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

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ABSTRACT: The metastable solubilities and the refractive indices in the aqueous ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K were determined with the method of isothermal evaporation, and the metastable phase diagram and the diagram of refractive index versus composition were plotted. Four two-salt cosaturated points of epsomite ($MgSO_4 \cdot 7H_2O$, Eps) + hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), Hex + pentahydrite ($MgSO_4 \cdot 5H_2O$, Pen), Pen + tetrahydrite ($MgSO_4 \cdot 4H_2O$, Tet), and Tet + bischofite ($MgCl_2 \cdot 6H_2O$, Bis), five isothermal univariant curves, and five metastable crystallization fields corresponding to Eps, Hex, Pen, Tet, and Bis were formed in the metastable ternary system. A comparison of the stable and metastable phase diagrams of the ternary system at 308.15 K shows that one more metastable crystallization field is formed. Neither a solid solution nor double salts are found. The solubility predictions of the metastable ternary system at 308.15 K based on Pitzer's ion-interaction model and its extended Harvie−Weare (HW) model are presented, and the calculated results were in good agreement with the experimental results.

INTRODUCTION

There are a large number of salt lakes in the Qinghai-Tibet Plateau, China. The salt lakes in the Qaidam Basin are rich in magnesium and lithium resources, and the reserves for magnesium sulfate and magnesium chloride are as high as 16.7×10^8 and 30.9×10^8 tons, respectively.[1] To adequately exploit and utilize this magnesium resource, it is essential to predict the crystallization path for the salt lake brines.

The stable system ($MgCl_2 + MgSO_4 + H_2O$) has previously been investigated over a wide temperature range (273.15 to 413.15) K. It was found that the metastable phenomena in the ternary system ($MgCl_2 + MgSO_4 + H_2O$) were obvious at (328.15 and 353.15) K.[2] For the crystallized minerals of tetrahydrite ($MgSO_4 \cdot 4H_2O$, Tet), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), epsomite ($MgSO_4 \cdot 7H_2O$, Eps), and bischofite ($MgCl_2 \cdot 6H_2O$, Bis) in the stable system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K, the stable crystallization fields for kieserite ($MgSO_4 \cdot H_2O$, Kie), Tet, pentahydrite ($MgSO_4 \cdot 5H_2O$, Pen), Hex, Eps, and Bis were yielded from the Harvie−Weare (HW) model,[3,4] whereas the metastable equilibrium behavior of the ternary system at 308.15 K has not been reported. In the present work, the metastable solubilities and the crystallized solid phases in the system at 308.15 K have been investigated experimentally and theoretically.

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) was used with a temperature controller to control the temperature.[5] An electric fan on the box was used to accelerate the evaporation of water from the solutions. The solid phase minerals were identified by combined use of an XP-300 digital polarizing microscope (Shanghai Caikon Optical Instrument Co,. Ltd., China) and an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands).

The chemicals used were of analytical grade and obtained from Tianjin Kermel Chemical Reagent Ltd. [magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, mass fraction 0.99) and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, mass fraction 0.99)] and were recrystallized before use. Doubly deionized water (DDW) with conductivity less than 1×10^{-4} $S \cdot m^{-1}$ at room temperature (298.15 K) was used to prepare the series of artificial synthesized brines and for chemical analysis.

Experimental Method. The isothermal evaporation method was used in this study. According to the statistical data from 1971 to 2000, the temperature of the brine in the Qaidam Basin is between (293.15 and 313.15) K from June to August, and the average temperature is 308.15 K. The climate conditions in the region of Qaidam Basin are generally windy, arid, little rainfall, and great evaporating capacity.[1] From an approximate knowledge of the phase equilibrium composition, an appropriate quantity of salts and DDW were mixed together to produce a series of artificial synthesized brines. These were loaded into clean polyethylene containers (15 cm in diameter, 6 cm high), and then the containers were put into the box for isothermal evaporation at (308.15 ± 0.1) K. The experimental conditions were 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) $mm \cdot d^{-1}$. These conditions are similar to the climate of Qaidam Basin. The solutions were always kept in no stirring conditions to

