

SOLID-LIQUID STABLE PHASE EQUILIBRIA OF THE TERNARY SYSTEMS $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ AND $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ AT 308.15 K

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Abstract - The solubilities and the relevant physicochemical properties of the ternary systems $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K were investigated using an isothermal dissolution method. It was found that there is one invariant point, two univariant curves, and two crystallization regions of the systems. The systems belong to a simple co-saturated type, and neither double salts nor solid solutions were found. Based on the extended HW model and its temperature-dependent equations, the single-salt Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^θ for MgCl_2 , MgSO_4 , and $\text{Mg}(\text{B}_6\text{O}_7)(\text{OH})_6$, the mixed ion-interaction parameters $\theta_{\text{Cl},\text{B}_6\text{O}_{10}}$, $\theta_{\text{SO}_4,\text{B}_6\text{O}_{10}}$, $\Psi_{\text{Mg},\text{Cl},\text{B}_6\text{O}_{10}}$, $\Psi_{\text{Mg},\text{SO}_4,\text{B}_6\text{O}_{10}}$ of the systems at 308.15 K were fitted. In addition, the average equilibrium constants of the stable equilibrium solids at 308.15 K were obtained by a method using the activity product constant. Then the solubilities of the ternary systems are calculated. The calculated solubilities agree well with the experimental values.

Keywords: Phase equilibrium; Phase diagram; Solubility; Pitzer modeling; Mcallisterite.

INTRODUCTION

There are more than one thousand salt lakes in China, and a number of salt lakes with an abundance of lithium and boron resources are widely distributed in the Qaidam Basin of Qinghai-Tibet Plateau, China (Zheng *et al.*, 1988). These brines belong mostly to the complex system $\text{Li} + \text{Na} + \text{K} + \text{Mg} + \text{Cl} + \text{SO}_4 + \text{borate} + \text{H}_2\text{O}$. It is well known that the thermodynamic phase equilibria and phase diagrams play an important role in exploiting the brine resources and describing the geochemical behavior of the brine and mineral system. Therefore, simulative experimental studies on stable phase equilibria containing magnesium and boron are essential for predicting the path of mineral crystallization for the effective separation and purification of the boron-containing mixture

salt effectively. Although it has been pointed out that the structure of boron ion of mcallisterite is $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$, $\text{B}_6\text{O}_{10}^{2-}$ is used in this paper for convenience (Li and Gao, 1993).

The ternary systems $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ are subsystems of the seven-component system. Although the stable phase equilibrium of the system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 298.15 K and 323.15 K, the system $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 323.15 K, and the system $\text{MgCl}_2 + \text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 323.15 K have been reported (Bi *et al.*, 1997; Meng *et al.*, 2012; Meng *et al.*, 2011), the stable phase equilibria of the ternary systems $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K are not reported in the literature. In this paper, the stable solubilities and the relevant physicochemical properties (densities and

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pH) of the ternary systems $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 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 equilibria. When the solution temperature in the container was under (308.15 ± 0.1) K, the apparatus for controlling the temperature formed a circuit, and the heating apparatus began to heat with temperature at 308.15 K. Conversely, the circuit was broken, and the heating apparatus stopped working. Therefore, the temperature in the thermostatic shaker was always maintained at (308.15 ± 0.1) K. The solid phase minerals were identified using Schreinemaker's method (Song, 1991) 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. [epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.99 by mass fraction), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.99 by mass fraction)], and were recrystallized before use. Mcallisterite ($\text{MgB}_6\text{O}_{10} \cdot 7.5\text{H}_2\text{O}$, 0.99 by mass fraction) was synthesized in our laboratory with the method described in the literature (Meng *et al.*, 2010). Doubly deionized water (DDW) with conductivity less than $1.2 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ at 298.15 K was used to prepare the series of artificial synthesized brines and for chemical analysis.

