SOLUBILITY MEASUREMENT AND SOLID-LIQUID EQUILIBRIUM MODEL FOR THE TERNARY SYSTEM MgBr$_2$ + MgSO$_4$ + H$_2$O AT 288.15 K

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Abstract - The solubility of magnesium minerals and the refractive index of the ternary system MgBr$_2$ + MgSO$_4$ + H$_2$O at 288.15 K were investigated using an isothermal dissolution method. It was found that there are two invariant points in the phase diagram and the solubility isotherm of this ternary system consists of three branches, corresponding to equilibrium crystallization of Epsomite (MgSO$_4$·7H$_2$O, Eps), hexahydrite (MgSO$_4$·6H$_2$O, Hex) and magnesium bromide hexahydrate (MgBr$_2$·6H$_2$O, Mb). Neither solid solutions nor double salts were found. The refractive indices calculated from empirical equation are in good agreement with the experimental data. Combining the results from solubility measurements with the single-salt parameters for MgBr$_2$ and MgSO$_4$, and the mixed ion-interaction parameter θ_{Br,SO_4}, the parameter ψ_{Mg,Br,SO_4} at 288.15 K was fitted using the Pitzer theory and Harvie-Weare (HW) approach. In addition, the average equilibrium constants of the stable equilibrium solids at 288.15 K were obtained by a method using the activity product constant. A chemical model, which combined the Pitzer parameters and the average equilibrium constants, was constructed to calculate the solid + liquid equilibria in the ternary system MgBr$_2$ + MgSO$_4$ + H$_2$O at 288.15 K. The model agreed well with the equilibrium solubility data for the magnesium salts.
Keywords: Phase equilibrium; Phase diagram; Magnesium bromide; Solubility; Pitzer model.

INTRODUCTION

Bromine-containing brine is widely distributed in the Qinghai-Tibet Plateau and the Sichuan basin of China (Zheng *et al.*, 1988; Sang *et al.*, 2011). These brines belong mostly to the complex system Li + Na + K + Mg (Ca) + Cl +SO$_4$ + Br + borate + H$_2$O. The phase equilibria and phase diagrams are the theoretical foundations for exploiting the brine resources and describing the geochemical behaviour of the brine and mineral systems. Therefore, investigations of the thermodynamics and the phase diagram of bromine-containing systems at different temperatures are valuable, because this investigation provides the theoretical foundation and scientific guidance for the comprehensive and effective exploitation of bromine resources.

The phase equilibria of some three-, four- or five-component bromine-containing systems have been reported (Sang *et al.*, 2011; Cui *et al.*, 2013; Christov,

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2012a, 2012b and 2012c; Christov, 2011). The ternary system $MgBr_2$ + $MgSO_4$ + H_2O has previously been investigated at 273.15, 298.15 and 308.15 K since the 1960s, but the solubility data and the reports of the corresponding equilibrium solid phases are not complete. In the literature (Howard and Silcock, 1979), both $MgSO_4·7H_2O$ and $MgSO_4·6H_2O$ occur at 273.15 K, but no invariant points saturated with $MgSO_4·7H_2O$ + $MgSO_4·6H_2O$ have been reported yet. More complicatedly, at 298.15 K, there are five crystallisation fields, corresponding to $MgSO_4·7H_2O$, $MgSO_4·6H_2O$, $MgSO_4·5H_2O$, $MgSO_4·H_2O$ and $MgBr_2·6H_2O$, but there is only one invariant point saturated with $MgBr_2·6H_2O$ + $MgSO_4·H_2O$. At 308.15 K, there are only two crystallisation fields ($MgBr_2·6H_2O$ and $MgSO_4·7H_2O$). All the data for the system $MgBr_2$ + $MgSO_4$ + H_2O system at 273.15, 298.15 and 308.15 K need to be investigated again. Recently, we reported a detailed study on the system at 323.15 K (Meng *et al.*, 2013). It was found that there are four crystallisation fields $MgSO_4·6H_2O$, $MgSO_4·4H_2O$, $MgSO_4·H_2O$ and $MgBr_2·6H_2O$. As it is known, the temperature in the Qinghai-Tibet Plateau in summer is nearly 288.15 K, but the ternary system at 288.15 K has not been reported in the literature to date.

