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Measurement and thermodynamic model study on equilibrium solubility in the aqueous system of magnesium chloride and magnesium bromide

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ABSTRACT

Solubilities of the ternary system $MgCl_2$–$MgBr_2$–H_2O at T=(288.15, 308.15, 323.15 and 333.15) K were investigated, and the crystallization behaviour of solid solution $Mg(Cl,Br)_2 \cdot 6H_2O$ was established. Combining our experimental results with other experimental data available in the literature at T=(298.15 and 313.15) K, the pure electrolyte solution parameters for binary systems, the T-variation mixing parameters $\theta_{Cl,Br}$ and $\psi_{Mg,Cl,Br}$ and the equilibrium constants equations of the solid solution were obtained. Based on Pitzer model and Harvie–Weare solubility approach, the solubility modelling approach achieved a very good agreement with chloride and bromide salts equilibrium solubility data. Temperature-dependent equation in the system provides reasonable mineral solubility at T=(288.15–333.15) K. This model expands the solubility calculation in the systems containing solid solution by evaluating chloride–bromide mixing solution parameters. Limitations of the mixed solution models due to data insufficiencies are discussed.

1. Introduction

The brines with bromine are widely distributed in the area of Qinghai-Tibet Plateau of China and Sichuan basin [1]. Recent field observations show that hydrothermal waters can be strongly enriched with bromide compare to the sea water [2,3]. Leybourne and Goodfellow [3] suggested that "elevated Br/Cl ratios of saline waters compared to sea-water may be explained by differential uptake of Br and Cl during groundwater evolution through water–rock reaction". The phase equilibria and the phase diagrams are both the theoretical foundation for exploitation of the brine resources and describing the geochemical behavior of brine and mineral system. Therefore, the investigation of the thermodynamics and phase diagram of the systems containing bromine are valuable in providing the theoretic foundation and scientific guidance in the comprehensive exploitation of the bromine resources effectively.

Chloride ion and bromide ions have the same chemical properties in the solution for that chlorine and bromine are in the same group of the periodic table, so chlorine and bromine can easily form to the solid solution. Moreover, the concentration is difficult to determine when chlorine and bromine coexist in the solution [4]. There are several studies on the solubility of the system $MgCl_2$–$MgBr_2$–H_2O in the literatures at T=(273.15 [5], 298.15 [6,7] and 308.15 K [5]). The solid solution $Mg(Cl,Br)_2 \cdot 6H_2O$, was found to form in the system, but the composition of $Mg(Cl,Br)_2 \cdot 6H_2O$ was not measured and the solubility data reported are not accurate and complete. Qiu et al. [8] and Weng [9] gave a detailed study on the system at T=(298.15 and 313.15) K. It is found that the composition of $Mg(Cl,Br)_2 \cdot 6H_2O$ is continuous from $MgCl_2$ to $MgBr_2$, the molecular formula of $Mg(Cl,Br)_2 \cdot 6H_2O$ can be written as $Mg(Cl_{1-N},Br_N)_2 \cdot 6H_2O$, where N is from 0 to 1. However, there are no reports in the literature about the system at the other temperatures.

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 [10]. Pitzer developed an ion-interaction model and published a series of papers [11,12],

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which gave a set of expressions for the osmotic coefficients of a solution and the mean activity coefficients of electrolytes in solution. On the basis of the semi-empirical equations of Pitzer, Harvie and Weare have developed the chemical equilibrium model, which are more convenient to use in solubility calculations [13,14]. Using Pitzer model and the extended Harvie–Weare (HW) solubility approach, the solubilities of many systems were predicted [15–18], and these predictions demonstrated that the Pitzer model and HW solubility approach could be expanded to calculate solubility in complex brines accurately and to predict the behaviour of natural fluids.

Comprehensive thermodynamic models that accurately predict the aqueous chemistry of bromides and the solubilities of bromide minerals as a function of composition and temperature are critical to understanding many important geochemical processes. Christov [19–23] gave the new thermodynamic model for the mixed systems Na+K+Ca+Br+SO_4+H_2O and Na+K+Mg+Ca+Br+H_2O to high solution concentration within the temperature range (273.15–373.15) K, which incorporates the Pitzer solution equations. Also some models were constructed for the system containing solid solution. Hu et al. [24] calculated the solubility of KCl–CsCl–H_2O system with the assumption that there is no solid solution in the system, so the calculated data did not agree well with the experimental data. Weng [9] measured the composition of the solid solution $Mg(Cl,Br)_2 \cdot 6H_2O$ in the system $MgCl_2$–$MgBr_2$–H_2O at 313.15 K and gave the calculation for the system using the equilibrium constant equations of the solid solution. Although the calculation agrees well with the experimental, there are great deviation in calculating the solubilities of the more complicated systems for that the mixing ion-interaction parameters $\theta_{Cl,Br}$ and $\psi_{Mg,Cl,Br}$ are considered as zero.

In this paper, the solubilities and the composition of the solid solution in the ternary system $MgCl_2$–$MgBr_2$–H_2O were determined at T=(288.15, 308.15, 323.15 and 333.15) K using the isothermal dissolution method. A chemical equilibrium model, incorporating the Pitzer model, the extended HW solubility approach and the T-variation mixing chloride–bromide interaction parameters, to high solution concentration over the T=(288.15–333.15) K temperature range is described. To validate the model, the solubility predictions in the system are compared with those given in the study or the literatures.

