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Metastable Phase Equilibrium in the Aqueous Quaternary System (Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O) at 288.15 K

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The metastable solubilities and the physicochemical properties (density, viscosity, refractive index, conductivity, and pH) of the aqueous quaternary system (Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O) at 288.15 K were determined with the isothermal evaporation method. According to the experimental data, the dry-salt phase diagram, water-phase diagram, and the physicochemical properties vs composition diagram were plotted. It was found that there are three invariant points, seven univariant curves, and five metastable crystallization regions corresponding to lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), arcanite (K_2SO_4), epsomite ($MgSO_4 \cdot 7H_2O$), double salt 1 ($LiKSO_4$), and picromerite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) formed in the metastable quaternary system. A comparison of the diagrams between the metastable equilibrium at 288.15 K and the stable equilibrium at 298.15 K shows that the metastable behavior of magnesium sulfate is obvious and the crystallizing regions of epsomite and arcanite are much larger than those in the stable phase diagram. The physicochemical properties of the quaternary system change gradually and regularly with the concentration of magnesium sulfate. No solid solution was found.

Introduction

Salt lakes are widely distributed in the west of China, especially in the area of the Qinghai-Tibet Plateau. Salt Lakes of the Qaidam Basin consist of a series of lakes including Caerhan Lake, Dongtai Lake, Xitai Lake, and Yiliping Lake that are a subtype of magnesium sulfate brines famous for their abundance of lithium, potassium, magnesium, and boron resources and also for the highest concentration ratio of magnesium to lithium in brines around the world (500 to 800). The climate conditions in the region of Qaidam Basin are generally windy, arid, little rainfall, and great evaporating capacity.[1] According to the statistical data from 1971 to 2000, the temperature of the brine in the Qaidam Basin from May to October in a year is between 285.35 K and 291.05 K, and the average temperature is 288.15 K. In order 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 sun, that is, solar pond techniques. Therefore, metastable phase equilibrium research is essential to predict the crystallized path of evaporation of the salt lake brine.

Although a number of papers describing the metastable equilibrium of the seawater system (Na + K + Mg + Cl + SO_4 + H_2O) from 293.15 K to 373.15 K and the stable equilibrium system (Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O) at 298.15 K have been previous reported,[2−6] the metastable equilibrium behavior of the quaternary system (Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O) at 288.15 K is not reported. Due to the fact that there is lithium sulfate monohydrate deposited in Dongtai Lake, this is needed to separate and purify the mixture sulfate salts. In this paper, the metastable solubilities and the physicochemical properties of the quaternary system (Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O) at 288.15 K are presented.

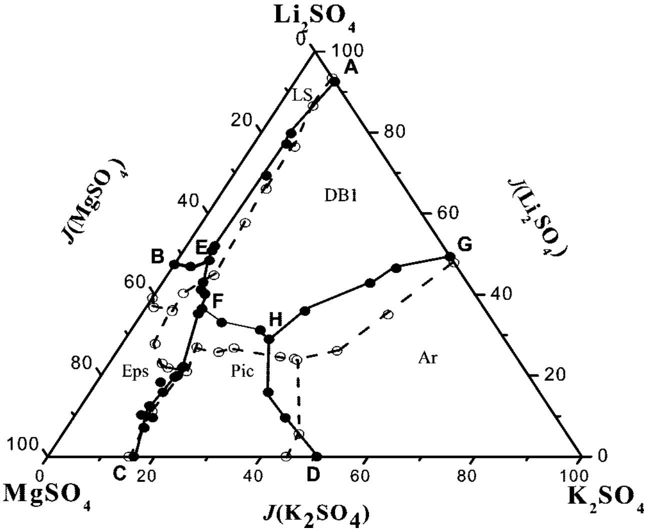

Figure 1. Metastable and stable equilibrium phase diagram of the quaternary system (Li_2SO_4 + K_2SO_4 + $MgSO_4$ + H_2O). ●, metal-stable experimental points at 288.15 K; ○, stable experimental points at 298.15 K; —, metastable isotherm curve; ---, stable isotherm curve; LS, $Li_2SO_4 \cdot H_2O$; DB1, $LiKSO_4$; Pic, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; Ar, K_2SO_4.