Computer models, which can predict the behaviour of solutions and solid + liquid equilibria with close to experimental accuracy, have wide applicability. The current theory for aqueous solutions of electrolytes is reliable for calculating the solubilities of a salt-water system. There are also studies that embrace currently available theories of electrolyte solution chemistry to simulate the physicochemical processes of solutes, and these studies are able to predict thermodynamic behaviour. These widely used models are important for studying the geochemistry of natural waters and mineral deposits, as well as for solving environmental problems and optimising industrial processes (Christov, 2012a). Pitzer and co-workers 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 a solution and the mean activity coefficients of electrolytes in solution. Single ion activity coefficients, which are more convenient to use in solubility calculations, are given in the Harvie and Weare modelling approach (Harvie and Weare, 1980; Harvie *et al*, 1984). On the basis of the Pitzer approach and its extension the Harvie-Weare (HW) model (denoted hereafter as the Pitzer and HW model), the solubilities of the systems containing bromine were predicted (Meng, 2013; Christov, 2012a, 2012b and 2012c; Christov, 2011), and these

predictions demonstrated that the Pitzer and HW model could be expanded to calculate the solubility of bromine minerals in complex brines accurately. However, studies modelling the ternary system $MgBr_2$ + $MgSO_4$ + H_2O at 288.15 K are still lacking in the literature.

In this study, the solubilities and the relevant refractive indices of the ternary system $MgBr_2$ + $MgSO_4$ + H_2O at 288.15 K were determined. Additionally, a chemical model incorporating Pitzer theory and the HW approach was constructed to calculate the solid + liquid equilibrium in the ternary system.

EXPERIMENTAL SECTION

Apparatus and Reagents

A thermostatic shaker (model THZ-82, Jintan Yitong Electronics Co., Ltd., China) was used to prepare the solution in its equilibrium state. The temperature in the thermostatic bath was maintained at a constant temperature of (288.15 ± 0.1) K, and the detailed experimental procedures were described previously (Meng *et al.*, 2011). The solid phase minerals were determined using Schreinemaker's method (Song, 1991) and an X-ray diffractometer (D8 Advance, Bruker Ltd., Germany). All the analytical grade chemicals, which were obtained from the Chengdu Aike Chemical Reagent Plant or the Shanghai Xinbao Fine Chemical Plant, were recrystallised before use, including magnesium bromide hexahydrate ($MgBr_2·6H_2O$, with mass fraction 0.98) and epsomite ($MgSO_4·7H_2O$, 0.99). Doubly deionised water (DDW) with a conductivity of less than $1.2×10^{-4}$ S·m^{-1} at 298.15 K was used to prepare the series of artificial, synthesised brines and for the chemical analysis.

Experimental Methods

The isothermal dissolution method was used in this study. A series of artificially synthesised brines were mixed from the appropriate quantities of salts and DDW, which were calculated according to the composition at phase equilibrium, and then were loaded into clean polyethylene bottles and capped tightly. The bottles were placed in a thermostatic rotary shaker, which was maintained at a constant temperature of (288.15 ± 0.1) K and a rotation speed of 120 rpm to accelerate equilibration of the 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 achieved. Otherwise, the solution was rotated continually until the equilibrium state was achieved. Generally, it took approximately 20 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 concentrations of the two liquid phases was within ± 0.3% in mass fraction, then the solubility of this equilibrium point, which was the average of the experimental data, was obtained. 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 (Song, 1991) (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). Another portion was dried, ground into powder and analysed by X-ray diffraction. The solid phase could then be identified.

Analytical Methods

The concentrations of the liquid phases and the wet residues were analysed with chemical analytical methods. The concentration of Mg^{2+} was determined with a precision of within ± 0.3% in mass fraction by titration with an EDTA standard solution in the presence of the indicator Eriochrome Black-T. The Br^- concentration was measured by titration with a standard solution of $Hg(NO_3)_2$ using a mixed indicator of diphenylcarbazone and bromophenol blue (precision: ± 0.3%) (Zhai et al., 1988). The SO_4^{2-} concentration was calculated by subtraction via charge balance. An Abbe refractometer (model WZS-1) was used to measure the refractive index (n_D) with an uncertainty of ± 0.0001. Through control with a thermostat, all measurements were conducted at the desired temperature of (288.15 ± 0.1) K.

