29,C	—	0.296	1.3869	—
30	1.2702	0.375	1.3852	9.35
31	1.2673	0.395	1.3846	9.30
32	—	0.417	1.3840	9.28
33	1.2244	0.567	1.3836	9.23
34	1.2136	0.596	1.3832	9.02
35	1.1982	0.665	—	—
36	—	0.763	1.3828	8.94
37	1.1787	0.842	1.3843	8.75
38,D	1.2642	0.377	1.4242	4.51
39,H	1.2635	—	1.4245	4.42

[a] The no. column corresponds to the no. column in Table 1. [b] —, means not detected.

containing lithium, sodium, chloride, and sulfate at 273.15 K are presented in Table 1 and Table 2. The ion concentration values in the metastable equilibrium solution are expressed by the Jänecke index [mol/100 mol dry salt].

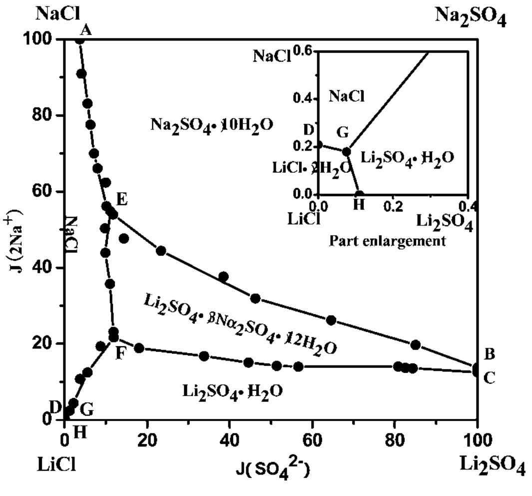


Figure 1. Metstable equilibrium phase diagram of the quaternary system ($LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O$) at 273.15 K. ●, experimental value; —, experimental isotherm curve.

Table 3. Comparisons of the Calculated and Experimental Values of Density and Refractive Index in the Quaternary System at 273.15 K

	density $\rho/(g\cdot cm^{-3})$			refractive index n_D		
no.	exptl value	calcd value	relative error, err %	exptl value	calcd value	relative error, err %
1,A	1.2146	1.2146	0.000	1.3830	1.3836	−0.043
2	1.2096	1.2071	0.207	1.3826	1.3830	−0.029
3	1.2062	1.2045	0.141	1.3822	1.3831	−0.065
4	1.2039	1.2022	0.141	1.3821	1.3832	−0.080
5	1.1988	1.1974	0.117	1.3820	1.3830	−0.072
6	1.1950	1.1952	−0.017	—	—	—
7	—	—	—	1.3823	1.3834	−0.080
8	1.1927	1.1927	0.000	1.3825	1.3832	−0.051
9,E	—	—	—	1.3831	1.3830	0.007
10	1.1884	1.1901	−0.143	1.3824	1.3836	−0.087
11	1.1827	1.1848	−0.178	1.3832	1.3834	−0.014
12	1.1822	1.1840	−0.152	—	—	—
13	—	—	—	1.3847	1.3862	−0.108
14,F	1.1813	1.1833	−0.169	1.3855	1.3865	−0.072
15	1.1758	1.1764	−0.051	1.3867	1.3866	0.007
16	1.1652	1.1659	−0.060	1.3871	1.3867	0.029
17	1.1636	1.1631	0.043	1.3875	1.3869	0.043
18	—	—	—	1.3901	1.3871	0.216
19	1.1603	1.1575	0.241	1.3910	1.3885	0.179
20,G	1.2645	1.2630	0.119	1.4250	1.4242	0.056
21,B	—	—	—	1.3858	1.3873	−0.108
22	—	—	—	—	—	—
23	1.2264	1.2272	−0.065	1.3821	1.3797	0.174
24	1.2115	1.2111	0.033	—	—	—
25	1.2048	1.2053	−0.042	1.3816	1.3806	0.072
26	—	—	—	—	—	—
27	—	—	—	1.3820	1.3823	−0.022
28	1.1942	1.1939	0.025	1.3828	1.3833	−0.036
29,C	—	—	—	1.3869	1.3875	−0.043
30	1.2702	1.2710	−0.063	1.3852	1.3838	0.101
31	1.2673	1.2690	−0.134	1.3846	1.3839	0.051
32	—	—	—	1.3840	1.3827	0.094
33	1.2244	1.2264	−0.163	1.3836	1.3831	0.036
34	1.2136	1.2146	−0.082	1.3832	1.3822	0.072
35	1.1982	1.1975	0.062	—	—	—
36	—	—	—	1.3828	1.3815	0.097
37	1.1787	1.1766	0.178	1.3843	1.3843	0.000
38,D	1.2642	1.2624	0.142	1.4242	1.4240	0.014
39,H	1.2635	1.2623	0.095	1.4245	1.4240	0.035