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

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Table 1. Metastable Equilibrium Solubility of the Quaternary System ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) at 288.15 K

	composition of liquid phase, w_b				composition of liquid phase Jänecke index, J_b				
	(mass %)				(g/100 g dry-salt)				
no.	K_2SO_4	Li_2SO_4	$MgSO_4$	H_2O	K_2SO_4	Li_2SO_4	$MgSO_4$	H_2O	equilibrium solid phase[a]
1,A	26.51	2.13	0.00	71.36	7.44	92.56	0.00	249.16	LS+DB1
2	1.83	25.45	4.64	68.08	5.73	79.73	14.54	213.28	LS+DB1
3	1.89	23.68	5.13	69.30	6.16	77.13	16.71	225.73	LS+DB1
4	2.08	23.24	8.18	66.50	6.21	69.37	24.42	198.51	LS+DB1
5	1.79	17.64	14.48	66.09	5.28	52.02	42.70	194.90	LS+DB1
6	1.79	16.99	14.65	66.57	5.35	50.82	43.83	199.13	LS+DB1
7,E	2.01	15.99	15.06	66.94	6.08	48.37	45.55	202.48	Eps+LS+DB1
8	1.56	17.34	18.33	62.77	4.19	46.58	49.23	168.60	Eps+LS
9,B	0.00	16.87	15.22	67.91	0.00	47.43	52.57	211.62	Eps+LS
10	2.68	13.57	16.68	67.07	8.14	41.21	50.65	203.67	Eps+DB1
11	3.12	13.37	16.80	66.71	9.37	40.16	50.47	200.39	Eps+DB1
12	3.60	12.34	17.92	66.14	10.63	36.44	52.93	195.33	Eps+DB1
13,F	3.57	11.88	18.23	66.32	10.60	36.27	54.13	196.91	Eps+DB1+Pic
14	4.53	7.04	20.13	68.30	14.29	22.21	63.50	215.46	Eps+Pic
15	4.22	5.93	19.57	70.28	14.20	19.95	65.85	236.47	Eps+Pic
16	4.22	5.90	21.66	68.22	13.27	18.57	68.16	214.66	Eps+Pic
17	2.87	2.22	16.69	70.28	13.18	10.19	76.63	359.14	Eps+Pic
18	4.12	4.79	21.29	69.80	13.64	15.86	70.50	231.12	Eps+Pic
19	3.83	3.69	22.56	69.92	12.73	12.27	75.00	232.45	Eps+Pic
20	4.34	2.83	22.13	70.70	14.81	9.66	75.53	241.30	Eps+Pic
21	4.07	3.40	25.43	67.10	12.37	10.33	77.30	203.95	Eps+Pic
22	4.27	2.13	23.24	70.36	14.40	7.19	78.41	237.38	Eps+Pic
23,C	4.60	0.00	24.00	71.40	16.09	0.00	83.91	249.65	Eps+Pic
24	4.81	10.54	15.27	69.38	15.71	32.42	49.87	226.58	DB1+Pic
25	6.69	8.63	12.35	72.33	24.18	31.19	44.63	261.40	DB1+Pic
26,H	7.10	7.62	11.61	73.67	26.97	28.94	44.09	279.79	DB1+Pic+Ar
27	11.83	5.58	17.88	64.71	33.52	15.81	50.67	183.37	Pic+Ar
28	13.05	3.15	16.69	67.11	39.68	9.58	50.74	204.04	Pic+Ar
29,D	10.44	0.00	10.29	79.27	50.36	0.00	49.64	382.39	Sch+Ar
30	8.31	9.90	9.31	72.48	30.20	35.97	33.83	263.37	Ar+DB1
31	14.73	16.19	6.89	62.19	38.97	42.81	18.22	164.48	Ar+DB1
32	18.32	17.27	5.20	59.21	44.91	42.34	12.75	145.16	Ar+DB1
33,G	8.92	9.17	0.00	81.91	50.69	49.31	0.00	452.79	Ar+DB1

[a] LS, $Li_2SO_4 \cdot H_2O$; DB1, $LiKSO_4$; Pic, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; Ar, K_2SO_4.

