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Solid−Liquid Metastable Equilibria of the Reciprocal Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K

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ABSTRACT: Experimental studies on the metastable solubilities and the physicochemical properties (density, pH value, conductivity, and viscosity) of the aqueous reciprocal quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 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 four invariant points, nine metastable solubility isotherm curves, and six metastable crystallization fields corresponding to lithium chloride monohydrate ($LiCl \cdot H_2O$), bischofite ($MgCl_2 \cdot 6H_2O$), starkeyite ($MgSO_4 \cdot 4H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), and the double salt lithium-carnallite ($LiCl \cdot MgCl_2 \cdot 7H_2O$). No solid solution was found. On the basis of the extended Harvie−Weare (HW) model and its temperature-dependent equation, the values of the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{φ} for Li_2SO_4, $MgCl_2$, and $MgSO_4$, the mixed ion-interaction parameters $\theta_{Li,Mg}$, θ_{Cl,SO_4}, $\Psi_{Li,Mg,Cl}$, Ψ_{Li,Mg,SO_4}, Ψ_{Li,Cl,SO_4}, and Ψ_{Mg,Cl,SO_4}, and the Debye−Hückel parameter A^{φ} of the quaternary system at 323.15 K were obtained. The calculated solubility of the quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K was done. A comparison between the calculated and the experimental results shows that the predicted solubility agrees well with the experimental data.

INTRODUCTION

The brines with high concentrations of lithium and magnesium resources are widely distributed in the area of Qinghai-Tibet Plateau of China. The mother brine mostly belongs to the complex five-component system ($Li + Mg + Cl + SO_4$ + borate + H_2O) in the evaporating anaphase when the minerals of NaCl and KCl were crystallized and separated.[1] The climatic conditions in the region of Qinghai-Tibet Plateau is windy, with weather aridity, little rainfall, and great evaporating capacity.[2] To economic exploit lithium resources in the mother liquor, it is important to adequately adopt the local natural resources such as the energy of the wind and sun resources for the solar pond technique. Therefore, metastable phase equilibrium research is essential to predict the crystallized path of evaporation of the mother liquor brine.

The reciprocal quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) is a subsystem of the five-component system. Although the phase equilibrium of the quaternary system at different temperatures had been reported,[3−10] the metastable phase equilibrium and the phase diagram of the reciprocal quaternary system at 323.15 K is not reported in the literature to describe the metastable behavior of the salt in the system. Due to the fact that there is lithium deposited in Dongtai Lake, this is needed to separate and purify the mixture salts. In this paper, the metastable solubilities and the physicochemical properties of the reciprocal quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 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) and an apparatus to control the temperature were installed. The temperature controlling apparatus is made up of an electric relay, an electrical contact thermograph, and the heating lamps. Therefore, the temperature in the box was always homogeneously maintained at (323.15 ± 0.2) K, which was described in literature.[11] The solid phase of the minerals was 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 Shanghai-Lithium Industrial Co., Ltd., lithium sulfate ($Li_2SO_4 \cdot H_2O$, in mass fraction 0.99), lithium chloride (LiCl, 0.99), epsomite ($MgSO_4 \cdot 7H_2O$, 0.99), and bischofite ($MgCl_2 \cdot 6H_2O$, 0.99) and were recrystallized before use. Doubly deionized water (DDW) with a conductivity less than $1.0 \cdot 10^{-4}$ $S \cdot m^{-1}$ at 298.15 K was used to prepare the series of artificial synthesized brines and for chemical analysis.

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Table 1. Metastable Equilibrium Solubility Data of the Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K

