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Stable Phase Equilibrium of the Aqueous Quaternary System ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) at 323.15 K

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ABSTRACT: The solubilities and relevant physicochemical properties including density and pH values of the aqueous quaternary system ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) at 323.15 K were determined for the first time with the method of isothermal dissolution. According to the experimental results, the dry-salt-phase diagram, water-phase diagram, and physicochemical properties versus composition diagrams were plotted. It was found that there are three three-salt cosaturated invariant points, seven univariant solubility isotherm curves, and five stable crystallization fields corresponding to bischofite ($MgCl_2 \cdot 6H_2O$, Bis), kieserite ($MgSO_4 \cdot H_2O$, Kie), tetrahydrite ($MgSO_4 \cdot 4H_2O$, Tet), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), and mcallisterite ($Mg(B_6O_7)(OH)_6 \cdot 4.5H_2O$, Mca). Neither solid solution nor double salts were found. On the basis of the extended Harvie−Weare (HW) model and its temperature-dependent equation, single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} for $MgCl_2$, $MgSO_4$, and $Mg(B_6O_7)(OH)_6$, mixed ion-interaction parameters θ_{Cl,SO_4}, $\theta_{Cl,B_6O_7(OH)_6}$, $\theta_{SO_4,B_6O_7(OH)_6}$, Ψ_{Mg,Cl,SO_4}, $\Psi_{Mg,Cl,B_6O_7(OH)_6}$, and $\Psi_{Mg,SO_4,B_6O_7(OH)_6}$, and the Debye−Hückel parameter A^{ϕ} at 323.15 K were obtained. In addition, the average equilibrium constants of stable equilibrium solids at 323.15 K were obtained with the method of the activity product constant. The prediction of solubilities of the quaternary system is then demonstrated. A comparison between the calculated and the experimental results shows that the predicted solubilities agree well with experimental data.

INTRODUCTION

The brines with high concentrations of magnesium and boron resources are widely distributed in the Qinghai-Tibet plateau.[1] These brines belong mostly to the complex system (Li + Na + K + Mg + Cl +SO_4 + borate + H_2O). It is well-known that the thermodynamic phase equilibrium and phase diagrams play an important role in exploiting the brine resources and describing the geochemical behavior of brine and mineral system. The investigation of the thermodynamics and phase diagram of the system is of theoretical and practical importance to predict the actual evaporation path of mineral crystallization for the separation and purification of the boron-containing mixture salts effectively. Although the literature has pointed out that the structure of boron ion of mcallisterite is $B_6O_7(OH)_6^{2-}$,[2] $B_6O_{10}^{2-}$ was used in this paper for convenience.

The quaternary system ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) is a subsystem of the seven-component system. Although the phase equilibrium of the systems containing $B_4O_7^{2-}$ over a wide temperature has been previously reported,[3−5] there are no reports in the literature concerning either the stable or metastable equilibrium of the systems containing $B_6O_{10}^{2-}$ except for ref 6 to describe the stable behaviors to separate and purify the boron-containing mixture salts. In this paper, the stable solubilities and the relevant physicochemical properties (densities and pH) of the quaternary system ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) at 323.15 K as well as the predicted solubilities using the Harvie−Weare (HW) solubility modeling approach which incorporates the Pitzer specific interaction formalism are presented.

EXPERIMENTAL SECTION

Apparatus and Reagents. A thermostatic shaker (model THZ-82) whose temperature can be controlled to ± 0.1 K was used for the measurement of phase equilibrium. When the solution temperature in the container was under (323.15 ± 0.1) K, the apparatus for controlling the temperature formed a circuit, and the heating apparatus began to heat with the temperature at 323.15 K. Therefore, the temperature in the thermostatic bath was always maintained at (323.15 ± 0.1) K. The solid phase minerals were identified using the Schreinemaker's method[7] and an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands).

The chemicals used were of analytical grade and were obtained from the Tianjin Kermel Chemical Reagent Manufactory: epsomite ($MgSO_4 \cdot 7H_2O$, $w = 0.990$ in mass fraction) and bischofite ($MgCl_2 \cdot 6H_2O$, $w = 0.990$), and were recrystallized before use. Mcallisterite ($MgB_6O_{10} \cdot 7.5H_2O$, $w = 0.990$) was synthesized in our laboratory with the method described in the literature.[8] Doubly deionized water (DDW) with a conductivity less than $1.2 \cdot 10^{-4}$ $S \cdot m^{-1}$ at 298.15 K was used to prepare the series of artificial synthesized brines and for chemical analysis.

