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Metastable Phase Equilibrium in the Aqueous Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K

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ABSTRACT: Experimental studies on the metastable solubilities and the physicochemical properties including density, viscosity, refractive index, conductivity, pH value, and total dissolved salts (TDS) in the aqueous quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K were determined with the isothermal evaporation method. According to the experimental results, the dry-salt phase diagram, water-phase diagram, and the physicochemical properties versus composition diagram were plotted. It was found that there are seven metastable crystallization fields corresponding to lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$, Ls), epsomite ($MgSO_4 \cdot 7H_2O$, Ep), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), tetrahydrite ($MgSO_4 \cdot 4H_2O$, Tet), bischofite ($MgCl_2 \cdot 6H_2O$, Bis), lithium-carnallite ($LiCl \cdot MgCl_2 \cdot 7H_2O$, Lic), and lithium chloride monohydrate ($LiCl \cdot H_2O$, Lc), 11 univariant curves, and five three-salt cosaturated points of Ls + Ep + Hex, Ls + Hex + Tet, Ls + Tet + Bis, Ls + Bis + Lic, and Ls + Lic + Lc formed in the metastable quaternary system. No solid solution is found.

INTRODUCTION

Salt lakes are widely distributed in the area of Qinghai-Xizang (Tibet) Plateau of China. The Salt Lake of Qaidam Basin, consisting with a series of lakes including Caerhan Lake, Dongtai Lake, Xitai Lake, and Yiliping Lake, is one of the subtype of magnesium sulfate brines famous for its abundant of lithium, potassium, magnesium, and boron resources and also for the highest concentration ratio of magnesium and lithium from 500 to 800 in brines around the world. The climate condition in the region of Qaidam Basin is windy, with weather aridity, little rainfall, and great evaporating capacity.[1] To economic exploit lithium resources, it is important to adequately adopt the local natural resources such as the energy of wind and sun resources for solar pond technique. Therefore, the metastable phase equilibrium research is essential to predict the crystallized path of the evaporation of salt lake brine. During the later period of the brine evaporation, the concentration of sodium and potassium is reduced to very low. The salt lake brines can be described in the quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$), which is completely different with the reported seawater system ($Na + K + Mg + Cl + SO_4 + H_2O$).[2−5] So it is necessary to research the metastable quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) under the conditions of the Qaidam Basin.

Although a number of papers describing the stable equilibrium of the quaternary system ($Li^+, Mg^{2+}//Cl^-, SO_4^{2-}-H_2O$) from (273.15 to 348.15) K and its metastable behaviors at 298.15 K have been reported,[6−12] the data reported are not completed. The quaternary system at 308.15 K is not reported in the literature to describe the metastable behaviors of the salts in the system. In this paper, the metastable solubilities and the physicochemical properties on the quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K are presented.

EXPERIMENTAL SECTION

Apparatus and Reagents. The isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermal 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 ± 0.2) 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 temperature in the box could always be kept at (308.15 ± 0.2) K. An electric fan installed on the box always worked to accelerate the evaporation quantity 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 a X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands).

The chemicals used were of analytical grade and obtained from either the Tianjin Kermel Chemical Reagent Ltd. or the Sinopharm Chemical Reagent Co. Ltd.: magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, in mass fraction 0.99), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, 0.99), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$, 0.99), and lithium chloride monohydrate ($LiCl \cdot H_2O$, 0.99) and were recrystallized before use. Doubly deionized water (DDW) with a conductivity less than

