Metastable Phase Equilibrium in the Aqueous Ternary System (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K[†]

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The metastable solubilities and physicochemical properties (densities and refractive index) of the aqueous ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K were determined for the first time by the method of isothermal evaporation, and the metastable phase diagram and the diagrams of physicochemical properties versus composition were plotted. It was found that there is one invariant point of ($Li_2SO_4 \cdot H_2O$ + $MgSO_4 \cdot 4H_2O$), two univariant curves, and two crystallization regions corresponding to lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$) and tetrahydrite ($MgSO_4 \cdot 4H_2O$) in the metastable ternary system. The system belongs to a hydrate type I, and neither double salts nor solid solutions were formed. A comparison of the stable and metastable phase diagrams at this temperature shows that the metastable phenomenon of magnesium sulfate is obvious, and the crystallizing region of tetrahydrite is much smaller than that in the stable phase diagram. The solution density and refractive index of the metastable ternary system changes regularly with the mass fraction of lithium sulfate and reaches a maximum value at an invariant point. The densities and refractive index were correlated with empirical equations.

Introduction

Salt lakes are a naturally occurring complex body of water and salt interaction. It is well-known that salt−water phase equilibrium plays an important role in exploiting the brine resources and describing the geochemical behavior of brine mineral. There are more than one thousand salt lakes in China, and a number of salt lakes with an abundance of lithium and magnesium resources are widely distributed in the Qaidam Basin of Qinghai-Tibet Plateau, China. 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 in solar ponds.[1] 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 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 metastable equilibria for the systems (KCl + K_2SO_4 + $K_2B_4O_7$ + H_2O) and (NaCl + KCl + $Na_2B_4O_7$ + $K_2B_4O_7$ + H_2O) at 308.15 K, (NaCl + KCl + $CaCl_2$ + H_2O) at 288.15 K, and (KCl + $CaCl_2$ + H_2O) and (Li_2SO_4 + $MgSO_4$ + H_2O) at (288.15 and 308.15) K and the stable equilibrium for (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K have been reported,[2−7] the metastable phase equilibrium on the ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K 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 (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K are presented.

Experimental Section

Apparatus and Reagents. An isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermally insulated box (70 cm long, 65 cm wide, 60 cm high) with an apparatus to control the temperature was installed. The schematic diagram of the apparatus and the temperature controlling have been satisfactorily described in our previous paper.[4] Therefore, the temperature in the box could always be kept within (348.15 ± 0.2) K. An electric fan installed on the box always worked to accelerate the evaporation of water from solutions. The solid phase minerals were identified combined with Schreinemaker's colinear principle (i.e., the solid phase mineral point lies in the extension line of the two composition points of the liquid phase and the wet residual) and an XP-300 digital polarizing microscope (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 ($MgSO_4 \cdot 7H_2O$, w = 99.0 %) and lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$, w = 99.0 %), and were recrystallized with doubly deionized water (DDW) before use. 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 Methods. 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

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Table 1. Solubility and Physicochemical Property of the Metastable Ternary System ($Li_2SO_4 + MgSO_4 + H_2O$) at 348.15 K[a]

	composition of liquid phase, w/%		composition of wet residue, w/%		density		
no.	Li_2SO_4	$MgSO_4$	Li_2SO_4	$MgSO_4$	ρ/g·cm^{-3}	n_D	equilibrium solid phase[b]
1(A)	25.34	0	ND[c]	ND	1.204	1.3727	Ls
2	20.76	8.7	36.18	6.45	1.2641	1.3812	Ls
3	19.09	10.82	ND	ND	1.279	1.384	Ls
4	17.93	13.2	ND	ND	1.2973	1.3876	Ls
5	16.39	16.24	30.5	13.22	1.3205	1.3922	Ls
6	14.65	19.15	ND	ND	1.3404	1.3953	Ls
7	13.96	20.86	ND	ND	1.3581	1.3982	Ls
8	12.63	24.47	ND	ND	1.3891	1.4026	Ls
9	11.32	27.31	30.25	20.61	1.4136	1.4057	Ls
10	9.53	30.75	ND	ND	1.4503	1.4097	Ls
11(E)	8.45	33.74	13.64	36.66	1.4801	1.415	Ls +Tet
12	4.85	36.73	3.02	42.74	1.4787	1.4135	Tet
13	4.38	36.47	ND	ND	1.4698	1.4125	Tet
14	2.26	36.54	2.07	39.31	1.4501	1.4081	Tet
15(B)	0	37.86	ND	ND	1.4408	1.405	Tet