Experimental Methods

The isothermal dissolution method was used in this study. The series of complexes of the ternary systems were loaded into clean polyethylene bottles and capped tightly. The bottles were placed in the thermostatic rotary shaker, whose temperature was controlled to (308.15 ± 0.1) K, and rotated at 120 rpm to accelerate the equilibration of those complexes. The rotary system rested for 2 h before sampling, and a 1.0 mL sample of the clarified solution was taken from each polyethylene bottle with a pipette at regular intervals and then used for a refractive index measurement. If the difference between two refractive index measurements was within ± 0.0002 , then the equilibrium state was assumed. Otherwise, the solution was rotated continually until

the equilibrium state was achieved. Generally, it took approximately 90 days to reach the equilibrium state. Twice, at different times, a sample of approximately 5.0 mL was taken, weighed and diluted to a final volume of 250 mL using a volumetric flask filled with DDW. Then, a quantitative analysis was performed. If the difference between the compositions of the two liquid phases was within $\pm 0.3\%$ in mass fraction, then the solubility of this equilibrium point, which was the average of the experimental data, was obtained. Some other solution samples were taken to determine the physicochemical properties. Meanwhile, some of the wet residue was separated from the solution, and one portion of the wet residue was weighed and dissolved to a final volume of 250 mL using a volumetric flask filled with DDW for chemical analysis by Schreinemaker's wet residue method (i.e., the solid phase mineral point lies on the extension of the line on the phase diagram through the composition points of the liquid phase and the wet residue) (Song, 1991). Another portion was dried, ground into powder and analysed by X-ray diffraction. The solid phase could then be identified.

Analytical Methods

The solid phases were analyzed by Schreinemaker's method and X-ray diffraction; magnesium borate in the two systems is mcallisterite ($\text{MgB}_6\text{O}_{10} \cdot 7.5\text{H}_2\text{O}$). It shows that mcallisterite is not converted, so $\text{B}_6\text{O}_{10}^{2-}$ can be used to express the boron ions in the aqueous and solid phases. The Mg^{2+} ion concentration was determined by titration with EDTA standard solution in the presence of the indicator Eriochrome Black-T. The average deviation of the determination was less than $\pm 0.3\%$ (by mass). For the ternary system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$, the Cl^- ion concentration was determined by titration with a standard solution of $\text{Hg}(\text{NO}_3)_2$ (uncertainty $\pm 0.3\%$) and the concentration of $\text{B}_6\text{O}_{10}^{2-}$ was evaluated using an ion balance (Zhai *et al.*, 1988). For the ternary system $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$, the concentrations of $\text{B}_6\text{O}_{10}^{2-}$ were determined by basic titration in the presence of mannitol (uncertainty $\pm 0.3\%$) and SO_4^{2-} was calculated by subtraction via charge balance (Zhai *et al.*, 1988). The densities (ρ) were measured by means of a pyknometer with a precision of $\pm 0.2 \times 10^{-6} \text{ kg} \cdot \text{m}^{-3}$. 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 a mixed phosphate of potassium dihydrogen phosphate and sodium dihydrogen phosphate (pH = 6.84), as well as potassium acid phthalate (pH = 4.02). All the

measurements were maintained at (308.15 ± 0.1) K through control of the thermostat.

RESULTS AND DISCUSSION

The solubility data and the relevant physicochemical property data of the aqueous systems $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K are presented in Tables 1 and 2. The ionic composition in the equilibrium solution of the isothermal dissolution is expressed as mass fraction. Using the experimental results in Tables 1 and 2, the phase diagrams of these systems at 308.15 K were plotted, as shown in Figures 1 and 2. Both of

the phase diagrams of the ternary systems in Figures 1 and 2 consist of one invariant point, two univariant curves and two crystallization fields. In Figure 1, the point labeled E is invariant for bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and mcallisterite ($\text{MgB}_6\text{O}_{10} \cdot 7.5\text{H}_2\text{O}$), and the compositions of MgCl_2 , $\text{MgB}_6\text{O}_{10}$ in the liquid phase with mass fraction ($w_b \times 10^2$) are 36.00 and 0.77, respectively. In Figure 2, the point labeled E is invariant for epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and mcallisterite ($\text{MgB}_6\text{O}_{10} \cdot 7.5\text{H}_2\text{O}$), and the compositions of MgSO_4 , $\text{MgB}_6\text{O}_{10}$ in the liquid phase with mass fraction ($w_b \times 10^2$) are 29.29 and 1.33, respectively. Both of the ternary systems belong to a simple eutectic type, and neither double salts nor solid solutions were found.

