

Metastable Phase Equilibrium in the Aqueous Ternary System $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 KTianlong Deng^{*,†,‡,§} Hongjun Yin,[§] and Yafei Guo^{†,‡}[†]Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine Science and Engineering, Tianjin University of Science and Technology, Tianjin, 300457, P. R. China[‡]Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, 810008, P. R. China[§]College of Materials, Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu, 610059, P. R. China

ABSTRACT: The metastable solubilities and physicochemical properties (densities and refractive index) of the aqueous ternary system ($\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at 323.15 K were determined by the isothermal evaporation method. According to the experimental results, the metastable phase diagram and the diagram of physicochemical properties versus composition were plotted. It was found that there are one eutectic point ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), two univariant curves, and two crystallization regions corresponding to lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) and hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) in the metastable ternary system. The system belongs to a simple eutectic type, and neither double salts nor solid solutions were found. It can be found that the solution density and refractive index of the metastable ternary system changed regularly with the content change of lithium sulfate, and all reach the maximum value at eutectic point. The calculated values of densities and refractive index with empirical equations are in good agreement with the experimental data.

■ INTRODUCTION

There are more than seven hundred salt lakes with an area larger than 1 km^2 in the Qinghai-Tibet Plateau, and a number of salt lakes with an abundance of lithium and magnesium resources are widely distributed in the Qaidam Basin. These salt lakes are famous for the highest concentration ratio of magnesium to lithium in brines around the world. The phenomena of supersaturation of brines containing magnesium sulfate are often found both in salt lakes and solar ponds.¹ The precipitation of salts of lithium sulfate and epsomite is recently observed in saline sediments in several salt lakes. It is well-known that studies on the thermodynamic phase equilibrium and phase diagrams are essential and important in exploiting the brine resources and understanding the geochemical behaviors of brine–mineral system. Therefore, the simulative experimental studies on metastable phase equilibrium are essential to predict the actual evaporation path of mineral crystallization for the separation and purification of the lithium-containing mixture salts effectively.

Although the phase equilibrium of $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ over a wide range of temperatures ranging from (298.15 to 348.15) K has been previously reported,^{2–6} the ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 K according to the climate conditions and the usual temperature during the evaporated seasons is studied, which is not reported in the literature, to describe the metastable behaviors to separate and purify the lithium-containing mixture salts. In this paper, the metastable solubilities and the solution physicochemical properties (densities and refractive index) in the ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 K are presented.

■ EXPERIMENTAL SECTION

Apparatus and Reagents. An 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 $(323.15 \pm 0.2) \text{ K}$, 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. Therefore, the temperature in the box could always be kept at $(323.15 \pm 0.2) \text{ K}$. An electric fan installed on the box always worked to accelerate the evaporation quantity of water from solutions. The solid phase minerals were identified combined with Schreinemaker's method and a XP-300 digital polarizing microscopy (Shanghai Caikon Optical Instrument Co. Ltd., China).

The chemicals used were of analytical grade and obtained from either the Tianjin Kermel Chemical Reagent Ltd. or the Shanghai-Lithium Industrial Co. Ltd.: epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.99 by mass fraction) and lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, 0.99) were recrystallized before use. Doubly deionized water (DDW) with a conductivity less than $1 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$ at 298.15 K was used to prepare the series of the 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), and then the containers were put into the box for the isothermal evaporation at $(323.15 \pm 0.2) \text{ K}$. Experimental conditions with an air flowing velocity of $(3.5 \text{ to } 4.0) \text{ m} \cdot \text{s}^{-1}$,

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Table 1. Solubility and Property Data of the Metastable System $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 K