RESULTS AND DISCUSSION

Solubility and Refractive Index Data

The solubility and the refractive index data of the system MgBr₂ + MgSO₄ + H₂O at 288.15 K are presented in Tables 1 and 2. The mineral concentrations

in the stable equilibrium solutions and the wet residue are expressed as mass percentage. Based on the experimental data (Table 1), the stable phase diagram of the system at 288.15 K was plotted, as shown in Figure 1.

Table 1: Solubility data of the ternary system MgBr₂ + MgSO₄ + H₂O at 288.15 K.

No.	Liquid phase, $10^2 w^a$		Wet residue, $10^2 w$		Equilibrium solid phase[b]
	MgBr₂	MgSO₄	MgBr₂	MgSO₄	
1, A	0.00	24.60	—[c]	—	Eps
2	4.37	20.10	1.82	36.34	Eps
3	7.38	17.22	3.31	35.75	Eps
4	10.15	14.99	4.51	35.14	Eps
5	13.34	12.19	5.78	34.31	Eps
6	17.59	9.67	7.32	32.81	Eps
7	21.62	7.24	8.85	32.24	Eps
8	24.06	6.06	10.77	30.3	Eps
9	27.51	4.43	12.46	29.45	Eps
10	29.50	3.83	13.58	28.55	Eps
11	32.82	2.69	15.08	27.95	Eps
12	35.71	2.55	16.43	28.09	Eps
13	38.25	2.31	18.13	27.33	Eps
14	39.61	2.14	18.69	26.70	Eps
15, E	43.33	1.87	20.47	27.40	Eps + Hex
16	44.52	1.72	22.34	27.21	Hex
17	45.60	1.57	27.67	21.34	Hex
18	46.89	1.29	28.05	21.76	Hex
19, F	49.10	1.03	28.41	24.12	Hex + Mb
20, B	49.70	0.00	—	—	Mb

[a] w, mass percentage; [b] Eps, MgSO₄·7H₂O; Hex, MgSO₄·6H₂O; Mb, MgBr₂·6H₂O; [c] —, means not detected.

Table 2: Experimental and calculated refractive index data of the ternary system at 288.15 K.

No.	Exp. value	Calc. value	Relative error/% [a]
1, A	1.3792	1.3777	0.11
2	1.3824	1.3798	0.19
3	1.3852	1.3817	0.25
4	1.3862	1.3842	0.14
5	1.3881	1.3867	0.10
6	1.3905	1.3922	-0.12
7	1.3951	1.3974	-0.17
8	1.3979	1.4011	-0.23
9	1.4034	1.4064	-0.22
10	1.4068	1.4102	-0.24
11	1.4122	1.4161	-0.28
12	1.4199	1.4229	-0.21
13	1.4273	1.4287	-0.1
14	1.4309	1.4317	-0.06
15, E	1.4428	1.4404	0.16
16	1.4465	1.4431	0.23
17	1.4508	1.4475	0.23
18	1.4542	1.4502	0.27
19, F	1.4593	1.4554	0.27
20, B	1.4549	1.4549	0.00

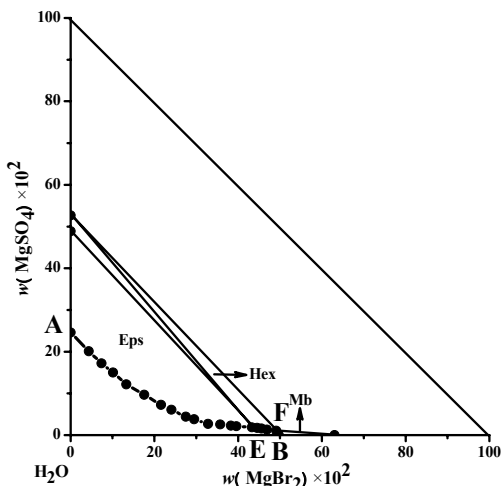[a] Relative error = (experiment value - calculated value)/ experiment value.

Figure 1: Stable phase diagram of the ternary system $MgBr_2$ + $MgSO_4$ + H_2O at 288.15 K; •, experimental solubility data; —, experimental stable isotherm curve.