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Table 1. Metastable Solubilities of the Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K

no.	composition in the solution, 100 w[a]					Jänecke index J/(mol/100 mol dry salts)			equilibrium solid phase[b]
	Li^+	Mg^{2+}	Cl^-	SO_4^{2-}	H_2O	$2Cl^-$	Mg^{2+}	H_2O	
1,A	1.58	4.49	0.00	28.67	65.26	0.00	61.90	1213.80	Ls+Ep
2,B	0.00	6.85	14.25	7.78	71.12	71.28	100.00	1400.13	Ep+Hex
3,C	0.00	9.05	23.26	4.24	63.45	88.14	100.00	946.33	Hex+Tet
4,D	0.00	9.44	24.57	4.03	61.96	89.20	100.00	885.36	Tet+Bis
5,E	4.78	3.53	34.71	0.00	56.98	100.00	29.64	646.16	Bis+Lic
6,F	6.58	1.65	38.41	0.00	53.36	100.00	12.51	546.72	Lic+Lc
7,G	7.71	0.00	39.35	0.030	52.91	99.94	0.00	528.80	Ls+Lc
8	0.066	9.35	24.81	3.79	61.98	89.86	98.77	883.82	Tet+Bis
9	0.091	9.30	25.11	3.36	62.14	91.01	98.31	886.57	Tet+Bis
10	0.091	9.28	25.22	3.12	62.29	91.64	98.32	890.84	Tet+Bis
11	0.094	9.26	25.26	3.04	62.35	91.85	98.26	892.59	Tet+Bis
12	0.11	9.26	25.38	3.01	62.24	91.96	97.90	887.78	Tet+Bis
13	0.17	9.14	25.70	2.47	62.52	93.38	96.92	894.17	Tet+Bis
14	0.19	9.14	25.96	2.22	62.50	94.07	96.57	891.35	Tet+Bis
15	1.55	4.49	0.24	28.11	65.61	1.16	62.33	1230.28	Ls+Ep
16	1.56	4.48	0.31	28.08	65.57	1.47	62.08	1227.04	Ls+Ep
17	1.58	4.52	0.52	28.09	65.29	2.43	62.03	1209.24	Ls+Ep
18	1.44	4.56	5.79	20.15	68.07	28.01	64.44	1296.87	Ls+Ep
19	1.41	4.64	7.01	18.58	68.36	33.84	65.29	1298.18	Ls+Ep
20,	1.19	5.18	11.75	12.75	69.13	55.54	71.36	1285.75	Ls+Ep
21,E1	1.12	5.47	13.82	10.67	68.92	63.71	73.54	1250.47	Ls+Ep+Hex
22	0.79	6.49	18.03	6.71	67.98	78.46	82.43	1164.59	Ls+Hex
23	0.57	8.12	23.24	4.54	63.53	87.39	89.06	940.18	Ls+Hex
24,E2	0.41	8.91	25.04	4.11	61.52	89.18	92.51	862.30	Ls+Hex+Tet
25	0.37	8.95	25.74	3.07	61.87	91.90	93.23	869.60	Ls+Tet
26	0.41	8.91	26.00	2.84	61.84	92.53	92.56	866.34	Ls+Tet
27	0.39	8.89	25.89	2.75	62.08	92.74	92.87	875.22	Ls+Tet
28	0.41	8.84	26.00	2.57	62.18	93.20	92.44	877.19	Ls+Tet
29,E3	0.38	8.89	26.05	2.51	62.17	93.36	92.97	876.95	Ls+Tet+Bis
30	0.46	8.73	26.40	1.89	62.53	94.98	91.61	885.51	Ls+Bis
31	0.49	8.71	26.62	1.75	62.43	95.36	90.99	880.41	Ls+Bis
32	0.55	8.66	26.85	1.63	62.31	95.70	90.06	874.19	Ls+Bis
33	0.57	8.54	26.96	1.14	62.80	96.97	89.58	889.03	Ls+Bis
34	1.57	7.28	29.11	0.19	61.85	99.51	72.65	832.17	Ls+Bis
35,E4	4.44	3.88	33.90	0.093	57.69	99.80	33.30	668.33	Ls+Bis+Lic
36	6.01	2.18	37.04	0.062	54.70	99.88	17.16	580.57	Ls+Lic
37,E5	6.45	1.72	37.93	0.031	53.87	99.94	13.23	558.70	Ls+Lic+Lc
38	6.55	1.70	38.38	0.028	53.35	99.95	12.92	546.89	Ls+Lic
39	6.55	1.70	38.37	0.037	53.35	99.93	12.92	546.85	Ls+Lic
40	6.93	1.07	38.52	0.035	53.44	99.93	8.11	545.73	Ls+Lic
41	7.54	0.042	38.57	0.058	53.79	99.89	0.32	548.26	Ls+Lc
42	7.56	0.043	38.67	0.070	53.66	99.87	0.32	545.33	Ls+Lc
43	7.54	0.044	38.58	0.069	53.77	99.87	0.33	547.80	Ls+Lc
44	7.55	0.029	38.60	0.072	53.75	99.86	0.22	547.42	Ls+Lc
45	7.55	0.023	38.57	0.082	53.77	99.84	0.17	547.82	Ls+Lc
46	0.10	6.89	15.07	7.54	70.39	73.02	97.44	1342.30	Ep+Hex
47	0.37	8.89	24.64	4.34	61.75	88.50	93.16	872.86	Hex+Tet
48	0.14	8.89	23.38	4.44	63.15	87.72	97.31	932.52	Hex+Tet