Experimental Method. The isothermal dissolution method was used in this study. A series of complexes of the quaternary system were loaded into clean polyethylene bottles and capped tightly. The bottles were placed in the thermostatic rotary shaker, whose temperature was controlled to (323.15 ± 0.1) K and rotated at 120 rpm to accelerate the equilibrium of those complexes. A 5.0 mL sample of the clarified solution was taken from the liquid phase of each polyethylene bottle with a pipet at

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Table 1. Stable Equilibrium Solubility of the Quaternary System ($MgCl_2$ + $MgSO_4$ + MgB_6O_{10} + H_2O) at 323.15 K

	composition of the solution, 10^2 w^a			Jänecke index J_b/(g/100 g dry salt)				
no.	$MgSO_4$	MgB_4O_7	$MgCl_2$	$MgSO_4$	MgB_4O_7	$MgCl_2$	H_2O	equilibrium solid phase^b
1(E_1)	0.00	1.45	36.77	0.00	3.79	96.21	161.64	Bis + Mb
2	0.20	1.37	35.87	0.54	3.66	95.8	167.07	Bis + Mb
3	0.58	1.33	35.34	1.55	3.57	94.88	168.49	Bis + Mb
4(E)	0.99	1.26	34.62	2.68	3.41	93.91	171.26	Bis + Kie + Mb
5(E_2)	0.95	0.00	36.60	2.53	0.00	97.47	166.31	Bis + Kie
6	0.94	0.38	36.04	2.52	1.03	96.45	167.63	Bis + Kie
7	0.97	0.85	35.33	2.61	2.29	95.1	169.22	Bis + Kie
8	1.00	1.12	34.87	2.71	3.04	94.25	170.27	Bis + Kie
9	2.88	1.23	31.27	8.14	3.48	88.39	182.68	Kie + Mb
10	4.51	1.27	28.67	13.1	3.68	83.22	190.26	Kie + Mb
11	7.08	1.38	25.77	20.68	4.02	75.3	192.2	Kie + Mb
12(F)	9.68	1.38	22.86	28.53	4.07	67.4	194.84	Kie + Tet + Mb
13(E_3)	6.54	0.00	26.9	19.56	0.00	80.44	199.04	Kie + Tet
14	6.74	0.23	26.52	20.13	0.68	79.19	198.56	Kie + Tet
15	7.25	0.56	25.75	21.62	1.66	76.73	197.96	Kie + Tet
16	7.55	0.84	25.25	22.45	2.48	75.07	197.26	Kie + Tet
17	8.47	1.19	24.16	25.05	3.51	71.43	195.72	Kie + Tet
18	10.24	1.36	22.12	30.36	4.03	65.61	196.64	Tet + Mb
19	11.44	1.35	20.32	34.55	4.08	61.37	202.06	Tet + Mb
20(G)	12.14	1.29	18.72	37.76	4.03	58.21	210.99	Tet + Hex + Mb
21(E_4)	10.7	0.00	21.1	33.65	0.00	66.35	214.47	Tet + Hex
22	11.03	0.32	20.85	34.26	1.01	64.74	210.52	Tet + Hex
23	11.21	0.50	20.46	34.84	1.57	63.6	210.87	Tet + Hex
24	11.64	0.80	19.51	36.42	2.5	61.08	213	Tet + Hex
25	11.87	1.12	18.98	37.13	3.49	59.38	212.79	Tet + Hex
26(E_5)	33.22	1.83	0.00	94.78	5.22	0.00	185.31	Hex + Mb
27	27.79	1.74	4.09	82.67	5.16	12.17	197.49	Hex + Mb
28	22.63	1.65	8.50	69.03	5.04	25.93	204.99	Hex + Mb
29	18.31	1.56	12.58	56.41	4.82	38.77	208.11	Hex + Mb
30	15.66	1.50	15.18	48.42	4.63	46.95	209.27	Hex + Mb

[a] w = mass fraction. [b] Mca, $MgB_6O_{10}\cdot 7.5H_2O$; Bis, $MgCl_2\cdot 6H_2O$; Kie, $MgSO_4\cdot H_2O$; Tet, $MgSO_4\cdot 4H_2O$; Hex, $MgSO_4\cdot 6H_2O$.

regular intervals and diluted to a 250.0 mL final volume in a volumetric flask filled with DDW. If the compositions of the liquid phase in the bottle became constant, then equilibrium was achieved. Generally, it takes about 90 days to reach equilibrium.

