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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Solid–Liquid Metastable Phase Equilibria in the Ternary System ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K[1]

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Abstract—The solubilities and the densities in the aqueous ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K were determined by the isothermal evaporation method. The phase diagram was drawn for this system at 323.15 K. The phase diagram consists of two invariant points, three univariant curves, and three crystallization regions corresponding to bischofite ($MgCl_2 \cdot 6H_2O$), tetrahydrate ($MgSO_4 \cdot 4H_2O$) and hexahydrite ($MgSO_4 \cdot 6H_2O$). Neither double salts nor solid solution was found. Based on the Pitzer and Harvie–Weare (HW) model, the solubility equilibrium constants for the salts were fitted with the solubilities in this research work, and the solubilities of the ternary system at 323.15 K were calculated. Comparisons between the calculated and measured solubilities show that the predicted data agree well with the experimental results.

Keywords: metastable phase equilibrium, solubility, Pitzer modeling

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A series of salt lakes in the Qaidam Basin, located in Qinghai, is famous for their abundance of magnesium resources [1]. These brines belong mostly to the complex system (Li + Na + K + Mg + Cl +SO_4 + borate + H_2O). The thermodynamic phase equilibria and phase diagrams play an important role in exploiting the brine resources and describing the geochemical behavior of brine and mineral system [2]. The solar pond technique is widely used in the exploitation of brine resources. The crystal formation of evaporated brines usually follows the metastable phase diagrams not the stable phase diagrams [3]. Therefore, the metastable phase equilibria of the brine system are necessary to exploit the brine resources.

The ternary system ($MgCl_2 + MgSO_4 + H_2O$) is a subsystem of the seven-component system. The stable phase equilibrium of the ternary system over a wide temperature had been previously reported [4]. The system at 323.15 K were studied in detail by Chr. Balarew [5], but the metastable phase equilibrium of the system at 323.15 K is not reported in the literature to describe the metastable behavior to separate and purify the magnesium sulfate salts and magnesium chloride salt. The isothermal equilibrium dissolution method (isothermal reduction of supersaturation method) is used to investigate the stable phase equilibrium, while the isothermal evaporation method is used for metastable phase equilibrium [3]. Therefore, the metastable solubilities and the densities of the ternary system of ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K were determined by the isothermal evaporation method in this study.

EXPERIMENTAL

The isothermal evaporation method is used to obtain the metastable phase diagram in this study. The isothermal evaporation box made in our laboratory was used for the isothermal evaporation, which was described in our previous study [6]. The solid phase of the minerals was identified using the Schreinemaker's method and a XP-300 Digital Polarizing Microscopy (Shanghai Caikon Optical Instrument Co. Ltd., China). The chemicals used were of analytical grade and obtained from either the Tianjin Kermel Chemical Reagent Ltd. or the Shanghai-Lithium Industrial Co. Ltd: epsomite ($MgSO_4 \cdot 7H_2O$, mass fraction purity 0.99), Bischofite ($MgCl_2 \cdot 6H_2O$, mass fraction purity 0.99), and were re-crystallized before use. The water used through the experiments was doubly dis-

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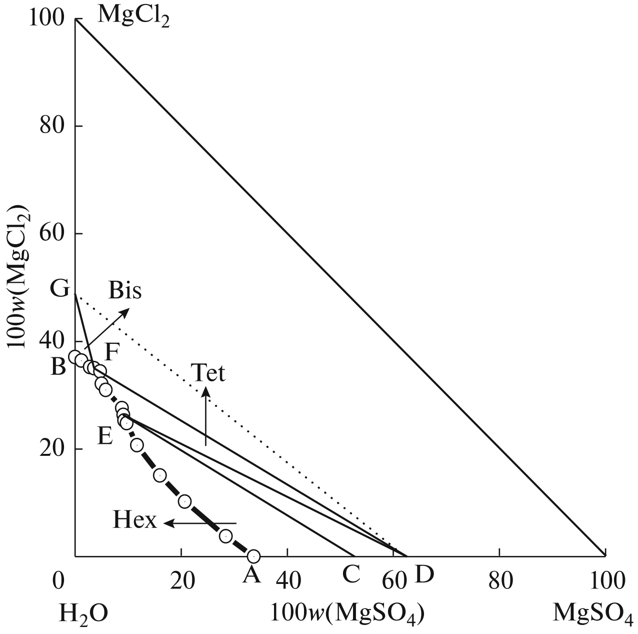