[a] w = mass fraction. [b] Ls, $Li_2SO_4 \cdot H_2O$; Ep, $MgSO_4 \cdot 7H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Lic, $LiCl \cdot MgCl_2 \cdot 7H_2O$; Lc, $LiCl \cdot H_2O$.

$1 \cdot 10^{-4}$ S·m^{-1} at 298.15 K was used to prepare the series of artificially synthesized brines and for chemical analysis.

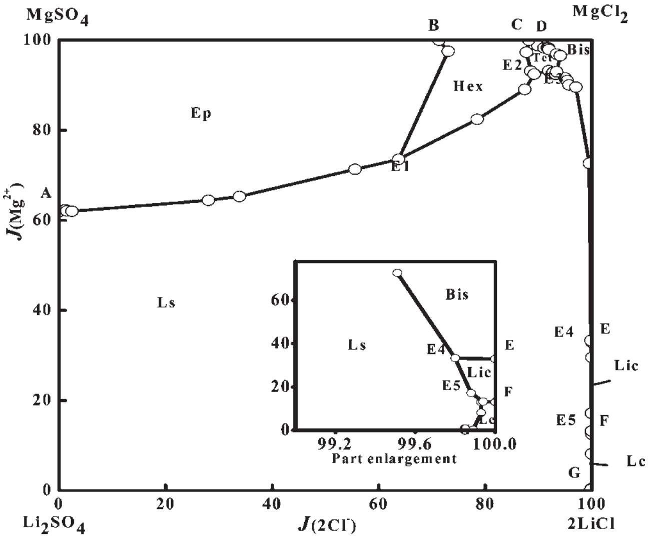
Experimental Method. The isothermal evaporation method was used in this study. According to phase equilibrium composition,

Table 2. Physicochemical Properties of the Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K