[a] w = mass fraction. [b] Ls, $Li_2SO_4\cdot H_2O$; Tet, $MgSO_4\cdot 4H_2O$. [c] ND means not determined.

isothermal evaporation at (348.15 ± 0.2) K. The experimental conditions with an air flowing velocity of (3.5 to 4.0) m·s^{-1}, a relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) mm·day^{-1} are presented. The solutions were always kept without stirring for metastable evaporation reasons, and the crystal behaviors of the solid phase were observed periodically. When enough new solid phases appeared, the wet residue mixtures were taken out from the solution. Meanwhile, a 5.0 mL sample of the clarified solution was taken out from the liquid phase of each polyethylene container through a pipet and then diluted to 250.0 mL volume 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 point.

Analytical Methods. The concentration of SO_4^{2-} in the liquids and their corresponding wet residues of the solid phases were analyzed in triplicate by gravimetric methods of barium chloride with a precision within ± 0.05 %. The Mg^{2+} ion concentration was determined by titration with standard EDTA solution in the presence of Eriochrome Black-T as an indicator.[8] It was observed that the measurement of Mg^{2+} concentration by the method of titration is significantly interfered with by the coexisted Li^+ in brine. We successfully eliminated the interference by using n-butyl alcohol and absolute alcohol as a masking agent, and the uncertainty for the analytical results in triplicate measurements is within ± 0.3 %.[9]

The densities (ρ) were measured in triplicate with a density bottle method with an uncertainty of ± 0.0002 g. An Abbe refractometer (model WZS-1) was used to measure the refractive index (n_D), and it was calibrated with the refractive index known superpure water standard (n_D = 1.3325) with an uncertainty of ± 0.0001 in triplicate measurements. All the measurements were maintained at the desired temperature ± 0.1 K through control of the thermostat.

Results and Discussion

The experimental data on the metastable solubilites and the solution densities and refractive index of the ternary system ($Li_2SO_4 + MgSO_4 + H_2O$) at 348.15 K were presented in Table 1. The ion concentration values in the metastable equilibrium solution were expressed in weight percentage. According to the experimental data in Table 1, the metastable phase diagram of the system at 348.15 K was plotted, as shown in Figure 1 with solid lines.

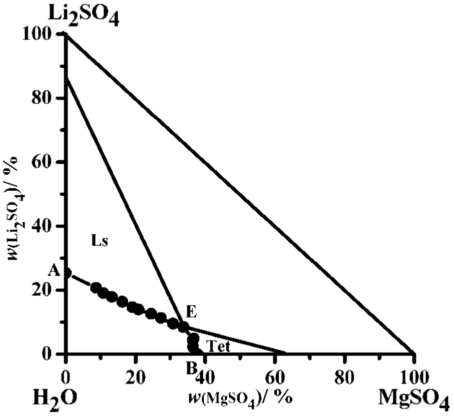


Figure 1. Metastable equilibrium phase diagram of the ternary system ($Li_2SO_4 + MgSO_4 + H_2O$) at 348.15 K. Tet, $MgSO_4\cdot 4H_2O$; Ls, $Li_2SO_4\cdot H_2O$.