(288.15 ± 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 decreased below the set temperature. Therefore, the temperature in the box could always be kept within (288.15 ± 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 combined with a XP-300 Digital Polarizing Microscope (Shanghai Caikon Optical Instrument Co. Ltd., China) and with an 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., lithium sulfate ($Li_2SO_4 \cdot H_2O$, 99.5 mass %), potassium sulfate (K_2SO_4, 99.0 mass %), magnesium sulfate ($MgSO_4 \cdot 7H_2O$, 99.5 mass %), and were recrystallized several times before use. Doubly deionized water (DDW) with conductivity less than $1 \cdot 10^{-4}$ $S \cdot m^{-1}$ at room temperature (298.15 K) was used to prepare the series of artificial synthesized brines and 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 calculated were mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high), which were put into the box for isothermal evaporation at (288.15 ± 0.2) K. The experimental conditions with an air flowing velocity of (3.5 to 4.0) $m \cdot s^{-1}$, a relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) $mm \cdot d^{-1}$ are presented, just like the climate of Qaidam Basin. The solutions were always kept without stirring for metastable evaporation reasons, and the crystal behavior of solid phase was observed periodically. When enough new solid phases appeared, the wet residue mixtures were taken out from the solution. Then solids were approximately evaluated from combined chemical analysis, observed with oil-immerse of XP-300D Digital Polarizing Microscopy, 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 250.0 mL in a volumetric flask 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.

Analytical Method. The compositions of K^+ and SO_4^{2-} in the liquids and their corresponding wet solid phases were analyzed by the gravimetric methods of sodium tetraphenyl borate and barium chloride, respectively both with the precisions within ± 0.05 mass %.[7] The Mg^{2+} ion concentration was determined using our previous modified EDTA titration method in the presence of Eriochrome Black-T as indicator.[8] In brief, the interference of the coexisted lithium ion in brine can be efficiently eliminated using *n*-butanol and anhydrous alcohol as a masking agent, and the relative error of the analytical results is less than ± 0.3 mass %. The concentration of Li^+ was evaluated using an ion balance and combined with analytical

Table 2. Physicochemical Property Data of the Metastable Quaternary System ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) at 288.15 K