Table 1: Solubility and physicochemical property data of the ternary system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K.

No.	Liquid phase, $10^2 w_b$		Wet residue, $10^2 w_b$		Density $10^{-3} \rho / (\text{kg} \cdot \text{m}^{-3})$	pH	Equilibrium solid phase ^a
	MgCl_2	$\text{MgB}_6\text{O}_{10}$	MgCl_2	$\text{MgB}_6\text{O}_{10}$			
1, A	0.00	2.88	— ^b	—	1.0129	6.97	Mb
2	2.51	2.60	—	—	1.0244	6.85	Mb
3	5.31	2.27	2.90	28.52	1.0397	6.70	Mb
4	7.32	2.05	—	—	1.0561	6.64	Mb
5	9.93	1.78	—	—	1.0805	6.57	Mb
6	15.02	1.35	8.75	26.76	1.1196	6.24	Mb
7	19.88	1.14	—	—	1.1680	5.73	Mb
8	25.93	0.96	—	—	1.2190	5.18	Mb
9	29.30	0.89	18.17	25.16	1.2586	4.59	Mb
10	33.80	0.82	—	—	1.3087	3.96	Mb
11, E	36.00	0.77	41.54	4.06	1.3388	3.71	Mb + Bis
12	36.03	0.58	—	—	1.3375	3.84	Bis
13	36.04	0.32	42.85	0.12	1.3361	3.71	Bis
14	36.03	0.19	—	—	1.3370	3.25	Bis
15, B	36.14	0.00	—	—	1.3365	3.21	Bis

^a Mb, $\text{MgB}_6\text{O}_{10} \cdot 7.5\text{H}_2\text{O}$; Bis, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; ^b —, means not detected.

Table 2: Solubility and physicochemical property data of the ternary system $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K.

No.	Liquid phase, $10^2 w_b$		Wet residue, $10^2 w_b$		Density $10^{-3} \rho / (\text{kg} \cdot \text{m}^{-3})$	pH	Equilibrium solid phase ^a
	MgSO_4	$\text{MgB}_6\text{O}_{10}$	MgSO_4	$\text{MgB}_6\text{O}_{10}$			
1, A	0.00	2.88	— ^b	—	1.0129	6.97	Mb
2	4.95	2.75	3.34	21.75	1.0580	6.31	Mb
3	10.37	2.62	—	—	1.1208	6.67	Mb
4	16.08	2.38	11.39	20.43	1.1792	6.53	Mb
5	20.63	2.06	—	—	1.2380	6.40	Mb
6	23.51	1.86	15.04	24.78	1.2753	6.32	Mb
7	26.37	1.66	—	—	1.3068	6.17	Mb
8	28.14	1.50	—	—	1.3283	6.12	Mb + Eps
9, E	29.29	1.33	35.86	6.75	1.3386	6.07	Eps
10	29.21	1.04	—	—	1.3370	6.02	Eps
11	29.26	0.47	36.15	0.30	1.3348	5.98	Eps
12, B	29.40	0.00	—	—	1.3320	5.92	Eps

^a Mb, $\text{MgB}_6\text{O}_{10} \cdot 7.5\text{H}_2\text{O}$; Hex, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; ^b —, means not detected.

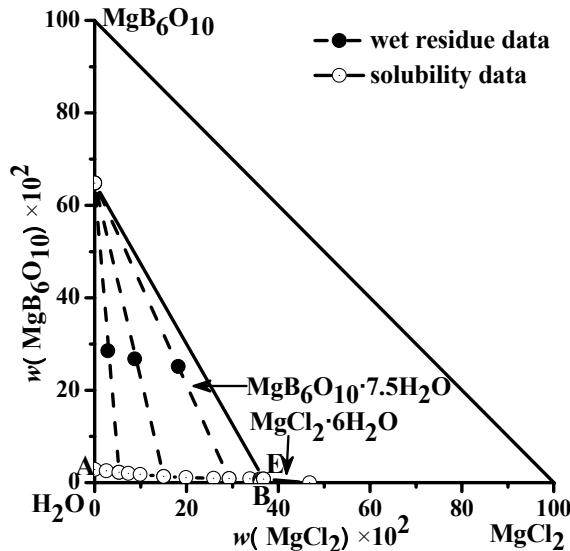


Figure 1: Stable equilibrium phase diagram of the ternary system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K; \circ , experimental solubility data; —, experimental stable isotherm curve; ●, wet residue data; ..., wet residue curve.