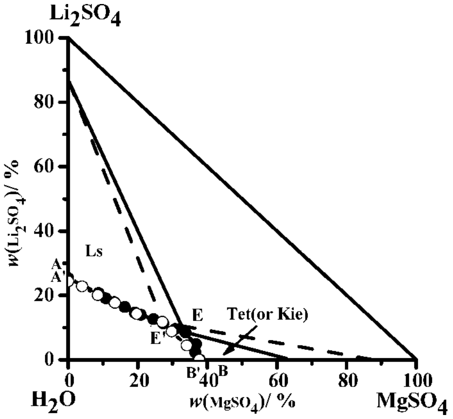


Figure 2. Metastable equilibrium phase diagram and stable equilibrium phase diagram for the ternary system ($Li_2SO_4 + MgSO_4 + H_2O$) at 348.15 K. ●, metastable experimental points; —, metastable isotherm curve; ○, stable experimental points; ---, stable isotherm curve; Tet, $MgSO_4\cdot 4H_2O$; Kie, $MgSO_4\cdot H_2O$; Ls, $Li_2SO_4\cdot H_2O$.

In Figure 1, points A and B are the metastable solubilities of the salts of $Li_2SO_4\cdot H_2O$ and $MgSO_4\cdot 4H_2O$ in mass fraction of (25.34 and 37.86) %, respectively. Point E is an invariant point of lithium sulfate monohydrate and tetrahydrite ($Li_2SO_4\cdot H_2O + MgSO_4\cdot 4H_2O$), and the compositions of Li_2SO_4 and $MgSO_4$ in the liquid phase in mass fraction are (8.45 and 33.74) %, respectively. There are two isotherm evaporation curves corresponding to curves AE and BE, indicating the saturation of single salts. The metastable phase diagram consists of two crystallization regions corresponding to the large area of $Li_2SO_4\cdot H_2O$ and the relative small area of $MgSO_4\cdot 4H_2O$. It obviously belongs to a hydrate type I, and neither double salts nor solid solution were found.

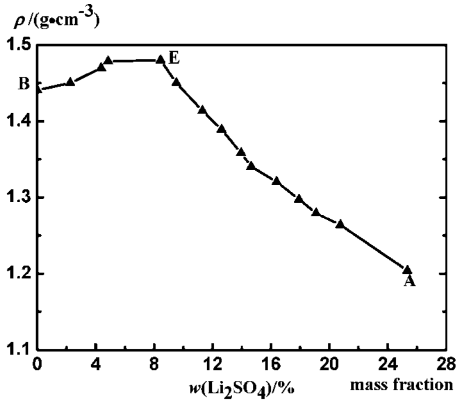
On the basis of experimental data in Table 1, the relationship of the solution physicochemical properties (densities and refractive index) with the concentration of lithium sulfate monohydrate was shown in Figure 3. It was found that the solution density and refractive index of the ternary system were changed regularly with the increase of weight percentage of lithium sulfate and to reach the maximum value at the invariant point E.

A comparison between the metastable and stable equilibrium phase diagrams on the system ($Li_2SO_4 + MgSO_4 + H_2O$) at 348.15 K was shown in Table 2 and Figure 2. It was found that

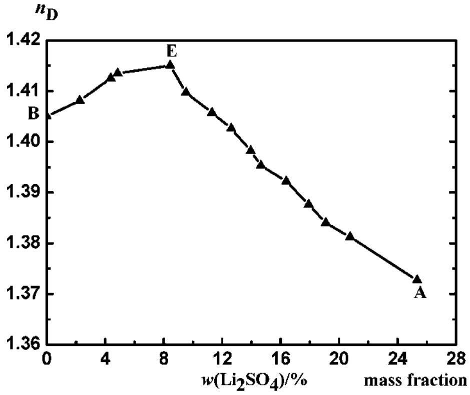
Table 2. Comparison of the Metastable and Stable Phase Equilibrium in the Invariant Point of the Ternary System (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K[a]

	composition of liquid phase *w*/%			
	Li_2SO_4	$MgSO_4$	H_2O	equilibrium solid phase[b]
metastable	8.45	33.74	57.81	Ls + Tet
stable[7]	11.75	27.03	61.22	Ls + Kie

[a] *w* = mass fraction. [b] Ls, $Li_2SO_4 \cdot H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Kie, $MgSO_4 \cdot H_2O$.