	density ρ		viscosity 10^{-3} η		conductivity κ	
no.[a]	($g \cdot cm^{-3}$)	n_D	($Pa \cdot s$)	pH	($S \cdot m^{-1}$)	TDS %
1,A	1.2643	ND	ND	ND	ND	ND
2	ND [b]	ND	ND	ND	ND	ND
3	1.2923	1.3871	12.3093	7.27	ND	ND
4	ND	1.3834	ND	7.28	ND	ND
5	1.3491	1.3951	ND	7.23	31.1	24.5
6	1.3454	1.3936	15.0837	ND	ND	ND
7,E	1.3460	1.3931	17.5066	7.03	34.2	26.2
8	1.3343	1.3901	10.6042	6.92	31.1	24.4
9,B	ND	ND	ND	ND	ND	ND
10	1.3445	1.3911	6.8412	6.26	34.9	27.2
11	1.3428	1.3921	17.3878	6.86	27.4	34.9
12	1.3485	1.3943	12.8639	6.84	34.2	27.1
13,F	1.3497	1.3938	ND	6.62	34.7	27.6
14	1.3374	1.3873	ND	ND	38.7	30.1
15	ND	1.3980	9.5017	7.03	43.7	33.9
16	1.3266	ND	ND	6.83	37.2	30.4
17	1.3433	1.3939	6.3832	6.46	35.6	27.6
18	1.3233	1.3720	8.0849	6.81	ND	ND
19	1.3147	1.3874	14.1238	6.65	39.4	32.2
20	1.3211	1.3840	6.7263	ND	39.8	32.4
21	1.3240	1.3902	4.9184	6.67	38.9	31.4
22	1.3268	1.3921	4.9458	6.65	39.4	32.2
23,C	1.3126	ND	ND	ND	ND	ND
24	ND	1.3875	ND	ND	42.5	35.9
25	1.2892	ND	2.7211	ND	62.7	52.1
26,H	1.2687	1.3919	4.3272	6.15	62.4	50.50
27	ND	1.3920	3.1293	6.81	37.1	28.9
28	ND	ND	20.9988	7.11	35.6	27.7
29,D	1.2169	1.3775	ND	ND	ND	ND
30	1.2678	ND	4.0083	7.24	67.6	58.1
31	ND	1.3838	ND	ND	ND	ND
32	ND	ND	ND	7.26	54.4	42.9
33,G	1.1872	ND	ND	ND	ND	ND

[a] Corresponds to the no. column in Table 1. [b] ND means not determined.

Table 3. Comparison of the Solubility Data in Invariant and Boundary Points for the Metastable and Stable Equilibrium System ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$)

		composition of liquid phase Jänecke index, J_b			
		(g/100 g dry-salt)			
invariant points		K_2SO_4	Li_2SO_4	$MgSO_4$	equilibrium solid phase[b]
E	298.15 K[a]	5.35	35.82	58.83	Eps+LS+DB1
	288.15 K	6.08	43.37	49.35	
F	298.15 K	15.48	21.05	63.47	Eps+Pic+DB1
	288.15 K	10.60	35.27	54.13	
H	298.15 K	34.75	23.84	41.41	Ar+Pic+DB1
	288.15 K	26.97	28.94	44.09	
A	298.15 K[a]	6.54	93.45	0.00	LS+DB1
	288.15 K	7.44	9.52	0.00	
B	298.15 K	0.00	39.16	60.84	LS+Eps
	288.15 K	0.00	47.43	52.57	
C	298.15 K[a]	15.20	0.00	84.75	Eps+Pic
	288.15 K	16.09	0.00	83.91	
D	298.15 K	44.60	0.00	55.40	Ar+Pic
	288.15 K	50.36	0.00	49.64	
G	298.15 K	52.15	47.85	0.00	Ar+DB1
	288.15 K	50.69	49.31	0.00	

[a] 298.15 K was from ref 6; 288.15 K was this work. [b] LS, $Li_2SO_4 \cdot H_2O$; DB1, $LiKSO_4$; Pic, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; Ar, K_2SO_4.

verified measurement occasionally by ICP-AES (IRIS Intrepid ICP, Thermo Electron Co.).

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 $g \cdot cm^{-3}$. The viscosities (η) were determined using an Ubbelohde capillary viscometer, which was placed in a thermostat at (288.15 ± 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. The uncertainty of the flow time measurements was ± 0.2 s. 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 Orion 145A+ Conductivity Meter (Thermo Electron Corporation, U.S.A.) with a precision of ± 0.0002 $S \cdot m^{-1}$. The physicochemical parameters of density, refractive index and pH were also all placed in a thermostat that electronically controlled the set temperature at (288.15 ± 0.1) K.