	composition of liquid phase, $100w_i$				Jänecke index, J/[mol/100 mol dry salt]			
no.	Li^+	Mg^{2+}	Cl^-	SO_4^{2-}	$J(Li_2^{2+})$	$J(Cl_2^{2-})$	$J(H_2O)$	equilibrium solid phase[a]
1(E_1)	7.86	0.00	40.22	0.068	100	99.87	507.81	Ls + Lc
2	7.4	0.83	40.19	0.051	93.95	99.91	504.08	Ls + Lc
3	6.92	1.57	39.89	0.049	88.53	99.91	508.48	Ls + Lc
4(F_1)	6.52	2.22	39.72	0.048	83.79	99.91	509.87	Ls + Lc + Lcar
5(E_2)	6.52	2.11	39.44	0.00	84.38	100	518.22	Lc + Lcar
6(E_3)	3.89	5.08	34.7	0.00	57.29	100	594.75	Bis + Lcar
7(F_2)	3.75	5.29	34.49	0.048	55.38	99.9	643.39	Ls + Bis + Lcar
8	3.14	5.6	32.31	0.068	49.51	99.84	716.17	Ls + Bis
9	1.84	7.18	30.3	0.057	30.97	99.86	786.35	Ls + Bis
10	1.05	8.34	29.58	0.15	18.09	99.62	806.89	Ls + Bis
11	0.57	8.85	27.83	1.22	10.18	96.86	842.87	Ls + Bis
12	0.5	9.02	26.85	2.7	8.79	93.1	831.41	Ls + Bis
13(F_3)	0.45	9.07	26.76	2.7	7.96	93.05	835.69	Ls + Bis + Tet
14	3.27	9.24	26.71	2.61	5.83	93.28	839.83	Bis + Tet
15	0.14	9.61	26.88	2.51	2.42	93.55	833.9	Bis + Tet
16(E_4)	0.00	9.66	26.07	2.88	0.00	92.47	857.01	Bis + Tet
17	0.39	9.12	25.88	3.66	6.92	90.54	839.12	Ls + Tet
18	0.52	8.17	20.29	8.38	9.95	76.64	931.27	Ls + Tet
19(F_4)	0.6	7.58	18.51	9.05	12.17	73.49	1004.37	Ls + Tet + Hex
20	0.54	7.78	18.8	9.02	10.85	73.84	987.11	Tet + Hex
21	0.15	8.51	19.92	7.71	3.05	77.79	978.95	Tet + Hex
22(E_5)	0.00	8.56	19.67	7.21	0.00	78.7	1016.59	Tet + Hex
23	0.74	7.32	17.74	10.03	15.08	70.55	1004.34	Ls + Hex
24	0.93	6.77	16.2	11.28	19.42	66.04	1040.06	Ls + Hex
25	1.16	5.44	12.39	12.69	27.12	56.95	1235.67	Ls + Hex
26	1.14	5.37	11.96	12.93	27.19	55.61	1255.52	Ls + Hex
27	1.12	5.69	7.46	20.11	25.62	33.46	1158.25	Ls + Hex
28	1.15	5.61	4.28	24.29	26.38	19.28	1146.13	Ls + Hex
29	1.14	5.53	3.21	25.44	26.57	14.58	1157.79	Ls + Hex
30	1.07	5.24	1.95	25.46	26.35	9.4	1257.77	Ls + Hex
31(E_6)	1.32	5.54	0.0	31.06	29.47	0.0	1065.69	Ls + Hex

[a] Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$; Lcar, $LiCl \cdot MgCl_2 \cdot 7H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$.

Experimental Method. The isothermal evaporation method was used in this study. According to the composition at the phase equilibrium, the appropriate quantity of salts and DDW calculated were mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high), and the containers were placed in the box for isothermal evaporation at (323.15 ± 0.2) K. The experimental conditions consisting of an air velocity of (3.5 to 4.0) $m \cdot s^{-1}$, relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) $mm \cdot d^{-1}$ 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 combined chemical analysis and observed with XP-300D digital polarizing microscope 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 a 250.0 cm^3 final volume in a volumetric flask filled with DDW for a 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 to reach a new isothermal evaporation equilibrium point.

Analytical Method. All samples were analyzed in triplicate. The concentration of Cl^- was measured by titration with a standard solution of mercury nitrate in the presence of mixed indicator of diphenylcarbazone and bromophenol blue with an uncertainty $\leq \pm 0.003$ in mass fraction. The SO_4^{2-} in the liquids was analyzed by the gravimetric methods using barium chloride with an uncertainty $\leq \pm 0.0005$.[12] The concentration of the Mg^{2+} ion was determined using our previously modified ethylenediaminetetraacetic acid (EDTA) complexometric titration method in the presence of Eriochrome Black-T as an indicator.[13] 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 uncertainty is less than ± 0.003. The concentration of Li^+ was evaluated according to ion balance and combined with analytical verified measurement occasionally by ICP-AES (IRIS Intrepid ICP, Therom Electron Co.) with an uncertainty $\leq \pm 0.005$ in mass fraction.