After the equilibrium was achieved, the rotary system was allowed to rest for 1 h to separate the solid phase from the liquid phase before sampling. The liquid phases were taken out, and a quantitative analysis was performed. Some of the filtrate was used to measure the relative physicochemical properties. One part of the solids, which were taken from the solution, was evaluated by combined chemical analysis, determined by Schreinemaker's method of wet residues. The other part was dried, ground into powder, and then analyzed by X-ray diffraction.

Analytical Method. The concentration of Mg^{2+} was determined by titration with ethylenediaminetetraacetic acid standard solution in the presence of indicator of Eriochrome Black-T with a precision within ± 0.3 in mass fraction. The Cl^- ion concentration was measured by titration with a standard solution of $Hg(NO_3)_2$ with a precision of ± 0.3 % in mass fraction. The concentrations of $B_6O_{10}{}^{2-}$ were determined by basic titration in the presence of mannitol with a precision within ± 0.3 % in mass fraction.[9] $SO_4{}^{2-}$ was calculated by subtraction via charge balance. The densities (ρ) were measured by means of a density bottle with a precision of $\pm 0.2\ kg\cdot m^{-3}$. A PHS-3C precision pH meter (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 6.83) as well as potassium acid phthalate (pH 4.06). All of the measurements were maintained at (323.15 ± 0.1) K through control of the thermostat.

RESULTS AND DISCUSSION

The solubility data and the relevant physicochemical property data of the aqueous system ($MgCl_2$ + $MgSO_4$ + MgB_6O_{10} + H_2O) at 323.15 K are presented in Tables 1 and 2. On the basis of the Jänecke index (J_b, J_b/(kg/100 kg dry salt)) in Table 1, the dry-salt phase diagram and the water-phase diagram of the system at 323.15 K were plotted, as shown in Figures 1 and 2.

In Figure 1, the stable dry-salt phase diagram of the system at 323.15 K consists of five stable crystallization fields corresponding to bischofite ($MgCl_2\cdot 6H_2O$, Bis), kieserite ($MgSO_4\cdot H_2O$, Kie), tetrahydrite ($MgSO_4 \cdot 4H_2O$, Tet), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), and mcallisterite ($MgB_6O_{10} \cdot 7.5H_2O$, Mca). There are three invariant points E, F, and G, which are saturated with salts (Bis + Kie +Mca), (Kie + Tet +Mca), and (Tet + Hex +Mca), respectively, and seven univariant curves corresponding to E_1E (Bis + Mca), E_2F (Bis + Kie), EF (Kie + Mca), E_3F (Kie + Tet), FG (Tet + Mca), E_4G (Tet + Hex), and E_5G (Hex + Mca), indicating the cosaturation of two salts. The crystallization area of mcallisterite is the largest, and the crystallized zone of bischofite is the smallest. These results indicate that mcallisterite is easy to saturate and crystallize from solution and that bischofite has a high solubility. Neither solid solution nor double salts were found in the system.

Table 2. Physicochemical Properties of the Quaternary System ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) at 323.15 K