According to the experimental data in Table 1, the metastable equilibrium phase diagram of the system at 273.15 K was plotted, as shown in Figure 1. The metastable phase diagram in Figure 1 consists of three invariant points, saturated with salts $NaCl + Na_2SO_4\cdot 10H_2O + Li_2SO_4\cdot 3Na_2SO_4\cdot 12H_2O$, $NaCl + Li_2SO_4\cdot 3Na_2SO_4\cdot 12H_2O + Li_2SO_4\cdot H_2O$, and $NaCl + Li_2SO_4\cdot H_2O + LiCl\cdot 2H_2O$; and five crystallization zones

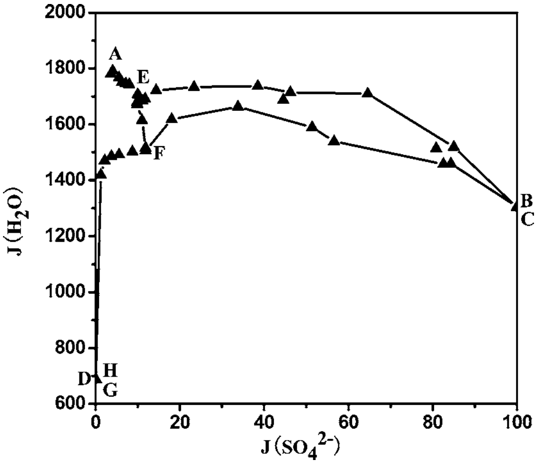
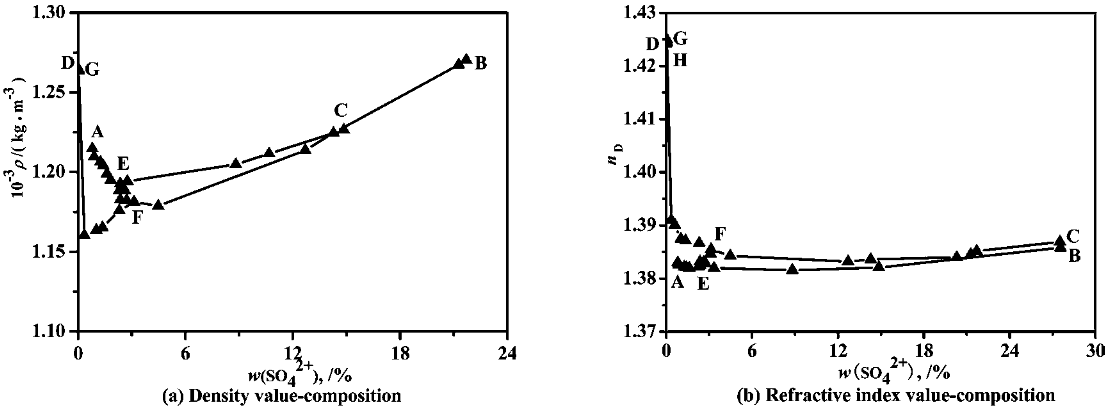
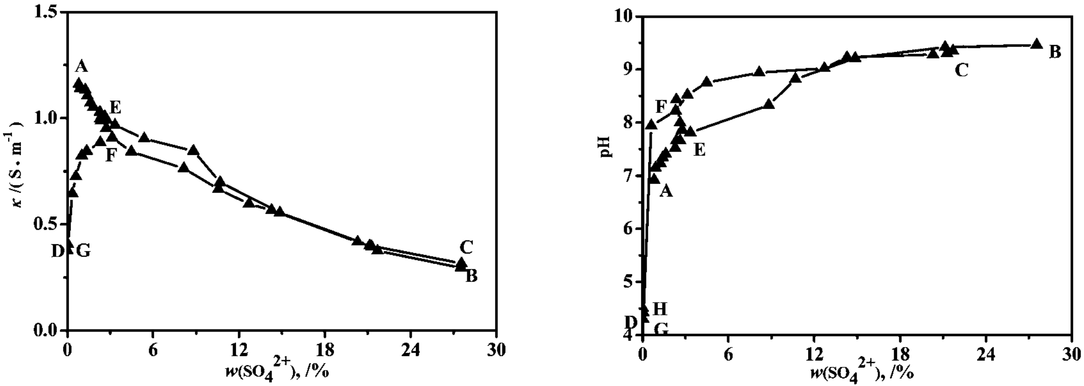