no.	composition of liquid phase, 100 w^a		composition of wet residue, 100 w		ρ $\text{g} \cdot \text{cm}^{-3}$	n_D	equilibrium solid phase ^b
	Li_2SO_4	MgSO_4	Li_2SO_4	MgSO_4			
1,A	27.23	0.00	ND ^c	ND	1.2383	1.3763	Ls
2	25.36	1.24	ND	ND	1.2390	ND	Ls
3	22.43	5.28	ND	ND	1.2559	1.3807	Ls
4	21.36	10.35	ND	ND	1.3088	1.3895	Ls
5	20.73	10.10	ND	ND	1.2999	1.3883	Ls
6	18.56	12.89	ND	ND	1.3036	1.3890	Ls
7	18.31	12.70	31.98	10.33	1.2917	1.3912	Ls
8	15.83	16.96	29.58	13.90	1.3353	1.3938	Ls
9	13.41	22.81	23.11	19.82	1.3782	1.4003	Ls
10,E	10.42	27.29	15.50	29.44	1.4146	1.4060	Ls + Hex
11	10.36	27.13	ND	ND	1.4162	1.4060	Hex
12	9.89	27.51	8.48	31.64	1.4137	1.4057	Hex
13	6.48	29.61	ND	ND	1.4046	1.4041	Hex
14	4.57	30.71	ND	ND	1.3975	1.4027	Hex
15	3.69	31.31	2.19	39.39	1.3930	1.4030	Hex
16,B	0.00	33.08	ND	ND	1.3829	1.4018	Hex

^a w , mass fraction. ^b Ls, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; Hex, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. ^c ND, not determined.

a relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) $\text{mm} \cdot \text{day}^{-1}$ are presented. The solutions were always kept with no stirring for reasons of metastable evaporation, and then the crystal behavior of solid phase was periodically observed. When enough new solid phase appeared, the wet residue mixtures were taken from the solution. Then solids were approximately evaluated, combining chemical analysis determined by Schreinemaker's method of wet residues. 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 diluted to a 250.0 cm^3 final volume in a volumetric flask with DDW for quantitative analysis of the compositions of the liquid phase. Some other filtrates were used to measure the relative physico-chemical 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 SO_4^{2-} in liquids and their corresponding wet residues of the solid phases were analyzed by gravimetric methods of barium chloride with an uncertainty within ± 0.0005 by mass fraction. The Mg^{2+} ion concentration was determined by titration with ethylenediaminetetraacetic acid (EDTA) standard solution in the presence of indicator of Eriochrome Black-T.⁷ It was observed that the measurement of Mg^{2+} with the method of titration is significantly impeded by the coexisting lithium ion in brine, so we successfully eliminated the interference by using *n*-butanol and anhydrous alcohol as a masking agent, and the relative error of the analytical results is no more than ± 0.003 by mass fraction.⁸ The densities (ρ) were measured with a density bottle method with an uncertainty of $\pm 0.0002 \text{ g} \cdot \text{cm}^{-3}$. An Abbe refractometer (model WZS-1) was used to measure the refractive index (n_D) with an uncertainty of ± 0.0001 . All of the measurements were maintained at the desired temperature within (323.15 \pm 0.1) K through control of the thermostat.

RESULTS AND DISCUSSION

The metastable solubilities and densities of the ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 K are presented in Table 1.

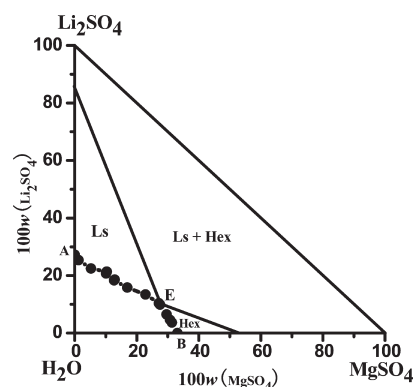


Figure 1. Metastable equilibrium phase diagram at 323.15 K and stable equilibrium phase diagram at 308.15 K of the ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$. Hex, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$; Ls, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

The ion concentration values in the metastable equilibrium solution were expressed in mass fraction. According to the experimental data in Table 1, the metastable phase diagram of the system at 323.15 K was plotted, as shown in Figure 1.

In Figure 1, points A and B are the metastable solubilities of the single salts of lithium sulfate and magnesium sulfate with a mass fraction (100 w) of 27.23 and 33.08, respectively. Point E is a eutectic point of lithium sulfate monohydrate and hexahydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), and the compositions of Li_2SO_4 , MgSO_4 in the liquid phase with mass fraction (100 w) are 10.42 and 27.29, respectively. There are two isotherm evaporation curves corresponding to curves AE and BE, indicating the saturation of single salts. The metastable phase diagram consisted with two crystallization regions corresponding to the large area of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and the relative small area of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. It obviously belongs to a simple eutectic type, and neither double salts nor solid solution were found.