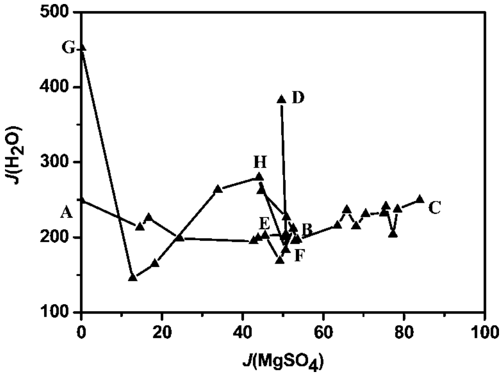
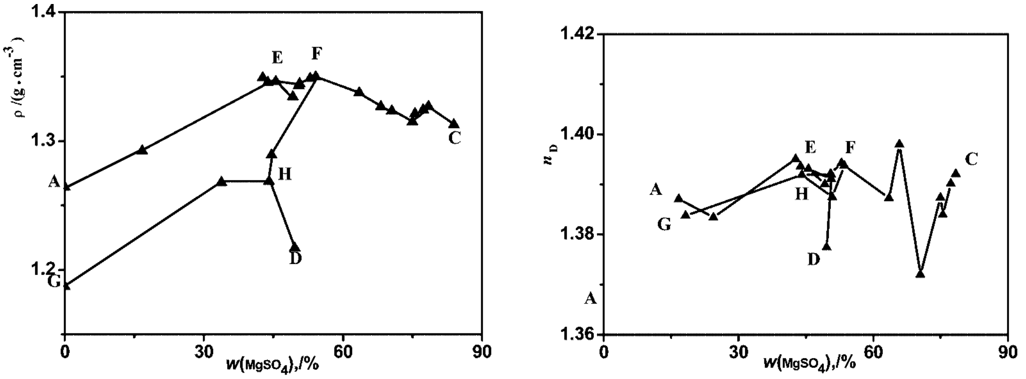


Figure 2. Water-phase diagram of the quaternary system ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) at 288.15 K.

Results and Discussion

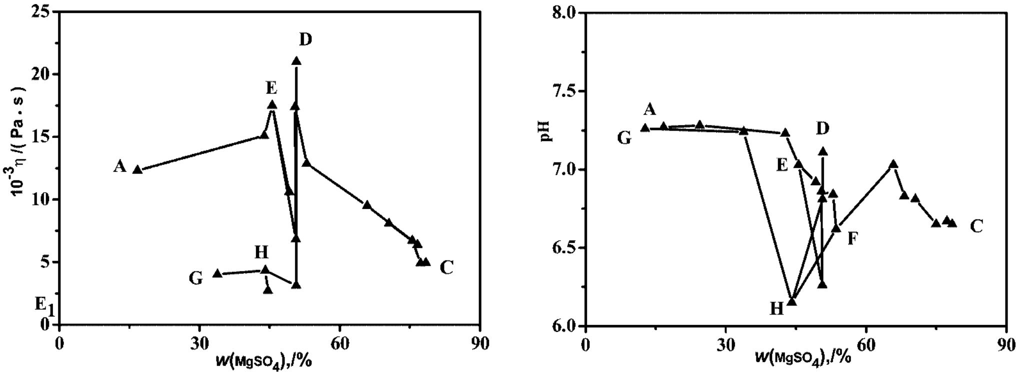
The experimental data on the metastable solubilites and the relevant physicochemical properties of the quaternary system ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) at 288.15 K are presented in Tables 1 and 2, respectively. The composition of the liquid phase in the metastable equilibrium solution is expressed both in weight percentage and Jänecke index (J_b). J_b expresses the *b*-th salt in the solution in gram per 100 g of dry-salt, that is, J_b (g/100 g dry-salt). On the basis of J_b in Table 1, the metastable equilibrium dry-salt phase diagram of the system at 288.15 K is plotted and shown in Figure 1 (solid lines).