Figure 2. Water-phase diagram of the quaternary system ($LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O$) at 273.15 K.



(a) Density value-composition

(b) Refractive index value-composition



(c) Conductivity value-composition

(d) pH value-composition

Figure 3. Property−composition diagrams for the metastable quaternary system ($LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O$) at 273.15 K. ▲, experimental data point; —, experimental relationship diagram. (a) Density vs composition; (b) refractive index vs composition; (c) conductivity vs composition; and (d) pH vs composition.

corresponding to sodium chloride (NaCl), mirabilite ($Na_2SO_4 \cdot 10H_2O$), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), lithium chloride dihydrate ($LiCl \cdot 2H_2O$), and a double salt $Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$. There are seven isotherm curves corresponding to curves AE, BE, CF, DG, HG, EF, and FG, indicating the cosaturation of two salts. The crystallization area of $Na_2SO_4 \cdot 10H_2O$ is the largest, which indicates that mirabilite is of low solubility, and the area of the crystallization zones decreases in the order of $Na_2SO_4 \cdot 10H_2O$, $Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$, $Li_2SO_4 \cdot H_2O$, NaCl, $LiCl \cdot 2H_2O$. Due to the high solubility of $LiCl \cdot 2H_2O$, there is a strong salting-out effect on $Li_2SO_4 \cdot H_2O$ and NaCl. There were no solid solutions formed in the reciprocal quaternary system.

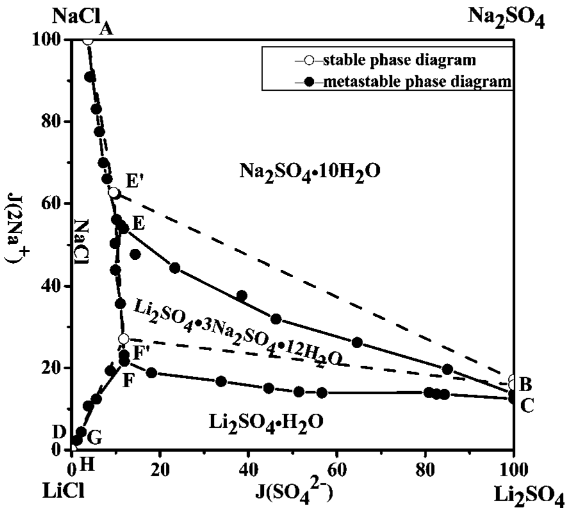


Figure 4. Comparison of the stable and metastable phase diagram of the quaternary system ($LiCl + NaCl + Li_2SO_4 + Na_2SO_4 + H_2O$) at 273.15 K. −●−, metastable curve; ···○···, stable curve.

The water phase diagram of the quaternary system at 273.15 K is shown in Figure 2. It is shown that the Jänecke index values $J(H_2O)$ gradually change with increasing $J(SO_4^{2-})$. At the invariant point G, the Jänecke index of $J(H_2O)$ is the smallest, which indicates that the water activity is quite small. On the basis of experimental data in Table 2, relationships between the solution physicochemical properties (density, refractive index, conductivity, and pH) and the mass fractions of sulfate are found, as shown in Figure 3. It can be concluded that the physicochemical properties change regularly with the mass fraction changes of sulfate.

Comparison of the dry-salt diagrams of the stable[8] and metastable equilibrium of the reciprocal quaternary system at 273.15 K is shown in Figure 4. The area of the metastable crystallization region of mirabilite is enlarged significantly, while the other mineral regions decrease.