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Table 1. Metastable Equilibrium Solubility for the Ternary System ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K

composition of liquid phase, 100*w*			composition of wet residue, 100*w*[a]				
$MgCl_2$	$MgSO_4$	H_2O	$MgCl_2$	$MgSO_4$	H_2O	n_D	equilibrium solid phase[c]
36.05	0.00	63.95	*b*				Bis
35.16	2.09	62.75	35.61	6.83	57.56		Bis
34.98	2.38	62.64					Bis
34.89	2.41	62.70				1.4367	Bis
34.40	3.36	62.24					Bis
34.35	3.31	62.34					Bis
34.31	3.34	62.35	35.67	5.75	58.58		Bis
33.98	3.95	62.07	34.53	7.76	57.71		Bis
33.80	3.86	62.34					Bis
33.73	4.39	61.88					Bis
33.39	4.57	62.04				1.4383	Bis
33.38	5.00	61.62					Bis
33.34	4.84	61.82					Bis
33.34	4.92	61.74				1.4377	Bis
33.33	5.12	61.55	35.02	5.42	59.56		Bis
33.31	4.72	61.97				1.4400	Bis
32.99	5.05	61.96				1.4370	Bis
32.78	5.66	61.56					Bis + Tet
32.59	5.26	62.15				1.4393	Tet
31.87	4.61	63.52					Tet
31.23	5.32	63.45				1.4321	Tet + Pen
30.92	5.12	63.96				1.4339	Pen
30.53	5.17	64.30				1.4325	Pen
30.16	5.16	64.68					Pen
29.83	5.18	64.99				1.4273	Pen
28.88	5.29	65.83					Pen
28.31	5.46	66.23					Pen
27.90	5.85	66.25					Pen
27.88	5.89	66.23				1.4262	Pen + Hex
26.02	6.22	67.76					Hex
25.91	6.54	67.55	12.50	30.69	56.81		Hex
25.88	6.32	67.80				1.4209	Hex
24.91	6.79	68.30					Hex
23.31	7.85	68.84					Hex
21.42	8.60	69.98					Hex
20.99	8.57	70.44	8.92	33.24	57.84		Hex
20.13	9.27	70.60				1.4107	Hex
19.94	9.29	70.77				1.4110	Hex
19.13	9.75	71.12					Hex + Eps
18.72	10.08	71.20					Eps
17.86	10.66	71.48					Eps
17.17	10.99	71.84					Eps
16.64	11.32	72.04					Eps
15.68	12.19	72.13					Eps
13.71	13.75	72.54				1.3961	Eps
12.35	14.97	72.68	5.33	34.38	60.29		Eps
11.68	15.46	72.86				1.3983	Eps
9.18	17.90	72.92					Eps
8.42	18.96	72.62				1.3948	Eps
0.00	29.82	70.18					Eps

[a] *w* = mass fraction; n_D = refractive index. [b] Not determined. [c] Eps, $MgSO_4 \cdot 7H_2O$, Hex, $MgSO_4 \cdot 6H_2O$; Pen, $MgSO_4 \cdot 5H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

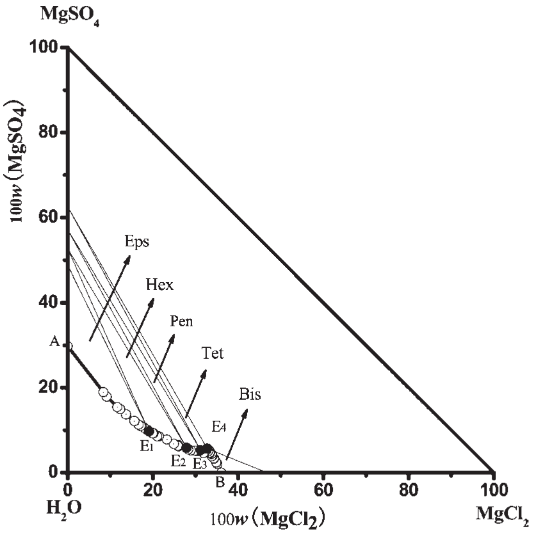

Figure 1. Metastable equilibrium phase diagram of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K. ⊙, experimental points; —, experimental isotherm curves; ●, experimental invariant points; Eps, $MgSO_4 \cdot 7H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Pen, $MgSO_4 \cdot 5H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

allow for metastable evaporation, and the crystal behavior of the solid phase was observed. When enough new solid phases appeared, the wet residue mixtures were taken out from the solution. Then the solid phase composition was determined by the wet residue method, observation of an oil-immersion by XP-300D digital polarizing microscopy, and further identification with X-ray diffraction. Meanwhile, a 5.0 cm^3 sample of the clarified solution was taken out from the liquid phase of each polyethylene container through a pipet and then diluted to a 250.0 cm^3 final volume in a volumetric flask with DDW for quantitative analysis of the composition of the liquid phase. Two drops of filtrate were used to measure the refractive index. The remainder of the solution continued to be evaporated and reached a new metastable equilibrium point.