Table 2. Physicochemical Properties of the Quaternary System ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K[a]

		ρ		κ	$10^{-3}\ \eta^{b}$
no.	Li^+	$g \cdot cm^{-3}$	pH	$S \cdot m^{-1}$	$Pa \cdot s$
$1(E_1)$	100	1.3088			
2	93.95	1.3218	4.6	95	8.5509
3	88.53				
$4(F_1)$	83.79	1.3397	4.51	81.8	10.3749
$5(E_2)$	84.38	1.3358			
$6(E_3)$	57.29	1.3477			
$7(F_2)$	55.38	1.3362	4.48	83	7.9354
8	49.51	1.323	4.62	96.1	6.3058
9	30.97				
10	18.09		4.7	96.2	5.693
11	10.18	1.3479	4.85	96.4	6.4364
12	8.79	1.386	3.07	90.1	7.2824
$13(F_3)$	7.96	1.3693	4.06	82.3	7.9733
14	5.83				
15	2.42	1.3772	4.57	90.2	7.3273
$16(E_4)$	0.00	1.3726			
17	6.92	1.3693	4.06	82.3	7.9733
18	9.95				
$19(F_4)$	12.17	1.3481	5.46	98	5.5593
20	10.85	1.3481	5.46	98	5.5593
21	3.05	1.3527	4.75	99.9	5.7015
$22(E_5)$	0.00	1.349			
23	15.08				
24	19.42				
25	27.12	1.2937	6.25	117.7	3.3432
26	27.19	1.2915	6.21	118.4	3.2201
27	25.62	1.3503	6.14	84.3	6.6848
28	26.38	1.3683	6.6	63.5	5.9473
29	26.57	1.3778	6.56	57.3	6.6734
30	26.35	1.3465	6.91	98	4.7738
$31\ (E_6)$	29.47	1.4125	6.65	42	8.9017

[a] Empty cells indicate undetected data. [b] $\eta_{H_2O} = 0.5468\ mPa \cdot s$ at 323.15 K in *Lange's Handbook of Chemistry*, 10.97.

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 in triplicate with an uncertainty within ± 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 an uncertainty within $\pm\ 0.0002\ g \cdot cm^{-3}$.

The viscosities (η) were determined using an Ubbelohde capillary viscometer. No fewer than five flow times for each equilibrium liquid phase were measured within 0.1 s using a stopwatch to record the flow time, and the results calculated were the average. Conductivities (κ) were measured with an Orion 145A+ conductivity meter (Thermo Electron Corporation, America) with an uncertainty of $\pm\ 0.001\ S \cdot m^{-1}$. The physicochemical parameters of density, refractive index, and pH were all placed in a thermostat at (323.15 ± 0.1) K.

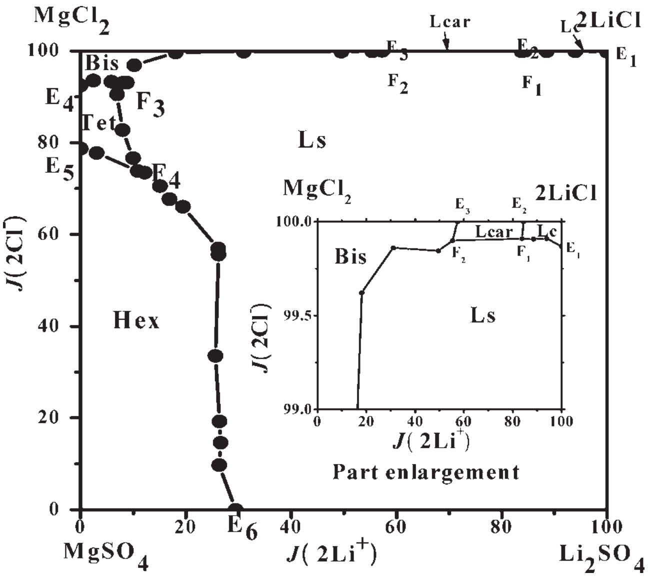


Figure 1. Dry-salt phase diagram of the system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K. ●, experimental data; —, metastable isotherm curve; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$; Lcar, $LiCl \cdot MgCl_2 \cdot 7H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$.