		density, $\rho/(10^3\ kg \cdot m^{-3})$		
no.	pH	experiments	calculation	relative error
1(E_1)	3.57	1.3620	1.3620	0.0000
2	3.92	1.3549	1.3536	−0.0010
3	4.20	1.3538	1.3522	−0.0012
4(E)	4.26	1.3465	1.3488	0.0017
5(E_2)	3.75	1.3578	1.3546	−0.0024
6	3.85	1.3568	1.3529	−0.0028
7	4.02	1.3578	1.3513	−0.0048
8	4.30	1.3468	1.3500	0.0024
9	4.52	1.3357	1.3364	0.0005
10	4.58	1.334	1.3298	−0.0032
11	4.69	1.3325	1.3333	0.0006
12(F)	4.82	1.3344	1.3358	0.0011
13(E_3)	3.91	1.3254	1.3214	−0.0030
14	4.21	1.3203	1.3227	0.0018
15	4.38	1.3263	1.3251	−0.0009
16	4.51	1.3271	1.3271	0.0000
17	4.70	1.3289	1.3317	0.0021
18	4.84	1.3375	1.3348	−0.0020
19	4.98	1.3348	1.3307	−0.0030
20(G)	5.12	1.3249	1.3216	−0.0025
21(E_4)	4.25	1.3132	1.3127	−0.0004
22	4.31	1.3204	1.3183	−0.0016
23	4.45	1.3142	1.3186	0.0034
24	4.80	1.3171	1.3176	0.0004
25	4.95	1.3196	1.3188	−0.0006
26(E_5)	5.89	1.4019	1.4045	0.0019
27	5.58	1.3758	1.3686	−0.0053
28	5.43	1.3543	1.3531	−0.0009
29	5.32	1.3384	1.3394	0.0007
30	5.27	1.3294	1.3320	0.0020

The water phase diagram of the quaternary system at 323.15 K is shown in Figure 2. It shows that the Jänecke index values of $J(H_2O)$ gradually change with increasing $J(MgSO_4)$. At the invariant point E_1, the Jänecke index of $J(H_2O)$ is the smallest, while at point E_4, the Jänecke index is the largest indicating the solubility of different salts.

On the basis of experimental data in Table 2, relationships between the solution physicochemical properties (density and pH) and the Jänecke index values of $J(MgSO_4)$ are shown in Figure 3. The physicochemical properties of the stable equilibrium solution vary regularly with $J(MgSO_4)$.

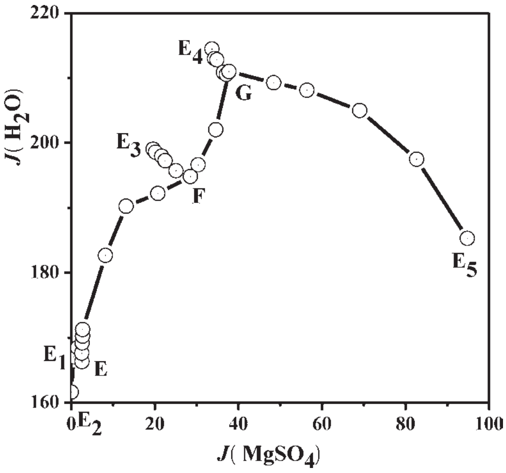


Figure 2. Water-phase diagram of the quaternary system ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) at 323.15 K.○, solubility data in this work; —, experimental water-phase isotherm curve.

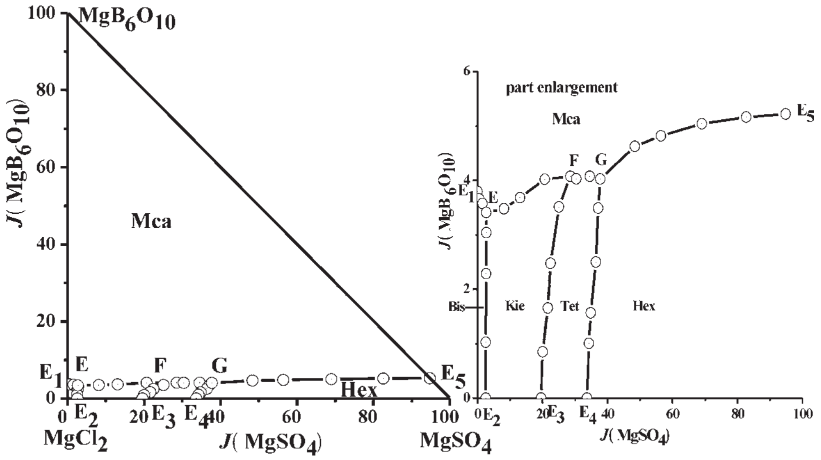
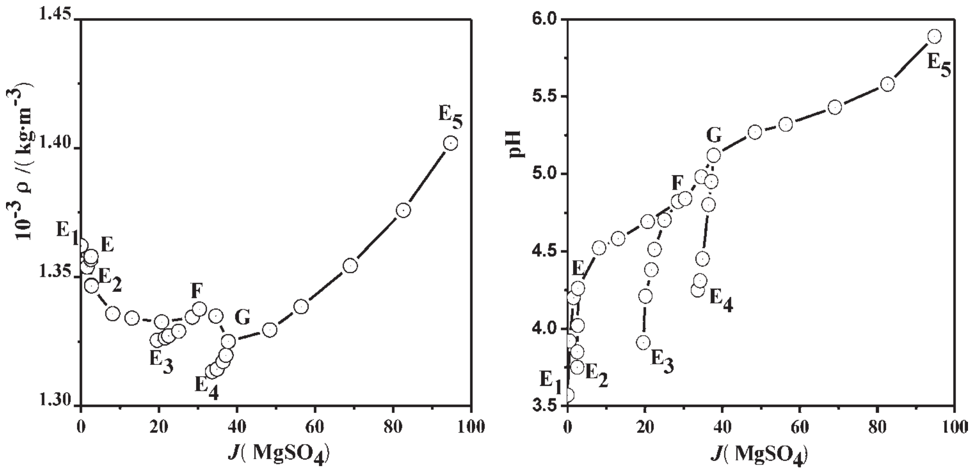