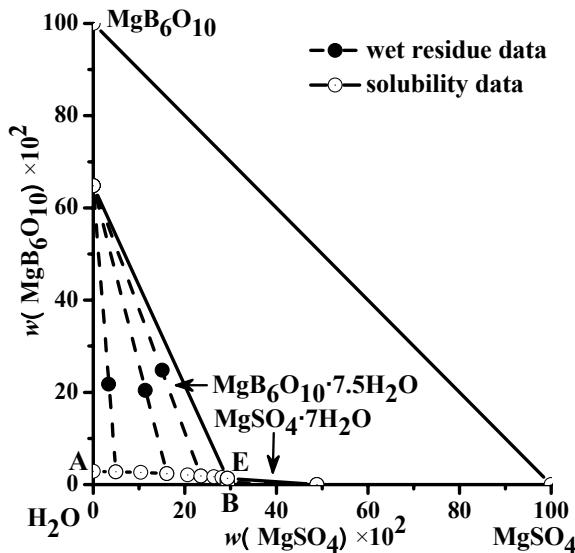


Figure 2: Stable equilibrium phase diagram of the ternary system $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at $T = 308.15$ K; \circ , experimental solubility data; —, experimental stable isotherm curve; ●, wet residue data; ..., wet residue curve.

Using the experimental results in Tables 1 and 2, the relationships of the solution physicochemical properties (densities and pH) with mass fraction of magnesium chloride or magnesium sulfate are

plotted in Figures 3 and 4. It was found that the solution densities of the ternary systems were changed regularly with the increase of mass fraction of magnesium chloride or magnesium sulfate and reached the maximum value at the invariant, while the pH values of the stable equilibrium aqueous solution generally decreased gradually with increasing magnesium chloride or magnesium sulfate concentration, because the solution with magnesium chloride or magnesium sulfate is acidic and the pH values will decrease with increasing concentration. Using the diagrams (Figures 3 and 4), the physicochemical properties (density and refractive index) could be used to roughly estimate the magnesium concentration in the ternary system.

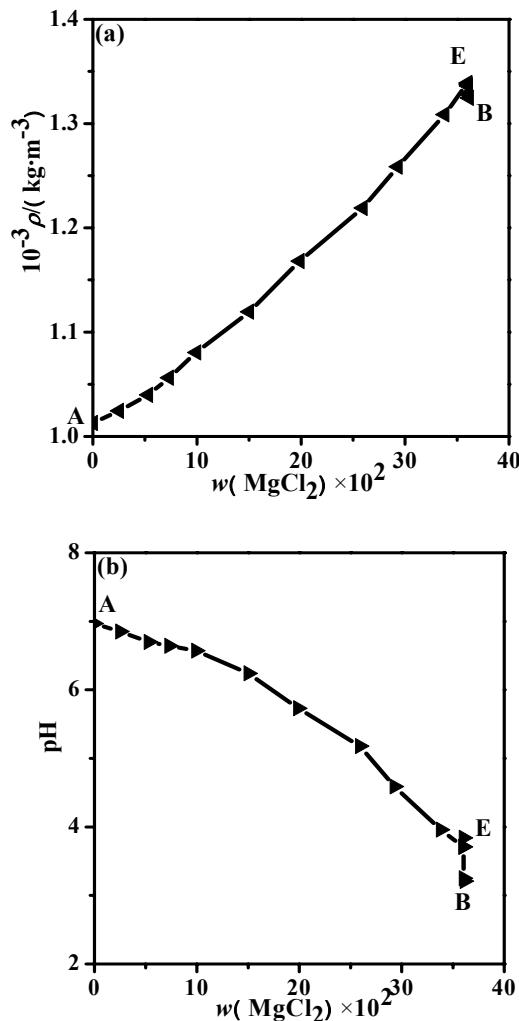


Figure 3: Physicochemical properties versus composition of the ternary system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K. (a) density vs. composition; (b) pH vs. composition.