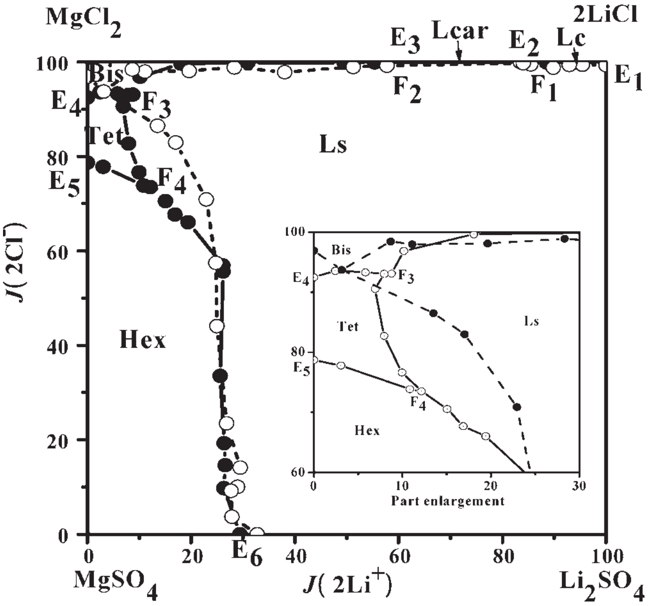


Figure 2. Comparison of the stable and metastable equilibria dry-salt phase diagram of the system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K. ●, metastable data; —, metastable curve; ○, stable data;[5] · · ·, stable curve; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$; Lcar, $LiCl \cdot MgCl_2 \cdot 7H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Hex, $MgSO_4 \cdot 6H_2O$.

■ RESULTS AND DISCUSSION

The experimental solubilities and the relevant physicochemical properties of the metastable quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K are presented in Tables 1 and 2. On the basis of the Jänecke index [J_b/(mol/100 mol dry salt)] in Table 1, the metastable equilibrium phase diagram of the system at 323.15 K was plotted in Figure 1.

In Figure 1, the metastable dry-salt phase diagram of the system at 323.15 K consists of six crystallization zones corresponding to lithium chloride monohydrate ($LiCl \cdot H_2O$, Lc), bischofite ($MgCl_2 \cdot 6H_2O$, Bis), starkeyite ($MgSO_4 \cdot 4H_2O$, Tet), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$, Ls), and the double salt of lithium-carnallite ($LiCl \cdot MgCl_2 \cdot 7H_2O$, Lcar) and four invariant points F_1, F_2, F_3, and F_4, which are saturated with salts (Lc + Ls + Lcar), (Lcar + Ls + Bis), (Bis + Ls + Tet), and (Tet + Hex + Ls), respectively. There are nine univariant isothermal evaporation curves corresponding to E_1F_1 (Lc + Ls), E_2F_1 (Lc + Lcar), F_1F_2 (Ls + Lcar), E_3F_2 (Lcar + Bis), F_2F_3 (Bis + Ls), E_4F_3 (Bis + Tet), F_3F_4 (Ls + Tet), E_5F_4 (Tet + Hex), and E_6F_4 (Hex + Ls), indicating the cosaturation of two salts. Due to the high solubilities of lithium chloride and magnesium chloride, there is a strong salting-out effect to lithium sulfate. Through a series of mineral identifications combined with a polarizing microscope and an X-ray diffractometer for the solid phase minerals existed in the system, no solid solution except for the double salt of lithium-carnallite and hydrated salts including lithium chloride monohydrate, bischofite, starkeyite, hexahydrite, and lithium sulfate monohydrate in the system was found. A comparison of the diagrams between the metastable and stable equilibrium at 323.15 K in Figure 2 shows that the metastable behavior of magnesium sulfate is obvious and the crystallization field of starkeyite ($MgSO_4 \cdot 4H_2O$) appears in the metastable phase diagram.