Figure 1. Dry-salt phase diagram of the quaternary system ($MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O$) at 323.15 K; ○, solubility data in this work; —, experimental stable isotherm curve; Mca, $MgB_6O_{10} \cdot 7.5H_2O$; Bis, $MgCl_2 \cdot 6H_2O$; Kie, $MgSO_4 \cdot H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Hex, $MgSO_4 \cdot 6H_2O$.



(a) density vs. composition (b) pH vs. composition

Figure 3. Physicochemical properties versus composition diagrams of the stable quaternary system $(MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O)$ at 323.15 K. ○, solubility data in this work; —, experimental water-phase isotherm curve; (a) density vs composition; (b) pH vs composition.

■ EMPIRICAL EQUATIONS FOR DENSITY

On the basis of the following empirical equation of the density in electrolyte solutions developed in the previous study,[10] the density of the solution was calculated.

$$\ln(d/d_0) = \sum A_i \cdot W_i$$

where $d_0 = 0.9880382 \cdot 10^3\ \mathrm{kg}^3 \cdot \mathrm{m}^{-3}$, the density of the water at 323.15 K; A_i is the constant of each possible component i in the system, and it 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 of $MgCl_2$, $MgSO_4$, and MgB_6O_{10} for the calculation of density are 0.00835947, 0.0100689, and 0.00942266. The calculated results and experimental values are presented in Table 2 for comparison, and all of the calculated results with the maximum relative error are less than 0.53 %.

■ SOLUBILITY PREDICTION

Ion-Interaction Model. Pitzer and co-workers have developed an ion-interaction model and published a series of papers,[11,12] which gave a set of expressions for the osmotic coefficients of the solution and mean activity coefficient of electrolytes in the solution. Single ion activity coefficients, which are more convenient to use in solubility calculations, are given in the HW modeling approach.[13,14] 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.[15−17] The following equations are the main expressions related to the solubility calculation of this model:

$$\begin{aligned}(\phi - 1) = {} & (2/\sum_i m_i)[-A^{\phi}I^{3/2}/(1 + bI^{1/2}) \\ & + \sum_c \sum_a m_c m_a (B^{\phi}_{ca} + ZC_{ca}) \\ & + \sum_c \sum_{<c'} m_c m_{c'} (\Phi^{\phi}_{cc'} + \sum_a m_a \Psi_{cc'a}) \\ & + \sum_a \sum_{<a'} m_a m_{a'} (\Phi^{\phi}_{aa'} + \sum_c m_c \Psi_{caa'})] \qquad (1)\end{aligned}$$

$$\begin{aligned}\ln \gamma_M = {} & ZM^2F + \sum_a m_a(2B_{Ma} + ZC_{Ma}) \\ & + \sum_c m_c(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca}) \\ & + \sum_a \sum_{<a'} m_a m_{a'} \Psi_{Maa'} + Z_M \sum_c \sum_a m_c m_a C_{ca} \qquad (2)\end{aligned}$$

$$\begin{aligned}\ln \gamma_X = {} & ZX^2F + \sum_c m_c(2B_{cX} + ZC_{cX}) \\ & + \sum_a m_a(2\Phi_{Xa} + \sum_c m_c \Psi_{cXa}) \\ & + \sum_c \sum_{<c'} m_c m_{c'} \Psi_{cc'X} + |Z_X| \sum_c \sum_a m_c m_a C_{ca} \qquad (3)\end{aligned}$$