The metastable phase diagram of the system in Figure 1 (solid lines) consists of three three-salt-cosaturation points, five crystallization fields, three-invariant points (points E, F, and H), and seven-univariant curves. Points E, F, and H are the invariant points of three cosaturated solid phases of E ($MgSO_4 \cdot 7H_2O + LiKSO_4 + Li_2SO_4 \cdot H_2O$), F ($MgSO_4 \cdot 7H_2O + K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + LiKSO_4$), and H ($K_2SO_4 + K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + LiKSO_4$) with the composition of K_2SO_4, Li_2SO_4, and $MgSO_4$ (mass %) 6.08, 48.37, 45.55 (point E), 10.60, 35.27, 54.13 (point F), and 26.97, 28.94, 44.09 (point H), respectively. The seven-univariant solubility isotherm curves correspond to AE ($Li_2SO_4 \cdot H_2O + LiKSO_4$), BE ($MgSO_4 \cdot 7H_2O + Li_2SO_4 \cdot H_2O$), EF ($MgSO_4 \cdot 7H_2O + LiKSO_4$), FC ($MgSO_4 \cdot 7H_2O + K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), FH ($LiKSO_4 + K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), HD ($K_2SO_4 + K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), and HG ($K_2SO_4 + LiKSO_4$). The five crystallization regions correspond to lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), arcanite (K_2SO_4), epsomite ($MgSO_4 \cdot 7H_2O$), double salt 1 ($LiKSO_4$),



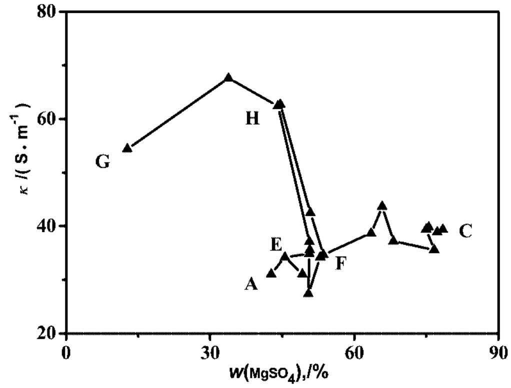
(a) density vs. composition

(b) refractive index vs. composition



(c) viscosity vs. composition

(d) pH value vs. composition



(e) conductivity vs. composition

Figure 3. Physicochemical property vs composition diagram for the metastable quaternary system ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) at 288.15 K. ▲, experimental data point; —, experimental relationship diagram. (a) Density vs composition; (b) refractive index vs composition; (c) viscosity vs composition; (d) pH vs composition; and (e) conductivity vs composition.

and picromerite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) formed in the metastable quaternary system. No solid solution was found in the system. Comparison of the solubility data in invariant and boundary points for the metastable and stable equilibrium system ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) are shown in Table 3. A comparison of the metastable equilibrium at 288.15 K and the stable equilibrium at 298.15 K (dashed lines) in Figure 1 shows that the metastable behavior of $MgSO_4$ is more obvious and the crystallizing regions of $MgSO_4 \cdot 7H_2O$ and K_2SO_4 are much larger than those in the stable phase diagram.

Figure 2 is the relevant water-phase diagram of the system at 288.15 K. The physicochemical properties of the quaternary system changed gradually and regularly with the content change of magnesium sulfate. It shows that the Jänecke index of water, that is, $J(H_2O)$, changes with the Jänecke index of magnesium sulfate. On the basis of the experimental data in Table 2, relationships between the solution physicochemical properties (density, pH, conductivity, refractive index, and viscosity) vs the composition of magnesium sulfate with weight percentage in solution are found, as shown in Figure 3. It can be found that the physicochemical properties of the equilibrium solution change with the change of the weight percentage of magnesium sulfate.

Conclusions

Metastable equilibria of the quaternary system ($Li_2SO_4 + K_2SO_4 + MgSO_4 + H_2O$) at 288.15 K were studied with the isothermal evaporation method. Solubilities and the physicochemical properties were determined experimentally. According to the experimental data, the metastable equilibrium phase diagram and the water-phase diagram of the system were plotted. The results show that there are no solid solutions formed in this quaternary system at 288.15 K.

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