Due to the fact that there are no data reported for the stable equilibrium system at 323.15 K, a comparison of the diagrams of

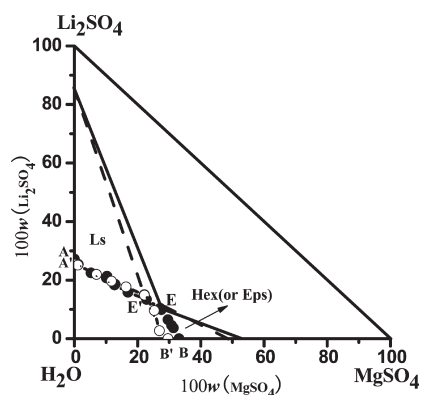
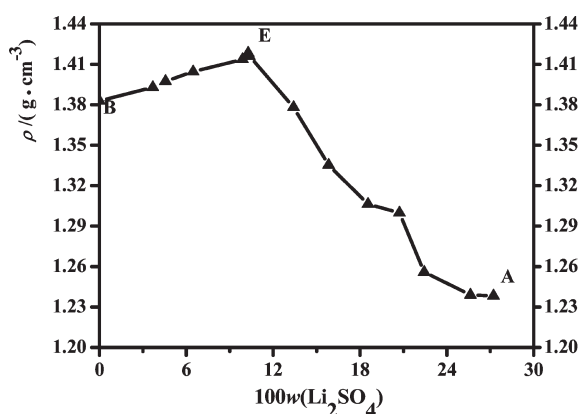
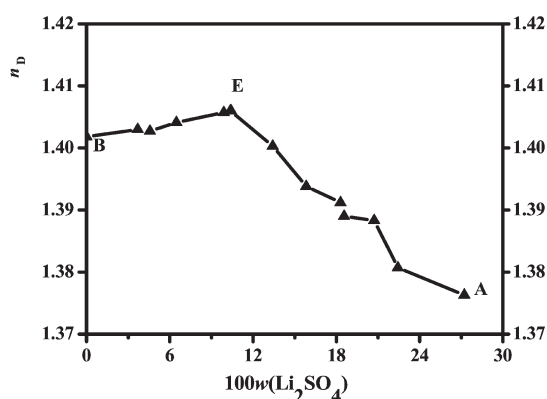


Figure 2. Comparison of the metastable phase diagram at 323.15 K and stable phase diagram at 308.15 K of the ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$. ●, metastable experimental points; —, metastable isotherm curve; Hex, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$; Ls, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; ○, stable experimental points; - - -, stable isotherm curve; Eps, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; Ls, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.



(a) density vs. composition



(b) refractive vs. composition

Figure 3. Physicochemical properties versus composition diagram for the metastable ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 K. ▲, experimental data point; —, experimental relationship diagram; (a) density versus composition; (b) refractive index versus composition.

the metastable equilibrium at 323.15 K with solid lines and the stable equilibrium at 308.15 K with dashed lines in the same system is shown in Figure 2.³ The area of the metastable

Table 2. Calculated and Experimental Properties in the Metastable System ($\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at 323.15 K

no. ^a	densities, $\rho/(\text{g} \cdot \text{cm}^{-3})$			refractive index, n_D		
	exp. value	calcd value	relative error ^b	exp. value	calcd value	relative error ^b
1,A	1.2383	1.2383	0.0000	1.3763	1.3763	0.0000
2	1.2390	1.2347	0.0035	ND ^c	1.3757	-
3	1.2559	1.2556	0.0002	1.3807	1.3795	0.0009
4	1.3088	1.3103	-0.0011	1.3895	1.3889	0.0004
5	1.2999	1.3002	-0.0002	1.3883	1.3873	0.0007
6	1.3036	1.3137	-0.0077	1.3890	1.3896	-0.0005
7	1.2917	1.3085	-0.0130	1.3912	1.3888	0.0017
8	1.3353	1.3386	-0.0025	1.3938	1.3939	-0.0001
9	1.3782	1.3923	-0.0102	1.4003	1.4027	-0.0017
10,E	1.4146	1.4195	-0.0035	1.4060	1.4072	-0.0009
11	1.4162	1.4185	-0.0016	1.4060	1.4070	-0.0007
12	1.4137	1.4185	-0.0034	1.4057	1.4070	-0.0009
13	1.4046	1.4087	-0.0029	1.4041	1.4056	-0.0011
14	1.3975	1.4021	-0.0033	1.4027	1.4047	-0.0014
15	1.3930	1.4004	-0.0053	1.4030	1.4044	-0.0010
16,B	1.3829	1.3829	0.0000	1.4018	1.4018	0.0000

^aNo. column corresponding to the no. in Table 1. ^bRelative error = (experimental value - calculated value)/experiment value. ^cND, not determined.

crystallization region of hexahydrate is obviously decreased, which illustrates that the MgSO_4 solution has a supersaturated phenomenon in the isothermal evaporation equilibrium system.