From eqs 1 to 3, M, C, and C' refer to cations, X, A, and A' refer to anions, N_c and N_a are referred to the number of cationics and anions, respectively. m_i and γ_i represent the concentration $(\mathrm{mol} \cdot \mathrm{kg}^{-1})$ and activity coefficient of the ions, respectively; Z_i refer to the valence of ions, and ϕ refers to the permeability coefficient. The other symbols from eqs 1 to 3, for example, F, C, Z, A^{ϕ}, Ψ, Φ, B^{ϕ}, and B could be obtained through some other references.[12,13]

Solubility equilibrium constants are used to calculate solubility; that is, a salt solution is saturated at a given temperature and pressure when the ion activity product is equal to the solubility equilibrium constant. For a hydrated salt $M_{\upsilon_M}X_{\upsilon_X} \cdot \upsilon_0\ H_2O$, the solubility equilibrium constant (K_{sp}) at a definite temperature and pressure for the dissolution reaction is expressed as following:

$$M_{\upsilon_M}X_{\upsilon_X} \cdot \upsilon_0 H_2O = \upsilon_M M^{+ZM} + \upsilon_X X^{-ZX} + \upsilon_0 H_2O \qquad (4)$$

$$\ln K_{sp} = \upsilon_M \ln(m_M \gamma_M) + \upsilon_X \ln(m_X \gamma_X) + \upsilon_0 \ln \alpha_w \qquad (5)$$

The activity of water is related to the osmotic coefficient ϕ, by the equation

$$\ln \alpha_w = -\phi(M_w/1000) \sum m_i \qquad (6)$$

where M_w is the molar mass of water and the sum covers all solute species. The activity coefficients, $\ln \gamma_i$, and the osmotic coefficients, ϕ, can be calculated using the Pitzer and its extended HW model.

Table 3. Single-Salt and Mixing Ion-Interaction Parameters of the Quaternary System $(MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O)$ at 323.15 K

species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{(\phi)}$	θ	Ψ	ref.
$MgCl_2$	0.337022	1.781700		0.0040144			17
$MgSO_4$	0.227487	3.614270	−40.26254	0.0197609	0.030000	−0.016425	17
$Mg(B_6O_7)(OH)_6$	−2.778218	5.622242	−71.621713	−0.158604	1.534600	0.0726886	this work
Cl^-, SO_4^{2-}					0.788038	−0.161438	17
Cl^-, $(B_6O_7)(OH)_6^{2-}$							this work
SO_4^{2-}, $(B_6O_7)(OH)_6^{2-}$							this work
Mg^{2+}, Cl^-, SO_4^{2-}							17
Mg^{2+}, Cl^-, $(B_6O_7)(OH)_6^{2-}$							this work
Mg^{2+}, SO_4^{2-}, $(B_6O_7)(OH)_6^{2-}$							this work