The stable phase diagram of the system at 288.15 K consists of three stable crystallisation fields corresponding to Epsomite ($MgSO_4 \cdot 7H_2O$, Eps), hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex) and magnesium bromide hexahydrate ($MgBr_2 \cdot 6H_2O$, Mb). Points E and F are the invariant points, which are saturated with Eps + Hex and Hex + Mb. Curves AE, EF and FB are the univariant curves, which are saturated with a single salt (Eps, Hex or, Mb). The Eps crystallisation area is relatively large; whereas, the Hex crystallisation area is relatively small. The smallest crystallisation area is that of Mb. These results indicate that magnesium sulphate is relatively easy to saturate and that magnesium bromide has a high solubility. Neither solid solutions nor double salts were found. Because it is known that the phase diagram of the $MgCl_2$ + $MgSO_4$ + H_2O system at 288.15 K (Howard and Silcock, 1979) also consists of crystallisation fields corresponding to Eps, Hex and $MgCl_2 \cdot 6H_2O$ (Bis), it is shown that magnesium bromide reacts with magnesium sulphate in solution similarly to magnesium chloride.

Using the refractive index data shown in Table 2, the relationships of the solutions' refractive index to the concentration of magnesium bromide were plotted in Figure 2. It is seen that the refractive indices of the solutions increase with the increase in magnesium bromide concentration, reach their maximum values at invariant point F (Hex + Mb), and then decrease. Using the diagram (Figure 2), the refractive index could be used to roughly estimate the magnesium bromide concentration in the ternary system.
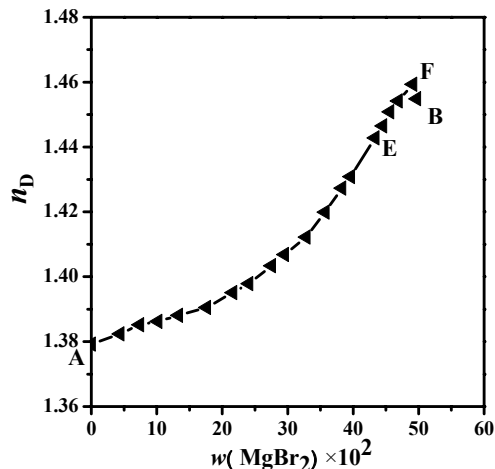

Figure 2: Refractive index data versus composition of the ternary system $MgBr_2$ + $MgSO_4$ + H_2O at 288.15 K. ▲, experimental data; —, experimental curve.

Comparison of the Ternary System at Different Temperatures

The comparison of the solubility data for the ternary system $MgBr_2$ + $MgSO_4$ + H_2O at 273.15, 298.15, 308.15 K (Howard and Silcock, 1979), 323.15 K (Meng *et al.*, 2013) and 288.15 K (this study) is shown in Figure 3. The patterns for the solubility curves at different temperatures are similar. The areas of the crystallised regions of magnesium bromide and magnesium sulphate decrease as the temperature increases, and these decreases indicate that the solubilities are positively correlated with temperature. The crystallisation zone for hydrated magnesium bromide was considerably smaller than that for hydrated magnesium sulphate. With this information, the mixture of magnesium bromide and magnesium sulphate salts can be separated and purified. There is one crystallisation field for hydrated magnesium bromide; whereas, there are many crystallisation fields for hydrated magnesium sulphate. Moreover, it is worthwhile to note that the crystallisation fields corresponding to hydrated magnesium sulphate differ greatly with temperature. Hydrated magnesium sulphate $MgSO_4 \cdot 7H_2O$ occurs when the temperatures are in the lower range (273.15, 288.15, 298.15 and 308.15 K); $MgSO_4 \cdot 6H_2O$ occurs at all five temperatures; whereas $MgSO_4 \cdot 4H_2O$ and $MgSO_4 \cdot H_2O$ occur at relatively higher temperatures (308.15, 323.15 K). The crystallisation water for the hydrated magnesium sulphate decreases as the temperature increases. It shows that the water sorption decreases as the temperature increases and the stability field of different hydrates depends on temperature. This crystallisation information for the