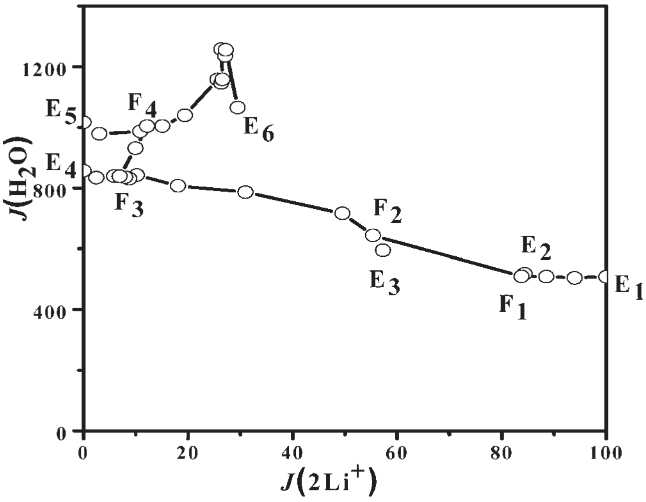
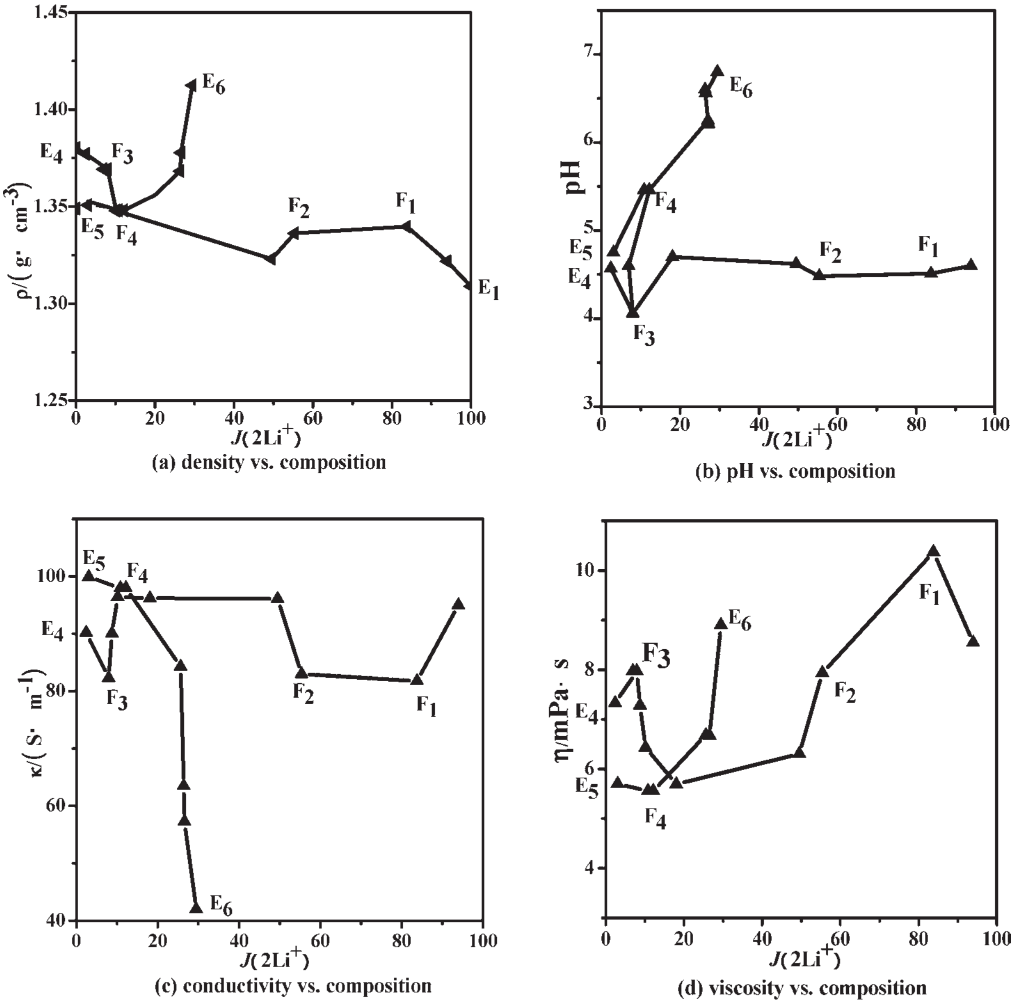


Figure 3. Water-phase diagram of the quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K. ○, solubility data; —, experimental curve.