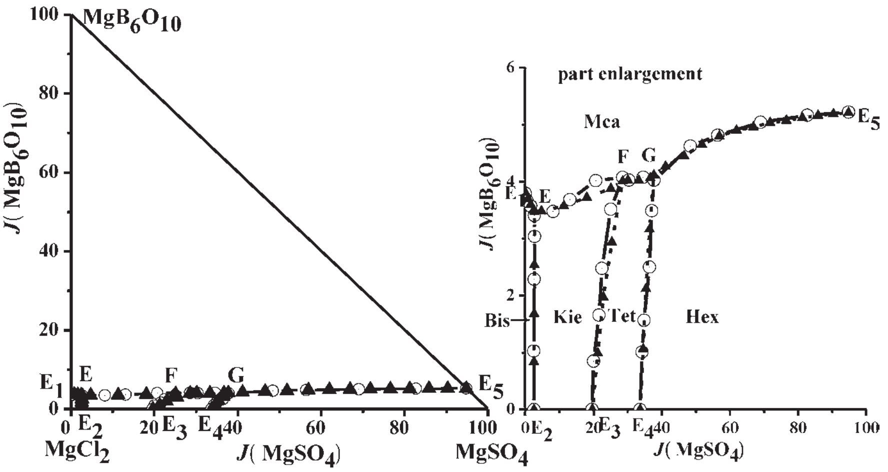


Figure 4. Comparison of the experimental and calculated phase diagram of the stable quaternary system $(MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O)$ at 323.15 K; ○, Experimental data; ▲, calculated data; —, experimental isotherm curve; · · ·, calculated isotherm curve; Mca, $MgB_6O_{10}\cdot 7.5H_2O$; Bis, $MgCl_2\cdot 6H_2O$; Kie, $MgSO_4\cdot H_2O$; Tet, $MgSO_4\cdot 4H_2O$; Hex, $MgSO_4\cdot 6H_2O$.

According to the Pitzer and its extended HW models, the activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}, and $\theta_{cc'}$; $\psi_{cc'a}$, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} are the parameters of a single salt, $\theta_{cc'}$ represents the interaction of the two ions with the same sign, and $\psi_{cc'a}$ represents the interactions among the three ions, in which the sign of the third one is different from the first two ions. The solubility of the quaternary system $(MgCl_2 + MgSO_4 + MgB_6O_{10} + H_2O)$ at $T = 323.15$ K could be calculated from eqs 1 to 6, when the Pitzer parameters and K_{sp} of the system are all known.

Model Parameterization. A high-temperature thermochemical model for the system $(Na + K + Mg + Cl + SO_4 + OH + H_2O)$ was presented by Pabalan et al., including a range of temperature for the model.[17] The single-slat parameters of $MgCl_2$ and $MgSO_4$, the mixing parameters θ_{C1,SO_4}, Ψ_{Mg,Cl,SO_4}, and Debye−Hückel parameter $A^{\phi} = 0.410330$ at 323.15 K were fitted in this paper based on the temperature-dependent equations presented in the literature.[16,17] The binary parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} of $Mg(B_6O_7)(OH)_6$ and the mixing parameters $\theta_{C1,B_6O_7\,(OH)_6}$, $\theta_{SO_4,B_6O_7(OH)_6}$, $\Psi_{Mg,Cl,B_6O_7(OH)_6}$, and $\Psi_{Mg,SO_4,B_6O_7(OH)_6}$ were available by a multiple linear regression procedure applied to the solubility data of the corresponding ternary systems in this work. All of the parameters used in the prediction are presented in Table 3. According to the parameters and the experimental solubilities of the quaternary system in this work, the average equilibrium constants of minerals that exist in the quaternary system at 323.15 K were fitted with the method of the activity product constant in each stable solution. These equilibrium constants ($\ln K_{aver}$) of equilibrium solid salts of $MgCl_2\cdot 6H_2O$, $MgSO_4\cdot H_2O$, $MgSO_4\cdot 4H_2O$, $MgSO_4\cdot 6H_2O$, and $Mg(B_6O_7)(OH)_6\cdot 4.5H_2O$ correspond to 9.834155, 0.136714, −2.412904, −3.729904, and −9.419733, respectively.

Calculated Solubility. To determine the accuracy of the parameters and the solubility equilibrium constants of the solids, the solubilities of the quaternary system at 323.15 K have been calculated based on the Pitzer ion-interaction model and the extended HW models for aqueous electrolyte solutions. It should be noted that solutes below their saturated solution molalities were fixed at some continuous values and the saturated solutes' solubilities were calculated. The phase diagrams according to the experimental and calculated data were constructed in Figure 4. It is shown that the calculated phase diagram and the experimental one are in good agreement, although there are slight deviations for the solubility curve EF (Kie + Mca). Generally, these results indicate that the Pitzer parameters and the equilibrium constants obtained in this work are reliable.