various minerals at different temperatures is important for the recovery of hydrated magnesium sulphate. Because of the lack of invariant points and of some crystallisation fields in the system at 273.15, 298.15 and 308.15 K, the differences between the diagrams at the five temperatures were not developed further.
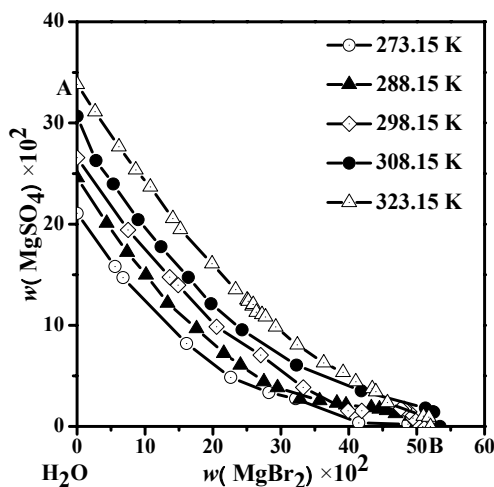

Figure 3: Comparison of the phase diagrams of the ternary system MgBr₂ + MgSO₄ + H₂O at different temperatures; ○, 273.15 K [11]; ▲, 288.15 K [11]; ◇, 298.15 K; ●, 308.15 K [11]; △, 323.15 K.

Empirical Equation for the Refractive Index

Song and Du (Song and Du, 1986) have given an expression, which has been widely used in brine systems, for the refractive index and solubility data. The following empirical equation was used to calculate the refractive index:

$$\ln\left(n/n_0\right) = \sum B_i \times W_i \qquad (1)$$

where $n_0 = 1.333390$, the refractive index of water at 288.15 K. B_i is the coefficients of each possible component i in the system. W_i is the salt of i in the solution in mass fraction. For the calculation of the refractive index of MgBr₂ and MgSO₄, coefficients B_i were set to be 0.001725, 0.001328, respectively. The calculated results and experimental values are presented for comparison in Table 2, and the maximum relative deviations for all of the calculated results are less than 0.28%. The reasons for the relative errors in the data in Table 2 are multifarious and include the error in the solubility data caused by temperature deviations, the uncertainty in the concentration, and the uncertainty in the measurements of refractive index. The calculated values agree well with the experimental data, and this agreement shows that the coefficients B_i obtained in this work are reliable and can be used for more complicated systems containing MgBr₂ and MgSO₄ at 288.15 K.

SOLUBILITY PREDICTION

Ion-Interaction Model

The Pitzer theory and HW approach, which incorporate concentration dependent equations showing the specific interactions of the solutes (Pitzer 1973; Pitzer 1992; Harvie and Weare, 1980; Harvie *et al*, 1984), were used for the aqueous solutions in this study. Additional work has centred on developing variable temperature models below 298.15 K, which have increased applicability to a number of diverse geochemical systems (Spencer *et al*., 1990; Marion and Farren, 1999). The following equations, which are described in the literature (Pitzer 1992), are the main expressions related to the solubility calculation of this model.

$$(\text{ø}-1) = (2/\sum_i m_i)\,[-A^{\varnothing}I^{3/2}/(1+bI^{1/2}) + \sum_c \sum_a m_c m_a (B^{\varnothing}_{ca} + ZC_{ca})$$

$$+\sum_c \sum_{<c'} m_c m_{c'}(\Phi^{\varnothing}_{cc'} + \sum_a m_a \Psi_{cc'a}) + \sum_a \sum_{<a'} m_a m_{a'}(\Phi^{\varnothing}_{aa'} + \sum_c m_c \Psi_{caa'})] \qquad (2)$$

$$\ln\gamma_M = z_M{}^2 F + \sum_a m_a\left(2B_{Ma} + ZC_{Ma}\right) + \sum_c m_c(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca})$$

$$+\sum_a \sum_{<a'} m_a m_{a'}\Psi_{Maa'} + z_M \sum_c \sum_a m_c m_a C_{ca} \qquad (3)$$

$$\ln\gamma_X = z_X{}^2 F + \sum_c m_c \left(2B_{cX} + ZC_{cX}\right) + \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \Psi_{cXa})$$

$$+ \sum_c \sum_{<c'} m_c m_{c'} \Psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} \tag{4}$$

In expressions (2) to (4), M, C and C' represent cations, X, A and A' represent anions, and N_C and N_A refer to the number of cations and anions, respectively. Additionally, m_i and γ_i represent the concentration (mol·kg⁻¹) and the activity coefficient of the ions, respectively, Z_i refers to the valence of the ions, and ø refers to the permeability coefficient. The other symbols in Eqs. (3) to (5), for example, F, C, Z, $A^Ø$, Ψ, Φ, $B^Ø$, and B, are all described in the references (Harvie and Weare, 1980; Harvie *et al*, 1984).