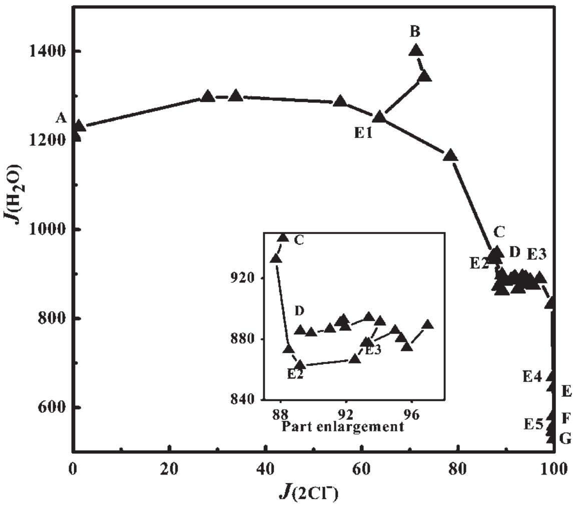
no.	physicochemical properties					
	pH	n_D	viscosity $\eta/(10^3\ Pa\cdot s)$	density $\rho/(10^3\ kg\cdot m^{-3})$	conductivity $\kappa/(S\cdot m^{-1})$	TDS[a]
1,A	—[b]	—	—	1.3754	—	—
2,B	—	—	—	—	—	—
3,C	—	1.4321	—	—	—	—
4,D	—	1.4370	—	—	—	—
5,E	—	—	—	—	—	—
6,F	—	—	—	—	—	—
7,G	5.02	1.4461	13.3004	1.3041	7.95	—
8	3.58	1.4377	10.9986	1.3699	5.64	30.9
9	3.79	1.4372	—	1.3660	5.71	31.2
10	—	1.4377	—	—	—	—
11	3.85	1.4377	10.2939	1.3645	6.05	33.7
12	—	1.4372	9.9635	1.3639	6.07	34.0
13	4.03	1.4372	9.5577	1.3587	6.35	35.4
14	—	1.4371	—	—	—	—
15	6.55	1.4017	9.1773	1.3728	4.02	21.6
16	6.47	—	—	1.3704	4.11	21.7
17	—	1.4045	—	—	—	—
18	—	—	—	—	—	—
19	6.24	1.4015	5.3796	1.3084	7.11	40.6
20	5.91	1.4047	4.3996	1.2879	9.12	53.7
21,E1	6.10	1.4089	4.3037	1.2838	9.78	57.7
22	—	1.4140	—	—	—	—
23	—	1.4328	—	—	—	—
24,E2	—	1.4404	11.3932	1.3693	6.21	34.5
25	—	1.4400	10.1708	1.3602	6.62	37.2
26	—	1.4393	—	—	—	—
27	—	1.4377	—	—	—	—
28	5.02	1.4377	9.4550	1.3546	6.02	33.8
29,E3	4.81	1.4416	9.5719	1.3556	6.89	39.0
30	—	—	—	—	—	—
31	—	—	—	—	—	—
32	—	1.4388	—	—	—	—
33	—	1.4390	—	—	—	—
34	4.52	1.4398	8.6255	1.3242	8.14	47.0
35,E4	4.32	1.4410	8.4534	1.3235	8.56	48.4
36	—	—	—	—	—	—
37,E5	4.96	1.4443	12.1169	1.3230	6.29	35.8
38	—	1.4439	—	—	—	—
39	4.94	1.4435	12.0617	1.3223	6.52	36.5
40	—	1.4437	—	—	—	—
41	5.14	1.4412	10.1960	1.3042	7.74	44.6
42	—	1.4407	—	—	—	—
43	5.52	1.4421	10.1121	1.3043	7.80	45.1
44	—	—	—	—	—	—
45	—	1.4418	—	—	—	—
46	5.72	1.4111	3.9043	1.2819	10.62	63.4
47	—	1.4401	10.4688	1.3639	6.37	35.6
48	—	1.4362	—	—	—	—

[a] Total dissolved salts. [b] Not detected.

the appropriate quantity of salts and DDW calculated were mixed together as a series of artificially synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high), then the containers were put into the box for isothermal evaporation at (308.15 ± 0.2) K. The experimental conditions of air flow velocity of (3.5 to 4.0) $m\cdot s^{-1}$, relative humidity of



(a) dry-salt phase diagram



(b) water-phase diagram

Figure 1. Metastable phase diagram of the quaternary system (Li^+, $Mg^{2+}//Cl^-$, $SO_4^{2-}-H_2O$) at 308.15 K. (a) dry-salt phase diagram; (b) water-phase diagram; Ls, $Li_2SO_4 \cdot H_2O$); Ep, $MgSO_4 \cdot 7H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Lic, $LiCl \cdot MgCl_2 \cdot 7H_2O$; Lc, $LiCl \cdot H_2O$.

(20 to 30) %, and an evaporation rate of (4 to 6) mm·d^{-1} are similar to those of the climate of Qaidam Basin. The solutions were not stirring for the 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 solid phase minerals were evaluated with the combined Schreinemaker's method (i.e., wet residue method) through the chemical analysis and observation with a XP-300 digital polarizing microscopy (Shanghai Caikon Optical Instrument Co. Ltd., China) and further identification with X-ray diffraction. Meanwhile, a 5.0 cm^{-3} sample of the clarified solution was taken from the liquid phase of each polyethylene container through a filter pipet and then diluted to 250.0 cm^{-3} final volume in a volumetric flask filled with DDW 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 point.