Analytical Methods. All samples were analyzed in triplicate. The concentration of SO_4^{2-} in the liquid phase and the corresponding wet solid residue was analyzed by gravimetric methods of barium chloride with an uncertainty $\leq \pm 0.05$ %. The concentration of Cl^- ion was measured by titration with mercury nitrate standard solution in the presence of mixed indicator of diphenylcarbazone and bromphenol blue with an uncertainty $\leq \pm 0.3$ %, and the concentration of Mg^{2+} ion was evaluated using an ion balance and combined with an EDTA complexometric titration method in the presence of indicator of Eriochrome Black-T with an uncertainty $\leq \pm 0.3$ %.[6]

An Abbe refractometer (model WZS-1), which was conducted in a thermostat that electronically controlled the set temperature at (308.15 ± 0.1) K, was used for measuring the refractive index (n_D) in triplicate with an uncertainty within ± 0.0001.

RESULTS AND DISCUSSION

The experimental data on the metastable solubilities and the refractive index of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K are presented in Table 1. According to the experimental data in Table 1, the metastable equilibrium phase diagram of the ternary system and refractive index versus composition diagram at 308.15 K are shown in Figures 1 and 2. The compounds concentration values in the metastable equilibrium solution are expressed in weight percentage.

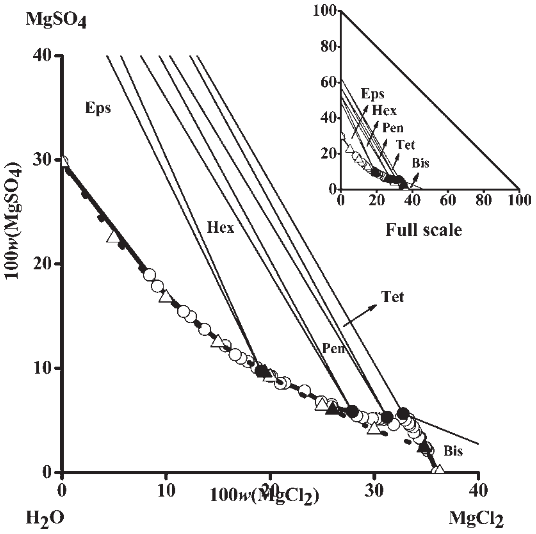

Figure 2. Metastable and stable equilibrium phase diagram of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K. ○, experimental points; ●, experimental cosaturated points; —, experimental isotherm curves; △, stable equilibrium points; ▲, stable cosaturated points; ..., stable isotherm curves; Eps, $MgSO_4 \cdot 7H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Pen, $MgSO_4 \cdot 5H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

According to the metastable phase diagram in Figure 1, there are five metastable crystallization regions corresponding to epsomite ($MgSO_4 \cdot 7H_2O$, Eps), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), pentahydrite ($MgSO_4 \cdot 5H_2O$, Pen), tetrahydrite ($MgSO_4 \cdot 4H_2O$, Tet), and bischofite ($MgCl_2 \cdot 6H_2O$, Bis). There are four isothermal invariant points corresponding to points E_1, E_2, E_3, and E_4, which are cosaturated with Eps + Hex, Hex + Pen, Pen + Tet, and Tet + Bis, respectively, and five isothermal evaporation curves (AE_1, E_1E_2, E_2E_3, E_3E_4, and E_4B), which are saturated with a single salt (Ep, Hex, Pen, Tet, and Bis). The crystallization area of Eps and Hex are relatively large, and the crystallization area of Pen and Tet are relatively small. The smallest crystallization area is Bis.