Fig. 1. Metastable phase diagram of the system ($MgCl_2$ + $MgSO_4$ + H_2O) at 323.15 K; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

tilled water (DDW) with a conductivity less than 1.2×10^{-4} S m^{-1}.

According to the composition at the phase equilibrium, the appropriate quantity of salts and DDW calculated were mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high). And then the containers were placed in the box for isothermal evaporation at $T = (323.15 \pm 0.2)$ K. The experimental conditions consisted of air flow (3.5 to 4.0) m s^{-1}, relative humidity (20 to 30)%, and evaporation rate (4 to 6) mm d^{-1}. It is pointed out that no stirring was applied to the solutions. The crystal behavior of the solid phase was observed periodically. When enough new solid phase appeared, the wet residue mixtures were taken from the solution. The solids were evaluated with chemical analysis and determined by Schreinemaker's method of wet residues [7]. Meanwhile, a 5.0 cm^{-3} sample of the clarified solution was taken out from the container through a filter pipette, and then diluted to a 250.0 cm^{-3} final volume in a volumetric flask filled with DDW for quantitative analysis. Some other filtrates was used to measure the physicochemical properties. The remainder of the solution in the container continued to be evaporated to reach a new isothermal evaporation equilibrium point. When two salts were crystallized from the solution in the ternary system, the point is the invariant points of the ternary system. The invariant points of the ternary system are unchangeable for some time. Therefore, the liquid phase for the invariant points of the ternary system were taken out for measurement twice at different times, If the difference between the concentrations of the two liquid phases was within ±0.003 in mass fraction, then the concentration of this invariant point, which was the average of the two experimental data, was obtained. It should be pointed out that the points on the isotherm evaporation curves are changing because the isothermal evaporation is continuous. Therefore, the concentration of these points are measured only one time. In this study, it took about 30 days to get the metastable phase diagram of the system ($MgCl_2$ + $MgSO_4$ + H_2O) at 323.15 K.

The Mg^{2+} ion concentration was determined by titration with EDTA standard solution in the presence of indicator of Eriochrome Black-T. The Cl^- ion concentration was measured by titration using a standard solution of $Hg(NO_3)_2$. The concentrations of Mg^{2+} and Cl^- were analyzed by the titrimetric analysis methods all with standard uncertainty 0.003 (0.68 level of confidence) in mass fraction [8]. The densities(ρ) were measured by means of a density bottle with a precision of ± 0.2 kg m^{-3}, and the bottle thermostatted at (323.15 ± 0.1) K.

RESULTS AND DISCUSSION

The experimental solubilities and the solution densities of the ternary system ($MgCl_2$ + $MgSO_4$ + H_2O) at 323.15 K are presented in Table 1. The mineral concentration values in the equilibrium solution of the isothermal evaporation are expressed as mass fraction. Using the experimental results in Table 1, the phase diagram of the system at 323.15 K is shown in Fig. 1.