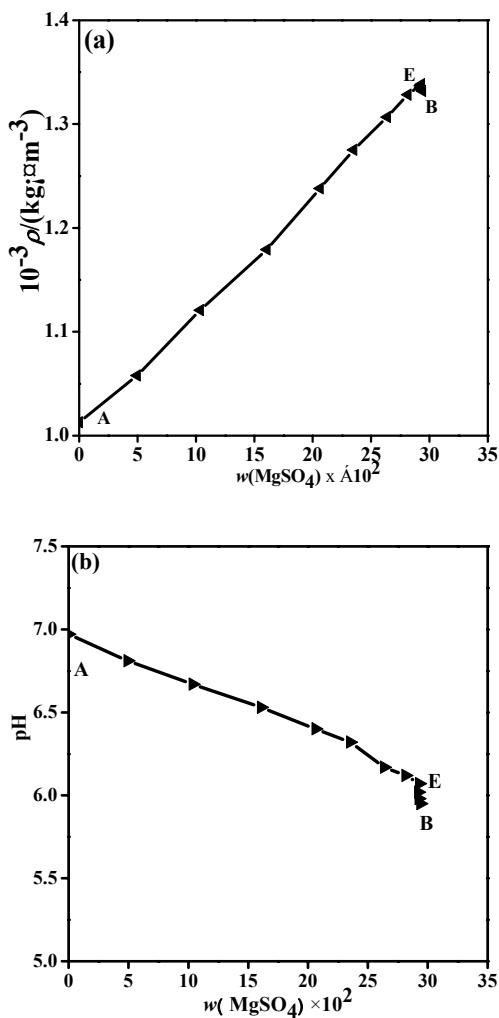


Figure 4: Physicochemical properties versus composition of the ternary system $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K. (a) density vs. composition; (b) pH vs. composition.

SOLUBILITY PREDICTION

Ion-Interaction Model

Pitzer has developed an ion-interaction model and published a series of papers (Pitzer 1973; Pitzer 1992), 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 Harvie and Weare modeling approach (Harvie and Weare, 1980; Harvie *et al.*, 1984). Because these equations are based on the excess free energy, all the activity

expressions are consistent and ready for application to different types of data (e.g., solubility data) for parameter evaluations and calculations of other thermodynamic functions. 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 (Møller, 1988; Greenberg and Møller, 1989; Pabalan and Pitzer, 1987). The following equations are the main expressions related to the solubility calculation of this model.

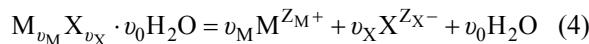
$$\begin{aligned} (\varnothing - 1) = & (2 / \sum_i m_i) [-A^\varnothing I^{3/2} / (1 + bI^{1/2})] \\ & + \sum_c \sum_a m_c m_a (B^\varnothing_{ca} + ZC_{ca}) \\ & + \sum_c \sum_{c' < c'} m_c m_{c'} (\Phi^\varnothing_{cc'} + \sum_a m_a \Psi_{cc'a}) \\ & + \sum_a \sum_{a' < a} m_a m_{a'} (\Phi^\varnothing_{aa'}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

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

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

In expressions (1) to (3), M, c and c' represent cations, and X, a and a' represent anions, respectively. Additionally, m_i and γ_i represent the molality ($\text{mol} \cdot \text{kg}^{-1}$) and the activity coefficient of the ions, respectively, z_i refers to the valence of the ions, and \varnothing refers to the permeability coefficient. The other symbols in expressions (1) to (3), for example, F, C, Z, A^\varnothing , Ψ , Φ , B^\varnothing , and B, are all described in the references (Harvie and Weare, 1980; Harvie *et al.*, 1984).

Solubility equilibrium constants are used to calculate solubility, i.e., 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 $M_{v_M}X_{v_X} \cdot v_0H_2O$, the solubility equilibrium constant (K_{sp}) at a definite temperature and pressure for the dissolution reaction is expressed as follows:



$$\ln K_{sp} = v_M \ln(m_M \gamma_M) + v_X \ln(m_X \gamma_X) + v_0 \ln \alpha_w \quad (5)$$

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

$$\ln \alpha_w = -\phi M_W \sum m_i \quad (6)$$

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 ion-interaction model and the extended HW model.