Nue et al has previously reported the solubility data of the stable system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K with the isothermal dissolution method, and the stable equilibrium time for this system in a closed boron glass jar, which was kept in continuous stirring, was at least nine months.[3] On the basis of the stable solubility data, the stable phase diagram plotted in Figure 2 shows that there are four stable crystallization fields of Bis, Tet, Hex, and Eps. Interestingly, although the presence of similar four stable crystallization fields in this ternary system at 323.15 K were presented by the method of isothermal dissolved equilibrium method, three metastable fields of Eps, Hex, and Tet had been found in the fields of the stable ones.[2]

A comparison of the solubility data of the metastable and the stable ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K is shown in Table 2. A comparison between the stable and metastable phase diagrams for the ternary system at 308.15 K shows that one more crystallization field of Pen ($MgSO_4 \cdot 5H_2O$) is found in the metastable system Moreover, it is worthy to point out that the concentration of magnesium sulfate in the cosaturation point of Bis and Tet in the metastble system increases by

Table 2. Comparison of the Solubility Data of Metastable and Stable System ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K

	composition of liquid phase, $100w$[a]				
	$MgCl_2$	$MgSO_4$	H_2O	equilibrium solid phase[b]	ref
metastable	36.05	0.00	63.95	Bis	this work
stable	36.10	0.00	63.90		3
metastable	32.78	5.66	61.56	Bis + Tet	this work
stable	34.80	2.40	62.80		3
stable	34.98	2.38	62.64	Tet + Hex	3
metastable	31.23	5.32	63.45	Tet + Pen	this work
metastable	27.88	5.89	66.23	Pen + Hex	this work
metastable	19.13	9.75	71.12	Hex + Eps	this work
stable	19.50	9.60	70.90		3
metastable	0.00	29.82	70.18	Eps	this work
stable	0.00	29.60	70.40		3

[a] w = mass fraction. [b] Eps, $MgSO_4 \cdot 7H_2O$, Hex, $MgSO_4 \cdot 6H_2O$; Pen, $MgSO_4 \cdot 5H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

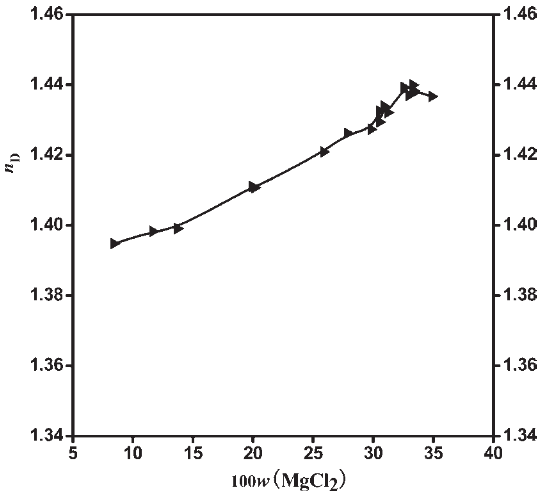

Figure 3. Diagram of the refractive index versus composition for the metastable ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K. ▲, experimental point; —, experimental curve.

Table 3. Pitzer Parameters in the System at 308.15 K

species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Θ_{Cl,SO_4}	Ψ_{Mg,Cl,SO_4}
$MgCl_2$	0.345458	1.69873		0.0548876	0.03	−0.0114584
$MgSO_4$	0.220933	3.71015	−35.2046	0.0246099		

2.36 times, and this result indicates that the metastable region of Tet is obvious in Figure 1 (data shown in Table 2).

Figure 3 is a diagram of refractive index versus magnesium chloride concentration in solution. It can be seen that the refractive index increases regularly with increasing magnesium chloride concentration.

■ SOLUBILITY PREDICTION

Pitzer and co-workers have developed an ion interaction model and published a series of papers[7,8] which gave a set of expressions for osmotic coefficients of the solution and mean activity coefficient of electrolytes in the solution. Expressions of the chemical equilibrium model (i.e., the extend HW model) for conventional single ion activity coefficients derived by HW[9,10] are more convenient to use in solubility calculations.

Table 4. Calculated Metastable Solubility of the Ternary System ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K

composition of liquid phase $100w$[a]			
$MgCl_2$	$MgSO_4$	H_2O	equilibrium solid phase
0.00	29.13	70.87	Eps
3.42	24.70	71.88	Eps
10.27	16.84	72.89	Eps
14.62	12.95	72.43	Eps
18.38	10.46	71.16	Eps + Hex
22.28	8.70	69.02	Hex
23.72	8.02	68.26	Hex
28.75	5.65	65.60	Hex + Pen
29.82	5.20	64.98	Pen
30.20	5.02	64.78	Pen
33.08	4.18	62.74	Pen + Tet
34.06	3.74	62.20	Bis + Tet
35.39	1.62	62.99	Bis
35.85	0.86	63.29	Bis
36.38	0.00	63.62	Bis

[a] w = mass fraction.