In Fig. 1, points A and B represent the solubility of the single-salts of magnesium sulfate and magnesium chloride with mass fraction ($100w_b$) of 33.70 and 37.10, respectively. The points E and F are invariant points for Hexahydrite ($MgSO_4 \cdot 6H_2O$, Hex), tetrahydrate ($MgSO_4 \cdot 4H_2O$, Tet) and tetrahydrate ($MgSO_4 \cdot 4H_2O$), Bischofite ($MgCl_2 \cdot 6H_2O$, Bis). The compositions of $MgSO_4$, $MgCl_2$ in the liquid phase with mass fraction ($100w_b$) of the invariant points are (9.10, 26.35) and (3.60, 34.99), respectively. There are three isotherm evaporation curves corresponding to curves AE, EF and BF saturated with single salt (Hex, Tet and Bis), and three single-salt crystallization regions corresponding to $MgCl_2 \cdot 6H_2O$ (BFG), $MgSO_4 \cdot 4H_2O$ (EDF) and $MgSO_4 \cdot 6H_2O$ (ACE) in the isothermal evaporation phase diagram. Points C, D and G are the points for the salts $MgSO_4{\cdot}6H_2O$, $MgSO_4 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ in Fig. 1. The regions CED and FDG are crystallization regions for $MgSO_4 \cdot 6H_2O$ + $MgSO_4 \cdot 4H_2O$, and $MgSO_4 \cdot 4H_2O$ + $MgCl_2 \cdot 6H_2O$, respectively. Neither double salts nor solid solutions were found.

The comparison between the metastable phase diagram (solid line) and stable phase diagram (dashed

Table 1. Solubility data and density data of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K

No.	Comp. of liquid phase, $100w_b$		Comp. of wet residue, $100w_b$		Density 10^{-3} $\rho/(kg\ m^{-3})$	Equilibrium solid phase[a]
	$MgSO_4$	$MgCl_2$	$MgSO_4$	$MgCl_2$		
1, A	33.70	0.00	—[b]	—	1.3872	Hex
2	28.43	3.77	—	—	1.3557	Hex
3	20.68	10.23	39.38	6.19	1.3202	Hex
4	16.00	15.10	—	—	—	Hex
5	11.69	20.71	—	—	—	Hex
6	9.74	24.79	—	—	—	Hex
7	9.29	25.30	—	—	—	Hex
8, E	9.10	26.35	29.92	14.99	—	Hex + Tet
9	8.85	27.58	—	—	—	Tet
10	5.77	30.94	—	—	—	Tet
11	4.98	32.12	—	—	—	Tet
12	4.74	34.43	31.69	18.50	1.3815	Tet
13, F	3.60	34.99	8.70	35.31	—	Tet + Bis
14	2.78	35.21	—	—	—	Bis
15	1.20	36.41	0.35	80.47	1.3596	Bis
16, B	0.00	37.10	—	—	1.3473	Bis

[a] Hex, $MgSO_4 \cdot 6H_2O$; Tet,$MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$. [b] "—", means not detected.

line) from Balarew Chr. [5] for the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K is shown in Fig. 2. The crystallizing zone corresponding to $MgSO_4 \cdot H_2O$ (Kie) disappears in the metastable equilibrium. As shown in Fig. 2, the metastable crystallization regions of $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 4H_2O$ and $MgSO_4 \cdot 6H_2O$ are bigger than those in the stable phase diagram.

Solubility Prediction

Pitzer [9, 10] published a series of papers and gave a set of expressions for the osmotic coefficient of solution and mean activity coefficient of electrolytes in the solution. Harvie et al. [11] have developed the electrolyte solution theory models (Harvie–Weare (HW) models), which reliably predict mineral solubility in the complex brine system (Na + K + Mg + Ca + H + Cl + SO_4+ OH + CO_3 + HCO_3 + CO_2 + H_2O) from low to high concentrations at 298.15 K (denoted hereafter as the Pitzer and HW model). Additional work has centered on developing variable temperature models, which will increase the applicability to demonstrate a number of diverse geochemical behaviors [12, 13].

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:

$$M_{\upsilon_M}X_{\upsilon_X} \cdot \upsilon_0 H_2O = \upsilon_M M^{+ZM} + \upsilon_X X^{-ZX} + \upsilon_0 H_2O, \quad (1)$$

$$\ln K_{sp} = \upsilon_M \ln(m_M \gamma_M) + \upsilon_X \ln(m_X \gamma_X) + \upsilon_0 \ln \alpha_w. \quad (2)$$

The water activity is a function of the osmotic coefficient ø, through the equation

$$\ln \alpha_w = -ø(M_w/1000)\sum m_i, \quad (3)$$

where M_w is the molar mass of water, 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. The following equations, which were described in reference [9], are the main expressions related to the solubility calculation in this study.