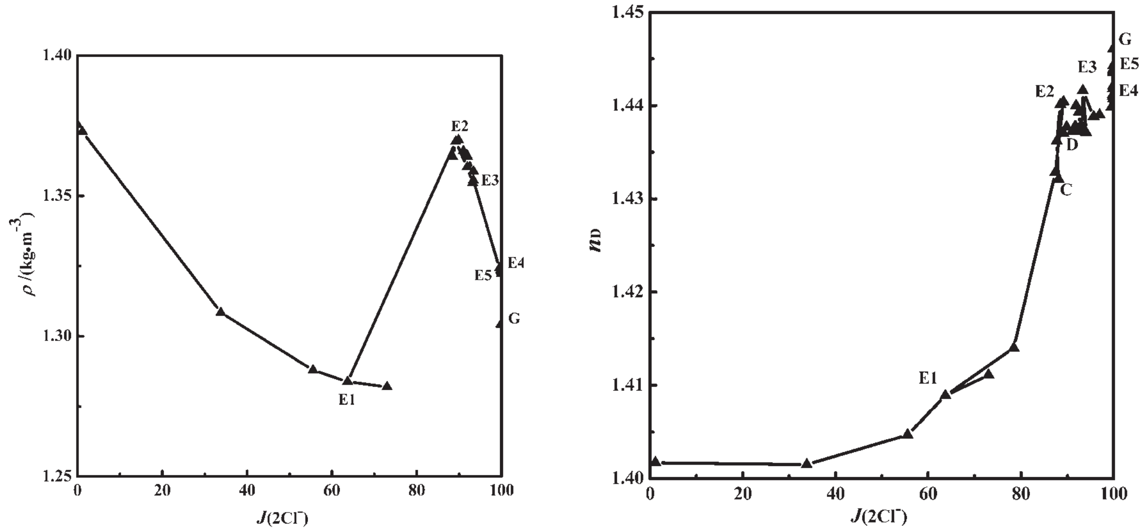
Analytical Method. The compositions of the SO_4^{2-} in the liquids and their corresponding wet solid phases were analyzed by the gravimetric method using barium chloride with a precision within ± 0.0005 in mass fraction.[13] The Cl^- ion concentration was determined by titration with hydrargyrum nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue with a precision of $\leq \pm 0.003$ in mass fraction,[13] and the concentration of Mg^{2+} ion was determined using our previous modified ethylenediaminetetraacetic acid (EDTA) complexometric titration method in the presence of Eriochrome Black-T as indicator.[13,14] In brief, the interference of the coexisted lithium ion in brine can be efficiently eliminated using butan-1-ol and anhydrous alcohol as a masking agent, and the relative error of the analytical results is less than ± 0.003 in mass fraction. The concentration of Li^+ was evaluated according to ion balance and combined with analytical verified measurement occasionally by inductively coupled plasma atomic emission spectroscopy (ICP-AES; IRIS Intrepid ICP, Therom Electron Co.) with a precision of $\leq \pm 0.005$ in mass fraction.

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 both mixing phosphate of potassium dihydrogen phosphate and sodium dihydrogen phosphate (pH = 6.84) and borax (pH = 9.18), respectively; the densities (ρ) were measured with a density bottle method with a precision of ± 0.0002 g·cm^{-3}. 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 precision of 0.1 s stopwatch 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 Orion 145A+ conductivity meter (Thermo Electron Corporation, America) with an accuracy precision of ± 0.001 S·m^{-1}. Measurements for the physicochemical properties of density, refractive index, and pH were conducted in a thermostat that electronically controlled the set temperature at (308.15 ± 0.1) K.