Theorized Calculation of the Densities and Refractive Index

On the basis of the following empirical equations of the density and refractive index in electrolyte solutions developed in the previous study,[9] the density and refractive index of the solutions were calculated.

$$\ln \frac{d}{d_0} = \sum A_i \cdot W_i$$
$$\ln \frac{D}{D_0} = \sum B_i \cdot W_i$$

where d and d_0 refer to the density value of the solution and pure water at the same temperature; and the d_0 value of pure water at 273.15 K is 0.99984 g.cm^{-3}. While D and D_0 refer to the refractive index value of the solution and pure water at the same temperature, the D_0 value of pure water at 273.15 K is 1.33395. A_i and B_i are the constants of each possible component i in the system. W_i is the weight percentage of salt i in the solution. Constants A_i of NaCl, Na_2SO_4, Li_2SO_4, and LiCl for calculation of density in solution are 0.007173, 0.008962, 0.008321, and 0.005735, and constants B_i of NaCl, Na_2SO_4, Li_2SO_4, and LiCl for calculation of the refractive index in solution are 0.001371, 0.001177, 0.001212, and 0.001609, respectively. The calculated and the experimental values are presented in Table 3 for comparison, and all the calculated results have a maximum relative error less than 0.3 %.

Conclusions

The metastable equilibria of the reciprocal quaternary system containing lithium, sodium, chloride, and sulfate at 273.15 K were studied by an isothermal evaporation method. Solubilities and the physicochemical properties were determined experimentally. In the dry-salt phase diagram, there are three invariant points, seven solubility isotherm curves, and five crystallization fields. There were no solid solutions formed in the quaternary system. When compared with the stable phase diagram, the phase region of mirabilite is enlarged significantly. The calculated values of density and refractive index in the quaternary system with empirical equations are in good agreement with the experimental values.

Acknowledgment

The authors thank Professor Z.H. Gao at Qinghai Institute of Salt Lakes for his kind help. Thanks also go to the Associate Editors Paul L. Brown and Anthony R. H. Goodwin and the anonymous reviewers for their critical comments and kind help on the manuscript.

Literature Cited

(1) Zheng, X. Y.; Tang, Y.; Xu, C.; *Tibet Saline Lake*; Science Press: Beijing, 1988; p 169 (in Chinese).
(2) Deng, T. L. Phase equilibrium for the aquous system containing Lithium, sodium, potassium, chloride, and borate ions at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1295–1299.
(3) Deng, T. L.; Li, D. C. Solid-liquid metastable equilibria in the quaternary system (NaCl - KCl - $CaCl_2$ - H_2O) at 288.15 K. *Fluid Phase Equilib.* **2008**, *269*, 98–103.
(4) Deng, T. L.; Wang, S. Q.; Sun, B. Metastable Phase Equilibrium in the Aqueous Quaternary System (KCl + K_2SO_4 + $K_2B_4O_7$ + H_2O) at 308.15 K. *J. Chem. Eng. Data* **2008**, *53* (2), 411–414.
(5) Deng, T. L.; Li, D. C.; Wang, S. Q. Metastable Phase Equilibrium in the Aqueous Ternary System (KCl - $CaCl_2$ - H_2O) at (288.15 and 308.15) K. *J. Chem. Eng. Data* **2008**, *53*, 1007–1011.
(6) Wang, S. Q.; Deng, T. L. (Solid + liquid) isothermal evaporation phase equilibria in the aqueous ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at T = 308.15 K. *J. Chem. Thermodyn.* **2008**, *40*, 1007–1011.
(7) Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. *Analytical methods of brines and salts*, 2nd ed.; Science Press: Beijing, 1988; pp 35−66 (in Chinese).
(8) Hu, K. Y. Phase equilibrium of the quaternary system LiCl-NaCl-Li_2SO_4-Na_2SO_4-H_2O. *Russ. J. Inorg. Chem.* **1960**, *5* (1), 191–196.
(9) Fang, C. H. A new model for predicting density of electrolyte solutions. *J. Salt Lake Res.* **1990**, *2*, 15–20.

Received for review April 15, 2010. Accepted August 20, 2010. Financial support from the State Key Program of National Natural Science Foundation of China (Grant. 20836009), the National Natural Science Foundation of China (Grant. 40773045), and Senior Professor Program in Tianjin Government for TUST (Grant. 20100405) is greatly acknowledged.

JE1003669