In Table 3, the values of the Pitzer single salt parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for $MgCl_2$ and $MgSO_4$ at 308.15 K have been calculated from the eq 1 for their temperature dependence.[11,12]

$$P(T) = a_1 + a_2 T + a_6 T^2 + a_9 T^3 + a_3/T + a_4 \ln T \qquad (1)$$

where $P(T)$ refers to the parameters of the solution model: the Pitzer single salt parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for $MgCl_2$ and $MgSO_4$; the values of the fitting constant terms of a_1, a_2, a_3, a_4, a_6, and a_9 were introduced.[11] The mixed ion-interaction parameters Θ_{ij} and Ψ_{ijk} at 308.15 K have been chosen using the assumptions of Pabalan and Pitzer of a temperature-independent value of Θ_{ij} and inverse proportion dependence of Ψ_{ijk} on temperature.[13]

$$\Psi_{ijk} = -0.1174 + 32.63/T(\mathrm{K}) \qquad (2)$$

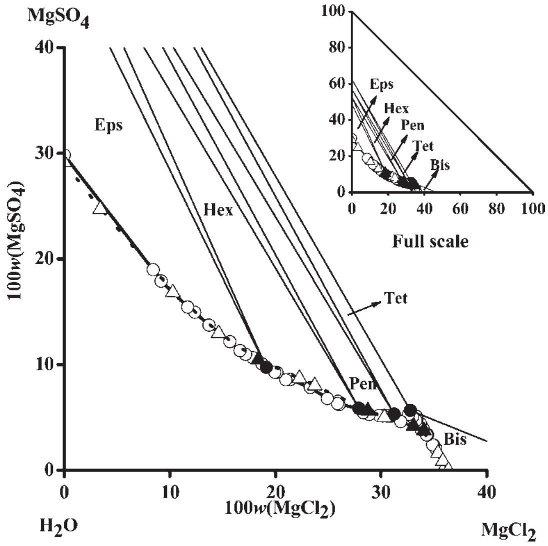

Figure 4. Calculated and experimental metastable equilibrium phase diagram of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K. ○, experimental points; ●, experimental cosaturated points; △, calculated points; ▲, calculated cosaturated points; —, experimental isotherm curves; ..., calculated isotherm curves; Eps, $MgSO_4 \cdot 7H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Pen, $MgSO_4 \cdot 5H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

where Ψ_{ijk} is linear with $1/T$ (K) as shown in Table 3. However, the value of Θ_{ij} is constant with temperature.[13] The value of the Debye−Hückel coefficient A^{φ} is 0.398535 at 308.15 K, which is calculated by using the equations for its temperature dependence.[4] The thermodynamic solubility products ln K for salts of Eps, Hex, Pen, Tet, and Bis crystallizing in the system at 308.15 K are calculated as 0.01634 ± 0.00002, 0.02449 ± 0.00002, 0.05618 ± 0.00002, 0.0172 ± 0.00005, and 30523 ± 0.5, respectively, using the experimental data in this work. Based on the Pitzer ion-interaction model and its extended HW model of electrolyte solutions, the solubilities of the ternary system at 308.15 K have been calculated, and are shown in Table 4 and Figure 4. It was also proved the metastable field of Pen exists in the metastable equilibrium system, and the metastable solubility of Pen is predicted successfully. When compared with the experimental data, the calculated data can be considered to be in good agreement with the experimental data at 308.15 K, although the calculated Eps solubilities are slightly lower and the calculated Bis solubilities are slightly higher. On the other hand, our further work demonstrates the extrapolation method of the solubilities in the supersaturated solution of $MgSO_4 \cdot xH_2O$ (x = 4, 5, 6, 7) at 308.15 K by Pabalan and Pitzer[13] is suitable for the salt-water metastable phase equilibrium system.

CONCLUSIONS

Metastable equilibria of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 308.15 K were studied with the isothermal evaporation method. Solubilities and the refractive index of solution were determined experimentally. The metastable solubilities of the system were calculated with the Pitzer ion-interaction model and its extended HW model of electrolyte solutions. According to the experimental and calculated data, the metastable equilibrium phase diagram and the refractive index versus composition diagram of the system were plotted. More comparisons of the metastable, stable and calculated results were also presented. Neither a solid solution nor double salts were found in the ternary system at 308.15 K.

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