■ RESULTS AND DISCUSSION

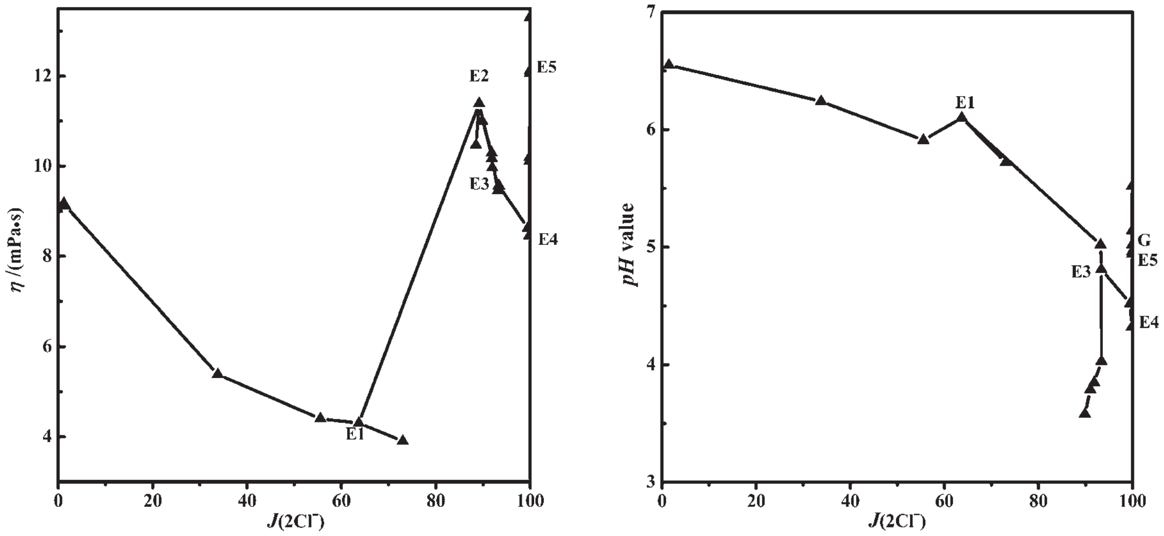
The experimental data on the metastable solubilites and the relevant physicochemical properties of the quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K were determined and presented in Tables 1 and 2, respectively. On the basis of the Jänecke index (J_b, J_b/(mol/100 mol dry salts)) in Table 1, the metastable equilibrium phase diagram of the system at 308.15 K was plotted (in Figure 1).

In Figure 1, the metastable dry-salt phase diagram of the system in Figure 1a consists of seven crystallization zones corresponding to Ls (lithium sulfate monohydrate, $Li_2SO_4 \cdot H_2O$), Ep (epsomite, $MgSO_4 \cdot 7H_2O$), Hex (hexahydrite, $MgSO_4 \cdot 6H_2O$), Tet (tetrahydrite, $MgSO_4 \cdot 4H_2O$), Bis (bischofite, $MgCl_2 \cdot 6H_2O$), Lic (lithium-carnallite, $LiCl \cdot MgCl_2 \cdot 7H_2O$), and Lc (lithium chloride monohydrate, $LiCl \cdot H_2O$), five invariant points E1, E2, E3, E4, and E5, which are saturated with salts (Ls + Ep + Hex), (Ls + Hex+ Tet), (Ls+ Tet + Bis), (Ls + Bis + Lic), and (Ls + Lic + Lc), respectively. There are 11