2. Experimental

The solubility data of $MgCl_2$–$MgBr_2$–H_2O system are critical for developing a temperature variable ion-interaction model, which describe solid–liquid equilibria of chloride and bromide minerals in brine system. Although the detailed solubility data at T=(298.15 and 313.15) K are available in the literature [9,10], they are not enough at all. To extend with temperature the application range of the solid solution model, the solubilities of the system at T=(288.15, 308.15, 323.15 and 333.15) K were investigated. The solubility of the ternary system was determined by the isothermal dissolution method described in our previous studies [25,26]. All the analytical grade chemicals were re-crystallized before usage, which were obtained from the Tianjin Kermel Chemical Reagent Manufactory or the Shanghai Xinbao Fine Chemical Plant, including bischofite ($MgCl_2 \cdot 6H_2O$, in mass fraction 0.99) and magnesium bromide hexahydrate ($MgBr_2 \cdot 6H_2O$, in mass fraction 0.98). Doubly deionized water (DDW) with conductivity less than 1.2×10^{-4} S m^{-1} at 298.15 K was used to prepare the series of artificial synthesized brines and for chemical analysis. According to the composition at the phase equilibrium, a series of artificial synthesized brines by mixing appropriate amount of salts and DDW were prepared, and loaded into clean polyethylene bottles. The bottles were capped tightly and placed in the thermostatic rotary shaker, which was controlled at a required temperature with a precision within $\pm$0.1 K and rotation speed of 120 rpm to accelerate the equilibrium of the complexes. The rotary system was allowed to rest for 1 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, which was then used to measure the refractive index. If the refractive index became a constant, a sample of about 5.0-mL was taken to 250-mL final volume using a volumetric flask filled with DDW twice at different time, then a quantitative analysis was performed. If the compositions of the liquid phase were nearly the same within $\pm$0.3% in mass fraction, then it was the equilibrium point. Meanwhile, the solid phase was separated from the solution and approximately evaluated. Chloride and bromide ions were determined by volumetric procedures titration with indicators with a precision of $\pm$0.3% in mass fraction [27]. Based on the Schreinemaker's method of wet residues [28], the solid phase mineral point lies in the extension line of the two composition points of the liquid phase and the wet residual. Also the solid solution $Mg(Cl,Br)_2 \cdot 6H_2O$ would be in the line of the two composition points of $MgCl_2 \cdot 6H_2O$ and $MgBr_2 \cdot 6H_2O$, so the composition of the solid solution would be calculated, and N, which is in the chemical formula $Mg(Cl_{1-N},Br_N)_2 \cdot 6H_2O$ would be obtained.

The solubilities of the $MgCl_2$–$MgBr_2$–H_2O system at T=(288.15, 308.15, 323.15 and 333.15) K are presented in Tables 1–4. Each of the experimental results represents the arithmetical mean of two parallel determinations. There is only one crystallization field of the solid solution $Mg(Cl,Br)_2 \cdot 6H_2O$. N, which is in the chemical formula $Mg(Cl_{1-N},Br_N)_2 \cdot 6H_2O$, is continuous from 0 to 1. The solubility changes at different temperatures show a similar trend. The solubilities become larger as the temperature increases, which indicates that the crystallized region of $Mg(Cl,Br)_2 \cdot 6H_2O$ become smaller.

3. Modeling approach

Pitzer model and HW solubility approach was used for the aqueous solutions in this study, which incorporate the concentration dependent equations showing the specific interactions of the solutes [11–14]. Since these equations are based on the excess free energy, all the activity expressions are consistent, which will be ready for the application of different kinds of data (e.g., the solubility data) in the parameter evaluations and the calculation of other thermodynamic functions. Using the activity coefficients

Table 1
Experimental solubility data of the system ($MgCl_2$+$MgBr_2$+H_2O) at 288.15 K.

No.	Liquid phase, 10^2 w		Liquid phase, molality (m mol^{-1} kg^{-1})		Wet solid phase, 10^2 w		Solid phase
	$MgCl_2$	$MgBr_2$	$MgCl_2$	$MgBr_2$	$MgCl_2$	$MgBr_2$	
1	0.00	49.70	0.00	5.37	0.00	60.15	$MgBr_2 \cdot 6H_2O$
2	4.42	43.73	0.90	4.58	3.76	51.82	$Mg(Cl,Br)_2 \cdot 6H_2O$
3	8.04	38.81	1.59	3.97	6.30	48.24	$Mg(Cl,Br)_2 \cdot 6H_2O$
4	11.39	34.38	2.21	3.44	12.59	36.66	$Mg(Cl,Br)_2 \cdot 6H_2O$
5	13.83	31.82	2.67	3.18	14.83	34.44	$Mg(Cl,Br)_2 \cdot 6H_2O$
6	15.67	28.60	2.95	2.79	16.79	35.04	$Mg(Cl,Br)_2 \cdot 6H_2O$
7	16.80	28.04	3.2	2.76	22.01	27.74	$Mg(Cl,Br)_2 \cdot 6H_2O$
8	18.50	25.28	3.46	2.44	25.82	22.18	$Mg(Cl,Br)_2 \cdot 6H_2O$
9	21.77	20.03	3.93	1.87	26.90	22.17	$Mg(Cl,Br)_2 \cdot 6H_2O$
10	24.89	15.11	4.36	1.37	32.15	12.40	$Mg(Cl,Br)_2 \cdot 6H_2O$
11	27.24	12.85	4.78	1.16	34.36	10.08	$Mg(Cl,Br)_2 \cdot 6H_2O$
12	30.29	8.62	5.21	0.77	40.38	8.00	$Mg(Cl,Br)_2 \cdot 6H_2O$
13	35.22	0.00	5.71	0.00	42.58	0.00	$MgCl_2 \cdot 6H_2O$