(a) density vs. composition



(b) refractive index vs. composition

Figure 3. Physicochemical properties versus composition diagram for the metastable ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 K. ▲, experimental data point; —, experimental relationship diagram; (a) density vs composition; (b) refractive index vs composition.

the magnesium sulfate crystallization regions for metastable and stable equilibria are tetrahydrite ($MgSO_4 \cdot 4H_2O$) and kieserite ($MgSO_4 \cdot H_2O$), respectively. It is obvious that the area of the metastable crystallization region of tetrahydrite ($MgSO_4 \cdot 4H_2O$) is more decreased than it was in the stable phase diagram, illustrating that the $MgSO_4$ solution has a supersaturated phenomenon in the isothermal evaporation equilibrium system.

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,[3,10] the density and refractive index of the solution were also calculated.

$$\ln \frac{d}{d_0} = \sum A_i \cdot w_i \qquad (1)$$

$$\ln \frac{D}{D_0} = \sum B_i \cdot w_i \qquad (2)$$

where *d* and d_0 refer to the density values of the solution and the pure water at 348.15 K; the $d_0$value for pure water at 348.15 K is 0.97486 g·cm^{-3}.[11] *D* and D_0 refer to the refractive index of the solution and the pure water at the same temperature, respectively; the D_0 value of pure water at 348.15 K is 1.32410.[11]

Table 3. Comparisons of the Calculated and Experimental Values of Density and Refractive Index in the Metastable Ternary System at 348.15 K

	density, *ρ*/g·cm^{-3}			n_D		
no.[a]	experimental value	calculated value	*δ*[b]	experimental value	calculated value	*δ*
1(A)	1.204	1.2022	0.0015	1.3727	1.374	0.001
2	1.2641	1.2658	−0.0013	1.3812	1.3836	0.0017
3	1.279	1.2759	0.0024	1.384	1.3848	0.0006
4	1.2973	1.2951	0.0017	1.3876	1.3876	0
5	1.3205	1.3193	0.0009	1.3922	1.3911	−0.0008
6	1.3404	1.34	0.0003	1.3953	1.394	−0.001
7	1.3581	1.3559	0.0016	1.3982	1.3963	−0.0014
8	1.3891	1.3918	−0.0019	1.4026	1.4015	−0.0008
9	1.4136	1.4175	−0.0028	1.4057	1.405	−0.0005
10	1.4503	1.447	0.0023	1.4097	1.4089	−0.0005
11(E)	1.4801	1.4789	0.0008	1.415	1.4133	−0.0012
12	1.4787	1.4803	−0.0011	1.4135	1.4125	−0.0007
13	1.4698	1.4706	−0.0005	1.4125	1.411	−0.0011
14	1.4501	1.4461	0.0028	1.4081	1.4068	−0.001
15(B)	1.4408	1.4387	0.0015	1.405	1.405	0

[a] The no. column corresponds to the no. in Table 1. [b] *δ* = (A_{exp} − A_{calc})/A_{exp}, and *A* stands for density and refractive index, respectively.

A_i and B_i are the constants for the *i*th component in the solution, and they can be obtained from the densities or refractive index versus compositions of the two boundary values in the ternary system with weight percentage (i.e., the saturated solubilites of the two binary systems) at 348.15 K. Constants A_i and B_i of Li_2SO_4 and $MgSO_4$ for calculation of density and refractive index of solution are 0.008272, 0.01028, and 0.001461, 0.001567, respectively. Comparison between the calculated physicochemical properties (density and refractive index) and the experimental results was shown in Table 3, and the maximum relative error was within 0.23 %.

Conclusions

Metastable equilibrium of the ternary system (Li_2SO_4 + $MgSO_4$ + H_2O) at 348.15 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 data, the metastable phase diagram and the diagrams of physicochemical properties vs composition were plotted. The results show that the ternary system belongs to a simple invariant type, and neither double salts nor solid solution formed. When comparing the stable and metastable diagrams on the ternary system at 348.15 K, the area of the metastable crystallized region of tetrahydrite ($MgSO_4 \cdot 4H_2O$) is decreased compared to the crystallized region of kieserite ($MgSO_4 \cdot H_2O$) in the stable phase diagram. The calculated values of densities and refractive index using empirical equations are in good agreement with the experimental values.

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