On the basis of experimental data in Table 1, the relationship of the solution physicochemical properties (densities and refractive index) with the concentration of lithium sulfate is shown in Figure 3. It can be found that the solution density and refractive index of the ternary system changed regularly with the content change of lithium sulfate, and all reach a maximum value at the eutectic point E.

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 solution were also calculated.

$$\ln \frac{d_{50}}{d_0} = \sum A_i \cdot w_i$$

$$\ln \frac{D_{50}}{D_0} = \sum B_i \cdot w_i$$

where $d_0 = 0.98803 \text{ g} \cdot \text{mL}^{-1}$, the density of water at 323.15 K; $n_0 = 1.3290$, the refractive index of water at 323.15 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 323.15 K. w_i is the salt of i in the solution in mass fraction. Constants A_i and B_i of Li_2SO_4 and MgSO_4 for calculation of density and refractive index of solution are (0.008292, 0.01016) and (0.001284, 0.001612), respectively. The calculated results and experimental values are presented in Table 2 for comparison, and all of the calculated results with the maximum relative deviations are within $\pm 0.53\%$.

CONCLUSIONS

The metastable equilibrium of the ternary system $\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$ at 323.15 K was studied with the isothermal evaporation method. Solubilities and the solution physicochemical properties (densities and refractive index) were determined experimentally. According to the experimental and predictive solubility data, the metastable phase diagrams and the diagrams of physicochemical properties versus composition were plotted. Those results show that the ternary system belongs to a simple eutectic type, and neither double salts nor solid solution formed. 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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REFERENCES

- (1) Chen, J. Q.; Liu, Z. Q.; Fang, C. H. Studies on evaporation-crystallization of salt lake brines in China. *J. Salt Lake Res.* **1994**, *2*, 43–51.
- (2) Lepeshkov, I. N.; Romashova, N. N. The ternary system $\text{Li}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ at 35 °C. *Russ. J. Inorg. Chem.* **1960**, *5*, 2512–2517.
- (3) Shevchuk, V. G. Phase equilibrium of the ternary system $\text{Li}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ at 35 °C. *Russ. J. Inorg. Chem.* **1961**, *6* (8), 1955–1958.
- (4) Aravamudan, G. The system lithium sulphate–magnesium sulphate–water at 30 °C. *Can. J. Chem.* **1962**, *40* (5), 1035–1037.
- (5) Li, B.; Fang, C. H.; Wang, Q. Z.; Li, J.; Song, P. S. A study on the phase diagram and solution properties of ternary system $\text{Li}^+, \text{Mg}^{2+}/\text{SO}_4^{2-}\text{-H}_2\text{O}$ at 25 °C. *J. Salt Lake Res.* **1993**, *1* (3), 1–5.
- (6) Wang, S. Q.; Deng, T. L. (Solid + liquid) isothermal evaporation phase equilibria in the aqueous ternary system ($\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at $T = 308.15$ K. *J. Chem. Thermodyn.* **2008**, *40*, 1007–1011.
- (7) Qinghai Institute of Salt Lakes of the Chinese Academy of Sciences. *Analytical Methods of Brines and Salts*, 2nd ed.; Science Press: Beijing, 1988; pp 39–52.
- (8) Wang, S. Q.; Gao, J.; Yu, X.; Sun, B.; Deng, T. L. Study on the interference of coexisting lithium ion on the measurement of magnesium ion. *J. Salt Lake Res.* **2007**, *15* (1), 44–48.
- (9) Lin, L. J.; Fang, C. H.; Fang, Y.; Qin, X. F. A new model for predicting density of electrolyte solutions. *J. Salt Lake Res.* **2006**, *14* (2), 56–61.