(a) density vs. composition

(b) pH vs. composition

(c) conductivity vs. composition

(d) viscosity vs. composition

Figure 4. Physicochemical properties versus composition of the quaternary system ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 323.15 K. (a) Density vs composition; (b) pH vs composition; (c) conductivity vs composition; (d) viscosity vs composition. ▲, experimental points; —, experimental curve.

Table 3. Single-Salt and Mixing Ion-Interaction Parameters of the Quaternary System $(LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O)$ at 323.15 K

species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{(\Phi)}$	θ	Ψ
LiCl	0.191584	−0.278		−0.00407		
Li_2SO_4	0.139751	1.321205		−0.00779		
$MgCl_2$	0.337022	1.7817		0.004014		
$MgSO_4$	0.227487	3.61427	−40.2625	0.019761		
Cl^-, SO_4^{2-}					0.03	
Li^+, Mg^{2+}					0.068708	
Li^+, Cl^-, SO_4^{2-}						0.027492
Mg^{2+}, Cl^-, SO_4^{2-}						−0.01643
Li^+, Mg^{2+}, Cl^-						0.007298
Li^+, Mg^{2+}, SO_4^{2-}						0.044631

Figure 3 is the water-phase diagram of the quaternary system at 323.15 K, and it shows that the Jänecke index values of $J(H_2O)$ gradually change with increasing $J(2Li^+)$.

The relationships between the solution physicochemical properties (density, pH, conductivity, and viscosity) and $J(2Li^+)$ were plotted in Figure 4. The physicochemical properties of the metastable equilibrium solution vary regularly with $J(2Li^+)$.

SOLUBILITY PREDICTION

Ion-Interaction Model. Pitzer and co-workers have published a series of papers and given a set of expressions for the osmotic coefficient of solution and mean activity coefficient of electrolytes in the solution.[14,15] Expressions of the chemical equilibrium model for conventional single ion activity coefficients derived by Harvie et al.[16,17] are more convenient to use in solubility calculations for the complex brine system $(Na + K + Mg + Ca + H + Cl + SO_4 + OH + CO_3 + HCO_3 + CO_2 + H_2O)$ from low to high concentrations at 298.15 K. Using the activity coefficients and the solubility products of the equilibrium solid phases allowed us to identify the coexisting solid phases and their compositions at equilibrium. Additional work has centered on developing variable temperature models, which will increase the applicability to a number of diverse geochemical systems.[18−20] The necessary model parameters for the activity coefficients of electrolytes in the system at 323.15 K were fitted from obtained osmotic coefficients and the ternary subsystems by the multiple and single linear regression methods.

Model Parameterization. The literature reported osmotic coefficients of the aqueous LiCl solutions from (0.1 to 18.0) *m* at (273.15, 298.15, 323.15, 348.15, and 373.15) K.[21] The osmotic coefficients of aqueous lithium chloride solutions from (0.1 to 18.0) *m* at 323.15 K may be obtained in the literature.[21] Single-salt parameters of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{φ} of lithium sulfate, magnesium sulfate, and magnesium chloride, the mixing pair θ_{Cl,SO_4}, the mixing triplet parameter of Ψ_{Mg,Cl,SO_4}, and the Debye−Hückel parameter $A^{\Phi} = 0.410330$ at 323.15 K are calculated on the basis of the temperature-dependent equation of parameters presented in the literature.[18,22] The mixing pair $\theta_{Li,Mg}$ and the mixing triplet parameters of $\Psi_{Li,Mg,Cl}$, Ψ_{Li,Mg,SO_4}, and Ψ_{Li,Cl,SO_4} are fitted using the reliable solubility data in the relative ternary subsystem at 323.15 K.[23] All of the parameters used in the prediction are presented in Table 3. According to the data of metastable experimental solubilities in this quaternary system and its metastable subternary systems at 323.15 K,[24,25] the average equilibrium constants of minerals existed in the quaternary system at 323.15 K were fitted with the method of the activity product constant in each metastable solution. These equilibrium constants ($\ln K_{aver}$) of equilibrium solid salts of $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$, $LiCl \cdot MgCl_2 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 6H_2O$, and $MgSO_4 \cdot 4H_2O$ equal to 12.013663, 0.355074, 22.713215, 9.8335, −2.114489, and −3.677860, respectively.