For a hydrated salt, $M_{\upsilon_M} X_{\upsilon_X} \cdot \upsilon_0 H_2O$, the solubility equilibrium constant (K_{sp}) for the dissolution reaction at a definite temperature and pressure is expressed as follows:

$$M_{\upsilon_M} X_{\upsilon_X} \cdot \upsilon_0 H_2O = \upsilon_M M^{Z_M+} + \upsilon_X X^{Z_X-}$$

$$+ \upsilon_0 H_2O \tag{5}$$
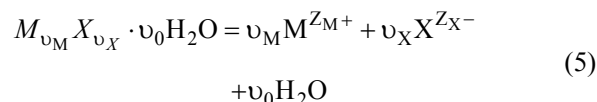
$$\ln K_{sp} = \upsilon_M \ln(m_M \gamma_M) + \upsilon_X ln(m_X \gamma_X) + \upsilon_0 \ln\alpha_w \tag{6}$$

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

$$\ln\alpha_w = -\text{ø} M_W \sum m_i \tag{7}$$

where M_w is the molar mass of water (kg·mol⁻¹), and the sum covers all the solute species. The activity coefficients γ_i, and the osmotic coefficients ø can be calculated using the Pitzer and HW model.

$$\gamma_\pm = (\gamma_M{}^{\nu_M} \times \gamma_X{}^{\nu_X})^{\frac{1}{(\nu_M + \nu_X)}} \tag{8}$$

The mean activity coefficients $\gamma_\pm$, which are a function of the activity coefficients γ_M and γ_X in Equation (8), can also be calculated using the Pitzer theory and HW approach.

According to the Pitzer theory and HW approach, the activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^Ø$, $\theta_{cc'}$ and $\psi_{cc'a}$; $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^Ø$ are the parameters of a single salt; $\theta_{cc'}$ represents the interaction between 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 ion is different from the first two ions. By combining the Pitzer parameters and the equilibrium constants of single salts, a chemical model could be constructed to calculate the solid + liquid equilibrium in the ternary $MgBr_2$ + $MgSO_4$ + H_2O system at 288.15 K from Eqs. (2)-(8).

Model Parameterization

The Debye–Hückel parameter $A^Ø = 0.385646$ at 288.15 K was obtained from the literature (Spencer *et al*., 1990). The Pitzer binary parameters for $MgBr_2$, and the mixing parameters θ_{Br,SO_4} were calculated from the temperature-dependent equations presented in the literature (Christov, 2011; Christov, 2012b). The Pitzer binary parameters for $MgSO_4$ can be gotten from the literature (Spencer *et al*., 1990; Marion and Farren, 1999), but the parameter $\beta^{(2)}$ for $MgSO_4$ is not mentioned in the literature (Spencer *et al*., 1990). Therefore, the parameters for $MgSO_4$ used in this study were calculated using the literature (Marion and Farren, 1999). The solubility data for the ternary system $MgBr_2$ + $MgSO_4$ + H_2O in this study were used to fit the mixing parameters Ψ_{Mg,Br,SO_4} via a multiple linear regression procedure. All the parameters used in the prediction are presented in Table 3. According to the parameters and the measured solubilities of the ternary system in this work, the equilibrium constants of the minerals in the ternary system at 288.15 K were fitted for each stable solution by a method using the activity product constant. For $MgBr_2 \cdot 6H_2O$ at 288.15 K, the $\ln K_{sp}$ is 11.6742, which is very close to the data in the literature (Christov, 2011; Meng, 2013). For $MgSO_4 \cdot 7H_2O$, the $\ln K_{sp}$ calculated using the pure electrolyte parameters and the solubility data in our study is -4.7194, which is very close to the data in the literature (Marion and Farren, 1999), but the $\ln K_{sp}$ for magnesium sulfate hydrate at the other points in the solubility isotherm are very different. The main reason may be that the parameters for $MgBr_2$ and $MgSO_4$ do not match. Another reason may be the deviation caused by the parameter fitting.