According to the Pitzer and extended HW models, the activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^θ , $\theta_{cc'}$ and $\psi_{cc'a}$. $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^θ 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. Solubility of the systems $MgCl_2 + MgB_6O_{10} + H_2O$ and $MgSO_4 + MgB_6O_{10} + H_2O$ at 308.15 K could be calculated from Eqs. (1)-(6) when the Pitzer parameters and K_{sp} of the system are all known.

Model Parameterization

A high-temperature thermo-chemical model for the system (Na + K + Mg + Cl + SO₄ + OH + H₂O)

was presented by Pabalan and Pitzer (1987), including a range of temperature for the model. Take MgCl₂ for example, the temperature-dependent equations for MgCl₂ are as follows:

$$P(T) = Q_1 T^2 + Q_2 T + Q_3 \quad (7)$$

where $P(T)$ in Eq. (7) refers to the binary parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^θ of MgCl₂ at 308.15 K of the solution model and the values of the fitting constant terms of Q_1 , Q_2 , and Q_3 were introduced (Pabalan and Pitzer, 1987). The Debye-Hückel parameter A^θ and the binary parameters of MgSO₄ at 308.15 K can be calculated based on the temperature-dependent equations presented in the literature (Møller, 1988; Pabalan and Pitzer, 1987). The binary parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^θ of Mg(B₆O₇)(OH)₆ and the mixing ion-interaction parameters $\theta_{Cl,B_6O_{10}}$, $\theta_{SO_4,B_6O_{10}}$,

$\Psi_{Mg,Cl,B_6O_{10}}$, $\Psi_{Mg,SO_4,B_6O_{10}}$ were available by a multiple linear regression procedure applied to the solubility data of the corresponding ternary system in this paper. All the parameters used in the prediction are presented in Table 3. According to the experimental solubility data in Tables 1 and 2, and Pitzer parameters in Table 3, the average equilibrium constants ($\ln K_{aver}$) for the solid phases were fitted in this study. These average equilibrium constants ($\ln K_{aver}$) of equilibrium solid salts for MgCl₂·6H₂O, MgSO₄·7H₂O, and Mg(B₆O₇)(OH)₆·4.5H₂O correspond to 10.7075, -4.114139 and -9.0057 at (308.15 ± 0.1) K. The uncertainties of the average equilibrium constants for MgCl₂·6H₂O, MgSO₄·7H₂O are ± 0.0278 and ± 0.0821, whereas the uncertainty for Mg(B₆O₇)(OH)₆·4.5H₂O is larger than ± 1.0000. The boron ions in the solution are very complicated, there are many different kinds of boron ions (Li and Gao, 1993), so the equilibrium constant of mcallisterite has a comparatively large uncertainty; a similar situation has been described for Li₂(B₄O₅)(OH)₄·H₂O (Meng, 2012).

Table 3: Single-salt and mixing ion-interaction parameters of the systems at 308.15 K.

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^θ	θ	Ψ
MgCl ₂	0.345373	1.699490		0.00547362		
MgSO ₄	0.220933	3.710150	-35.2046	0.0246099		
Mg(B ₆ O ₇)(OH) ₆	-1.731783	6.235616	-139.935780	-1.497872		
Cl ⁻ (B ₆ O ₇)(OH) ₆ ²⁻					1.054584	
SO ₄ ²⁻ (B ₆ O ₇)(OH) ₆ ²⁻					0.937438	
Mg ²⁺ , Cl ⁻ , (B ₆ O ₇)(OH) ₆ ²⁻						0.738305
Mg ²⁺ , SO ₄ ²⁻ , (B ₆ O ₇)(OH) ₆ ²⁻						-0.241503

Calculated Solubility

To determine the accuracy of the parameters and the solubility equilibrium constants of the solids, the solubilities of the two ternary systems at 308.15 K have been calculated based on the Pitzer ion-interaction model and the extended HW model for aqueous electrolyte solutions. It should be noted that solutes below their saturated solution molalities were fixed at their experimental values and the saturated solutes' solubilities were calculated. The phase diagrams according to the experimental and calculated data were constructed and are shown in Figures 5 and 6, respectively.