$$\begin{aligned}(ø - 1) = \left(2\Big/\sum_i m_i\right)\Big[&-A^{ø} I^{3/2}\big/(1 + bI^{1/2}) \\ &+ \sum_c \sum_a m_c m_a \left(B^{ø}_{ca} + ZC_{ca}\right) \\ &+ \sum_c \sum_{<c'} m_c m_{c'} \left(\Phi^{ø}_{cc'} + \sum_a m_a \Psi_{cc'a}\right) \\ &+ \sum_a \sum_{<a'} m_a m_{a'} \left(\Phi^{ø}_{aa'} + \sum_c m_c \Psi_{caa'}\right)\Big],\end{aligned} \quad (4)$$

Table 2. Single-salt and mixing ion-interaction parameters of the system ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{(\phi)}$	θ	Ψ	Ref.
$MgCl_2$	0.337022	1.781700		0.004014			[8]
$MgSO_4$	0.227487	3.614270	−40.262540	0.019761			[8]
Cl^-, SO_4^{2-}					0.03		[8]
Mg^{2+}, Cl^-, SO_4^{2-}						−0.016425	[8]

Table 3. Comparison of experimental and calculated values in invariant point of the ternary system at 323.15 K (experimental/calculated)

Comp. of liquid phase, $100w_b$			Equilibrium solid phase
$MgSO_4$	$MgCl_2$	H_2O	
9.10 9.12	26.35 26.31	64.55 64.57	Hex + Tet
3.60 3.65	34.99 34.97	61.41 61.48	Tet + Bis

$$\ln\gamma_M = z_M^2 F + \sum_a m_a\left(2B_{Ma} + ZC_{Ma}\right) + \sum_c m_c\left(2\Phi_{Mc} + \sum_a m_a\Psi_{Mca}\right) + \sum_a\sum_{<a'} m_a m_{a'}\Psi_{Maa'} + z_M\sum_c\sum_a m_c m_a C_{ca}, \quad (5)$$

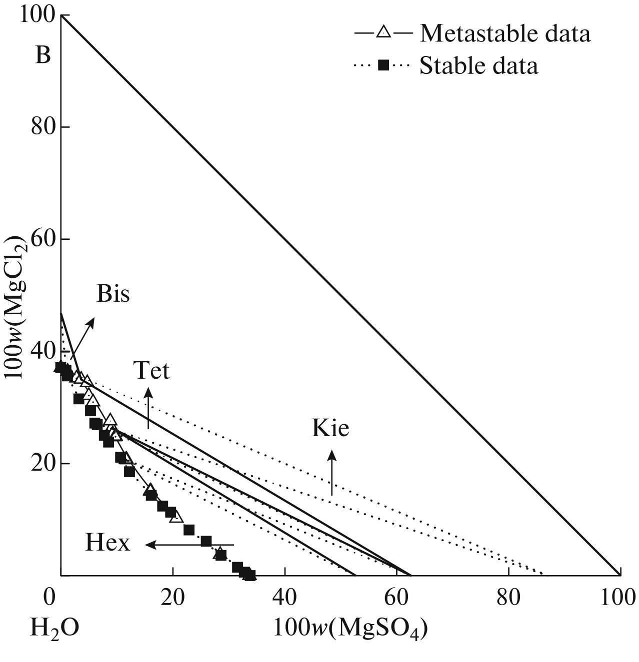

Fig. 2. Metastable and stable equilibrium phase diagram of the ternary system ($MgCl_2 + MgSO_4 + H_2O$) at 323.15 K; Hex, $MgSO_4 \cdot 6H_2O$; Tet, $MgSO_4 \cdot 4H_2O$; Kie, $MgSO_4 \cdot 4H_2O$; Bis, $MgCl_2 \cdot 6H_2O$.

$$\ln\gamma_X = z_X^2 F + \sum_c m_c\left(2B_{cX} + ZC_{cX}\right) + \sum_a m_a\left(2\Phi_{Xa} + \sum_c m_c\Psi_{cXa}\right) + \sum_c\sum_{<c'} m_c m_{c'}\Psi_{cc'X} + |z_X|\sum_c\sum_a m_c m_a C_{ca}. \quad (6)$$

In expressions (4) to (6), M, C and C' represent cations, X, A and A' are 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 expressions (4) to (6), for example, F, C, Z, A^{ϕ}, Ψ, Φ, B^{ϕ}, and B, are all described in references [9–11].