Therefore, the average equilibrium constants ($\ln K_{aver}$) of equilibrium solid salts were used to calculate the solubilities in this study. These average equilibrium constants ($\ln K_{aver}$) and uncertainties for the equilibrium solid salts of $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 6H_2O$ are presented in Table 4.

Table 3: Single-salt and mixing ion-interaction parameters of the systems at 288.15 K.

Parameters	Value	Reference
$\beta^{(0)}(MgBr_2)$	0.409524	Christov, 2011
$\beta^{(1)}(MgBr_2)$	1.945165	Christov, 2011
$C^{(\phi)}(MgBr_2)$	0.005198	Christov, 2011
$\beta^{(0)}(MgSO_4)$	0.109518	Marion and Farren, 1999
$\beta^{(1)}(MgSO_4)$	3.004927	Marion and Farren, 1999
$\beta^{(2)}(MgSO_4)$	0.725033	Marion and Farren, 1999
$C^{(\phi)}(MgSO_4)$	0.067418	Marion and Farren, 1999
θ_{Br,SO_4}	0.03	Christov, 2012b
Ψ_{Mg,Br,SO_4}	0.138242	This work

Table 4: Values for the average equilibrium constants of the ternary system at 288.15 K.

Species	$\ln K$sp	Uncertainty
$MgBr_2 \cdot 6H_2O$	11.6742	±0.0342
$MgSO_4 \cdot 7H_2O$	-3.4955	±0.6120
$MgSO_4 \cdot 6H_2O$	2.7152	±0.3701

Validation and Application of the Model

In Figure 4, we calculated the mean activity coefficients of magnesium bromide and magnesium sulphate in the solutions ($\gamma_\pm$ vs. molality) up to the saturation molality at 288.15 K using Equation (8). In Figure 4(a), the mean activity coefficients of magnesium bromide increase with increasing concentrations of magnesium bromide. The $\gamma_\pm$ values first decrease with concentration to a wide minimum at low to moderate concentration, and an additional increase in molality leads to a sharp increase up to the equilibrium precipitation of the corresponding solids. The trend for the curve at 288.15 K is similar to that for the curve at 323.15 K, but the activity coefficients in bromide electrolyte systems at 288.15 K are smaller than those for systems at 323.15 K (Meng *et al.*, 2013). This result represents another step that validates the present parameters for the bromide systems presented in Table 3. Compared with the curve in Figure 4(a), the curve in Figure 4(b) shows the opposite trend. The $\gamma_\pm$ values of magnesium sulphate first decrease sharply with concentration and then change relatively smoothly with concentration. The solubilities for the ternary system at 288.15 K were also calculated using Eqs. (2)-(7) to validate the accuracy of the model. It should be noted that solutes below their saturation molalities were fixed at their experimental values and the saturated solubilities were calculated. The comparison of the calculated and the experimental phase diagrams of the ternary system is shown in Figure 5. The calculated phase diagram and the experimental phase diagram are found to be 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 equilibrium in the system studied.
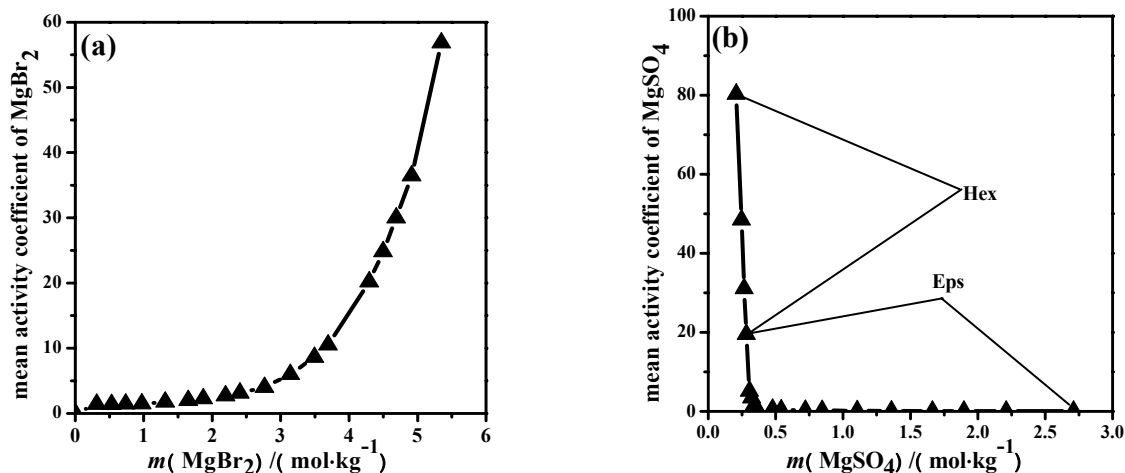