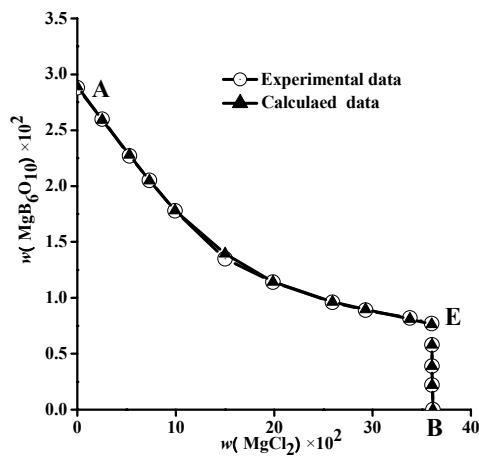


Figure 5: Comparison of the experimental and calculated phase diagram of the ternary system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K; ○, Experimental data; ▲, calculated data; —, experimental isotherm curve; ..., calculated isotherm curve.

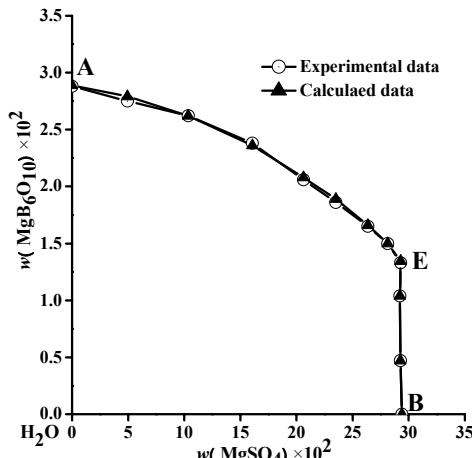


Figure 6: Comparison of the experimental and calculated phase diagram of the ternary system $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K; ○, Experimental data; ▲, calculated data; —, experimental isotherm curve; ..., calculated isotherm curve.

It is shown that the calculated and the experimental data for the ternary system $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ are in good agreement. These results indicate that the model obtained in this work that combines the Pitzer parameters and the equilibrium constants is reliable and is capable of predicting equilibria in the system studied.

CONCLUSIONS

The experimental solubility data and the relevant physicochemical property data of the aqueous systems $\text{MgCl}_2 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ and $\text{MgSO}_4 + \text{MgB}_6\text{O}_{10} + \text{H}_2\text{O}$ at 308.15 K were determined. The experimental stable phase diagrams and the variation of the physicochemical properties with composition were constructed for the first time. The results show that the systems belong to a simple co-saturated type and neither solid solutions nor double salts were formed in the two ternary systems. The single-salt Pitzer parameters, the mixing ion interaction parameters, the equilibrium constant of the minerals were fitted, and the Debye-Hückel parameter A^\ominus in the systems were calculated based on the temperature-dependent equations presented in the literature (Møller, 1988; Pabalan and Pitzer, 1987). Solubility calculations for the ternary systems at 308.15 K have been made using the Pitzer parameters and average equilibrium constants of the solids. The calculated solubilities agree well with experimental values. These results indicate that the parameters and the equilibrium constants obtained in this work are reliable.

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NOMENCLATURE

A^\ominus	Debye-Hückel parameter
B^\ominus	parametric functions of Pitzer parameter
B	parametric functions of Pitzer parameter
B'	parametric functions of Pitzer parameter

C^0	single-salt Pitzer parameter	
C	parametric functions of Pitzer parameter	
f'	parametric functions of Pitzer parameter	
$g(x), g'(x)$	parametric functions of Pitzer parameter	
I	ionic strength	mol/kg
K_{sp}	solubility equilibrium constant	
m	molality	mol/kg
M, C	cation	
n	neutral molecules	
X, A	anion	
z	valence of ions	
Z	parametric functions of the molality of species i	

Greek Letters

α_w	water activity
$\beta^{(0)}$	single-salt Pitzer parameter
$\beta^{(1)}$	single-salt Pitzer parameter
$\beta^{(2)}$	single-salt Pitzer parameter
v	number of ions in the molecule
γ	activity coefficient of the ions
σ	osmotic coefficients
θ	mixing ion interaction Pitzer parameter
Ψ	mixing ion interaction Pitzer parameter

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