■ CONCLUSION

The experimental solubility data and the relevant physicochemical property data of the aqueous quaternary system

($MgCl_2$ + $MgSO_4$ + MgB_6O_{10} + H_2O) at 323.15 K were determined. The experimental stable phase diagrams and the variation of the physicochemical properties with composition were constructed for the first time. On the basis of the extended HW model and its temperature-dependent equation, the single-salt Pitzer parameters, mixed ion-interaction parameters, and the Debye−Hückel parameter A^{ϕ} were fitted. Using the average equilibrium constants of equilibrium solids, the solubilities of the quaternary system were calculated. A comparison of the experimental and calculated solubilities shows that the predictive data obtained with the extended HW model agree well with experimental results.

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REFERENCES

(1) Zheng, X. Y.; Tang, Y.; Xu, C. *Tibet Saline Lake*; Science Press: Beijing, 1988; p 169 (in Chinese).

(2) Li, J.; Gao, S. Y. Chemistry of borates. *J. Salt Lake Res. (China)* **1993**, *1* (3), 62–67.

(3) Deng, T. L. Phase equilibrium for the aqueous system containing Lithium, sodium, potassium, chloride, and borate ions at 298.15 K. *J. Chem. Eng. Data* **2004**, *49* (5), 1295–1299.

(4) Deng, T. L.; Wang, S. Q.; Sun, B. Metastable phase equilibrium in the aqueous quaternary system (KCl + K_2SO_4 + $K_2B_4O_7$ + H_2O) at 308.15 K. *J. Chem. Eng. Data* **2008**, *53* (2), 411–414.

(5) Deng, T. L.; Meng, L. Z.; Sun, B. Metastable phase equilibria of the reciprocal quaternary system containing sodium, potassium, chloride, and sulfate Ions at 308.15 K. *J. Chem. Eng. Data* **2008**, *53* (3), 704–709.

(6) Bi, W. B.; Sun, B.; Song, P. S.; et al. Study on phase diagram of Mg^{2+}/Cl^{-}, borate-H_2O ternary system at 25 °C. *J. Salt Lake Res. (China)* **1997**, *5*, 42–46.

(7) Song, P. S. Studies on the application of the wet residues method in phase equilibrium for the salt-water systems. *J. Salt Lake Res. (China)* **1991**, *1*, 42–46.

(8) Meng, L. Z.; Deng, T. L.; Duan, C. W.; et al. A synthesis method for mcallisterite. *World Sci-Tech Res. Dev. (China)* **2010**, *32* (6), 825–826.

(9) Qinghai Institute of Salt Lakes, Chinese Academy of Science. *Analytical methods of brines and salts*, 2nd ed.; Chinese Science Press: Beijing, 1988; pp 47−66.

(10) Song, P. S.; Du, X. H. Phase equilibrium and properties of the saturated solution in the quaternary system $Li_2B_4O_7$-Li_2SO_4-LiCl-H_2O at 25 °C. *Chin. Sci. Bull. (China)* **1986**, *3*, 209–213.

(11) Pitzer, K. S. Thermodynamics of electrolytes I: theoretical general equation. *J. Phys. Chem.* **1973**, *77*, 268–277.

(12) Pitzer, K. S. *Semi-empirical equations for pure and mixed electrolytes. Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1995; pp 290−321.

(13) Harvie, C. E.; Weare, J. H. The prediction of mineral solubilties in nature waters: the Na-K-Mg-Cl-SO_4-H_2O system from zero to high concentration at 25 °C. *Geochim. Cosmochim. Acta* **1980**, *44*, 981–997.

(14) Harvie, C. E.; Møller, N.; Weare, J. H. The prediction of mineral solubilities in nature waters: the Na-K-Mg-Ca-H-SO_4-OH-HCO_3-CO_3-H_2O system to high ionic strengths at 25 °C. *Geochim. Cosmochim. Acta* **1984**, *48*, 723–751.

(15) Greenberg, J. P.; Møller, N. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO_4-H_2O system to high concentration from 0 to 250 °C. *Geochim. Cosmochim. Acta* **1989**, *53*, 2503–2518.

(16) Møller, N. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO_4-H_2O system to high temperature and concentration. *Geochim. Cosmochim. Acta* **1988**, *52*, 821–837.

(17) Pabalan, R. T.; Pitzer, K. S. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO_4-OH-H_2O. *Geochim. Cosmochim. Acta* **1987**, *51*, 2429–2443.