Figure 4: Mean activity ($\gamma_\pm$) calculated from the model of magnesium bromide and magnesium sulphate in the MgBr₂ + MgSO₄ + H₂O system at 288.15 K; ▲, calculated data; —, calculated curve; (a) MgBr₂; (b) MgSO₄.

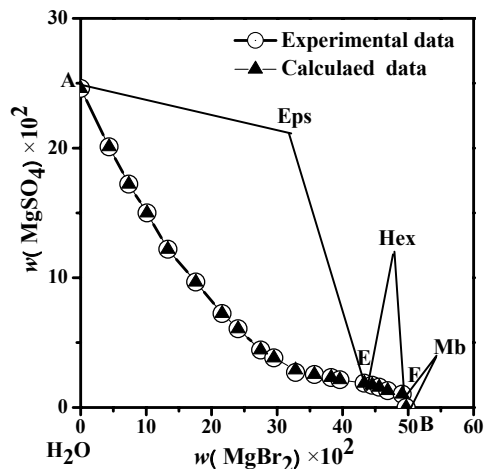**Figure 5:** Comparison of the experimental and calculated phase diagrams of the stable ternary system $MgBr_2 + MgSO_4 + H_2O$ at 288.15 K; ○, Experimental data; ▲, calculated data; —, experimental isotherm curve; …, calculated isotherm curve; Eps, $MgSO_4 \cdot 7H_2O$; Hex, $MgSO_4 \cdot 6H_2O$; Mb, $MgBr_2 \cdot 6H_2O$.

CONCLUSIONS

The stable equilibria of the aqueous ternary system $MgBr_2 + MgSO_4 + H_2O$ were investigated at 288.15 K. The phase diagram and diagram of the variation in the refractive indices with composition were plotted for this system at 288.15 K. It was found that there are two three-salt cosaturated invariant points, three univariant solubility isotherms, and three stable crystallisation fields in the ternary system. Neither solid solutions nor double salts are found. The refractive indices of the solution are positively correlated with the concentration of magnesium bromide, with the maximum value occurring at point F (Hex + Mb). No significant differences are found among the diagrams of the ternary system at different temperatures; however, the crystallisation fields are very different, especially the fields for hydrated magnesium sulphate. The empirical equations were used to calculate the refractive indices; the coefficients have been fitted, and the calculated values for the refractive index are in good agreement with the experimental data.

The parameter ψ_{Mg,Br,SO_4} at 288.15 K was fitted using the measured solubility data in this study, and the average equilibrium constants for stable equilibrium solids at 288.15 K were obtained with a method using the activity product constant. Based on Pitzer theory and the HW approach, a new chemical model, including the Pitzer parameters and the equilibrium constants, was constructed for the ternary system at 288.15 K. The model gave very good agreement with the equilibrium solubility data of the magnesium salts.

NOMENCLATURE

$A^{\varnothing}$	Debye–Hückel parameter	
$B^{\varnothing}$	parametric functions of Pitzer parameter	
B	parametric functions of Pitzer parameter	
B'	parametric functions of Pitzer parameter	
$C^{\varnothing}$	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
Ksp	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
υ	number of ions in the molecule
γ	activity coefficient of the ions
ø	osmotic coefficients
θ	mixing ion interaction Pitzer parameter
Ψ	mixing ion interaction Pitzer parameter

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