According to the Pitzer and HW model, the activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}, $\theta_{cc'}$ and $\psi_{cc'a}$; $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} 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. The K_{sp} can be calculated with the Pitzer parameters and solubility data with the Eqs. (1)–(6), which can be called method of the activity product constant. By combining the Pitzer parameters and the equilibrium constants of single salts, the solubility data of the ternary system can be calculated.

The Pitzer single salt parameters, mixing ion-interaction parameters and Debye–Hückel parameter A^{ϕ} = 0.410330 at 323.15 K were calculated with the temperature-dependent equations from the literature [12]. And all the parameters used in the prediction are presented in Table 2. The average metastable equilibrium constants of the crystallized single salts of $MgSO_4 \cdot 6H_2O$, $MgSO_4 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ were fitted with the method of the activity product constant, which correspond to −3.97, −2.64 and 9.83. The uncertainties of the average equilibrium constants for $MgSO_4 \cdot 6H_2O$, $MgSO_4 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ are ±0.13, ±0.10 and ±0.01, respectively. Combining the parameters noted and the equilibrium constants of single salts, the solubilities of the ternary system were calculated. It should be noted that solutes below their saturation molalities were fixed at continuous values

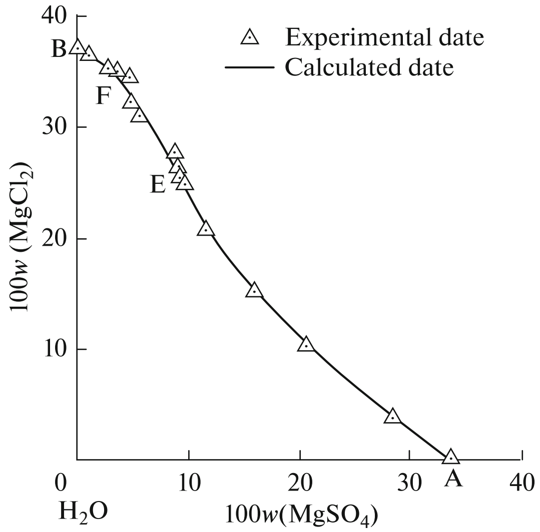

Fig. 3. Comparison of the experimental and calculated metastable phase diagram of the ternary system ($MgCl_2$ + $MgSO_4$ + H_2O) at 323.15 K.

and the saturated solutes' solubilities were calculated. The comparison of calculated and experimental solubilities at the invariant points of the ternary system is shown in Table 3. Based on the calculated and experimental data, the phase diagrams are shown in Fig. 3. The relative deviations between the calculated and measured solubilities ((calculated solubility – measured solubility)/measured solubility) are less than 0.05 in the system. The calculated phase diagram and experimental phase diagram are found to be in good agreement, which confirms that the equilibrium constants of equilibrium solid salts obtained in this work are reliable for predicting the metastable solubilities of the systems.

CONCLUSIONS

The solubilities and solution densities of the metastable equilibria of the ternary system ($MgCl_2$ + $MgSO_4$ + H_2O) at 323.15 K were experimentally determined with the isothermal evaporation method. In the metastable phase diagram of the system at 323.15 K, there are two invariant points, three univariant curves, and three crystallizing regions corresponding to $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 4H_2O$ and $MgSO_4 \cdot 6H_2O$. When compared with the stable diagram, the zone of kieserite disappears, the areas of the metastable crystallization regions of $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 4H_2O$ and $MgSO_4 \cdot 6H_2O$ are bigger than those in stable phase diagram. The calculated solubilities in the metastable ternary system are in good agreement with the experimental values.

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