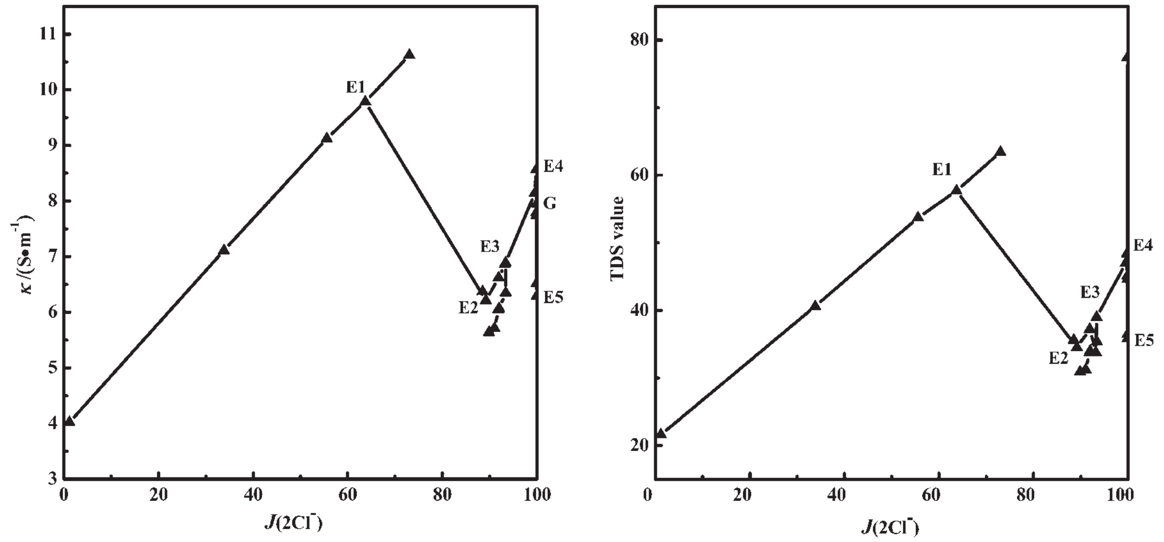
(a) density vs. composition

(b) refractive index vs. composition



(c) viscosity vs. composition

(d) *pH* vs. composition



(e) conductivity vs. composition

(f) TDS vs. composition

Figure 2. Physicochemical properties versus composition diagram for the quaternary system (Li^+, Mg^{2+}//Cl^-, SO_4^{2-}—H_2O) at 308.15 K. (a), density vs composition; (b), refractive index vs composition; (c), viscosity vs composition; (d), pH vs composition; (e), conductivity vs composition; (f), TDS vs composition.

Table 3. Comparison of the Calculated and Experimental Values of Density and Refractive Index in the Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 308.15 K

no.	density, $\rho/(10^3\ kg \cdot m^{-3})$		relative error, %	refractive index, n_D		relative error, %
	experiments	calculation		experiments	calculation	
1,A	1.3754	1.3754	0.00	–	1.4021	–
2,B	–	1.2831	–	–	1.4062	–
3,C	–	1.3559	–	1.4321	1.4322	0.01
4,D	–	1.3720	–	1.4370	1.4369	−0.01
5,E	–	0.9941	–	–	1.3313	–
6,F	–	0.9941	–	–	1.3313	–
7,G	1.3041	1.3041	0.00	1.4461	1.4461	0.00
8	1.3699	1.3699	0.00	1.4377	1.4369	−0.05
9	1.3660	1.3661	0.01	1.4372	1.4367	−0.03
10	–	1.3637	–	1.4377	1.4365	−0.08
11	1.3645	1.3624	−0.15	1.4377	1.4363	−0.10
12	1.3639	1.3632	−0.05	1.4372	1.4366	−0.04
13	1.3587	1.3575	−0.09	1.4372	1.4363	−0.07
14	–	1.3570	–	1.4371	1.4366	−0.03
15	1.3728	1.3708	−0.15	1.4017	1.4017	0.00
16	1.3704	1.3704	0.00	–	1.4018	–
17	–	1.3732	–	1.4045	1.4026	−0.14
18	–	1.3214	–	–	1.4022	–
19	1.3084	1.3145	0.46	1.4015	1.4028	0.10
20	1.2879	1.2941	0.48	1.4047	1.4064	0.12
21,E1	1.2838	1.2909	0.55	1.4089	1.4089	0.00
22	–	1.2964	–	1.4140	1.4157	0.12
23	–	1.3435	–	1.4328	1.4312	−0.11
24,E2	1.3693	1.3682	−0.08	1.4404	1.4378	−0.18
25	1.3602	1.3617	0.11	1.4400	1.4377	−0.16
26	–	1.3612	–	1.4393	1.4372	−0.15
27	–	1.3588	–	1.4377	1.4367	−0.07
28	1.3546	1.3565	0.14	1.4377	1.4364	−0.09
29,E3	1.3556	1.3569	0.09	1.4416	1.4366	−0.35
30	–	1.3500	–	–	1.4360	–
31	–	1.3497	–	–	1.4363	–
32	–	1.3497	–	1.4388	1.4367	−0.15
33	–	1.3425	–	1.4390	1.4357	−0.23
34	1.3242	1.3297	0.41	1.4398	1.4365	−0.23
35,E4	1.3235	1.3177	−0.44	1.4410	1.4410	0.00
36	–	1.3181	–	–	1.4454	–
37,E5	1.3230	1.3210	−0.15	1.4443	1.4475	0.22
38	–	1.3226	–	1.4439	1.4481	0.29
39	1.3223	1.3226	0.02	1.4435	1.4481	0.32
40	–	1.3134	–	1.4437	1.4466	0.20
41	1.3042	1.2982	−0.46	1.4412	1.4439	0.19
42	–	1.2992	–	1.4407	1.4443	0.25
43	1.3043	1.2983	−0.46	1.4421	1.4439	0.13
44	–	1.2983	–	–	1.4440	–
45	–	1.2980	–	1.4418	1.4439	0.14
46	1.2819	1.2878	0.46	1.4111	1.4082	−0.21
47	1.3639	1.3674	0.25	1.4401	1.4360	−0.28
48	–	1.3569	–	1.4362	1.4325	−0.26