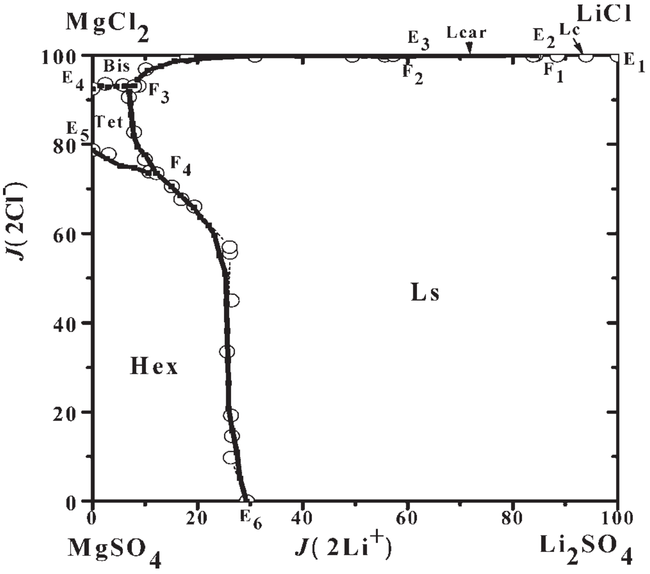


Figure 5. Comparison of the experimental and calculated dry-salt phase diagram of the system $(LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O)$ at 323.15 K. ○, Experimental point; · · ·, experimental curve; —, calculated curve; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$; Lcar, $LiCl \cdot MgCl_2 \cdot 7H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$.

Calculated Solubilities. Based on the Pitzer ion-interaction model and the extended HW models for aqueous electrolyte solutions and the above parameters, the calculated solubilities are shown in Figure 5 with hollow circles. A comparison between the experimental and predicted phase diagrams of the quaternary system at 323.15 K shows that the calculated phase diagram and the experimental one are in good agreement. These results indicate that the Pitzer parameters and the equilibrium constants obtained in this work are reliable.

CONCLUSIONS

Solubilities and the physicochemical properties of the metastable equilibria of the quaternary system $(LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O)$ at 323.15 K were studied with the isothermal evaporation method. According to the experimental data, the experimental metastable phase diagram and the diagrams of physicochemical properties versus composition are constructed for the first time. No solid solution is found. A comparison of the stable and metastable phase diagrams of the system at 323.15 K shows that the metastable behavior of magnesium sulfate is obvious, and the crystallization field of starkeyite appears in the metastable phase diagram.

On the basis of the extended Harvie—Weare (HW) model and its temperature-dependent equation, the values of the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{φ} for Li_2SO_4, $MgCl_2$, and $MgSO_4$, the mixed ion-interaction parameters $\theta_{Li,Mg}$, θ_{Cl,SO_4}, $\Psi_{Li,Mg,Cl}$, Ψ_{Li,Mg,SO_4}, Ψ_{Li,Cl,SO_4}, and Ψ_{Mg,Cl,SO_4}, and the Debye—Hückel parameter A^{φ} of the quaternary system at 323.15 K are fitted. The average equilibrium constants of the solid minerals existing in the system at 323.15 K are obtained with the method of the activity product constant in each metastable solution. The predictive metastable solubilities with the extended HW model agree well with the experimental data. These results indicate that the Pitzer parameters and the equilibrium constants obtained in this work are reliable.

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