isotherm evaporation curves corresponding to AE1 (Ls + Ep), BE1 (Ep + Hex), E1E2 (Hex + Ls), CE2 (Hex + Tet), E2E3 (Tet + Ls), DE3 (Tet + Bis), E3E4 (Ls + Bis), EE4 (Bis + Lic), E4E5 (Ls + Lic), GE5 (Ls + Lc), and FE5 (Lic + Lc), indicating the cosaturation of two salts. The crystallization area of lithium sulfate monohydrate is the largest, and the crystallized zone of lithium chloride monohydrate is the smallest. These results indicate that lithium sulfate monohydrate is easy to saturate and crystallize from solution and that lithium chloride monohydrate has a high solubility. There is one double salt and no solid solution formed in the system.

Figure 1b is the relevant water-phase diagram of the system at 308.15 K. Figure 1b shows that the Jänecke index values of $J(H_2O)$ gradually change with increasing $J(2Cl^-)$.

On the basis of experimental data in Table 2, relationships between the solution physicochemical properties (density, pH, conductivity, refractive index, and viscosity) and the Jänecke index values of $J(2Cl^-)$ were plotted in Figure 2. It can be found that the physicochemical properties are in regular changes with the Jänecke index values of $J(2Cl^-)$.

EMPIRICAL EQUATIONS FOR DENSITY 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,[15] 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 $d_0 = 0.99406\ \mathrm{g \cdot mL^{-1}}$, the density of the 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 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. Constants A_i and B_i of LiCl, $MgCl_2$, Li_2SO_4, and $MgSO_4$ for calculation of density and refractive index of solution are 0.00576341, 0.0100253, 0.81334659, and 0.00823297 and 0.00175671, 0.00207763, 0.00141313, and 0.00153500, respectively. The calculated results and experimental values are presented in Table 3 for comparison, and all of the calculated results with the maximum relative error are less than 0.55 %.

CONCLUSIONS

Metastable equilibria of the quaternary system (Li^+, Mg^{2+}// Cl^-, SO_4^{2-} - H_2O) at 308.15 K were studied by isothermal evaporation method. The solubilities and physicochemical properties were determined experimentally. According to the experimental data, the metastable equilibrium dry-salt phase diagram, water-phase diagram, and the physicochemical properties versus composition diagrams of the system were plotted. The results show that there is neither double salt nor solid solution formed in this quaternary system. The calculated values of density an refractive index using empirical equations are in good agreement with the experimental values.

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