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Experiment and Pitzer Model Prediction for the Solid + Liquid Equilibria of the Ternary System LiCl–CaCl₂–H₂O

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1 Introduction

Lithium resources are widely distributed in the oilfield brine from the Nanyishan district in the Qaidam Basin (Fan et al., 2007). The investigation of the thermodynamics and phase diagram of the brine system is valuable in providing the theoretic foundation and scientific guidance in the comprehensive exploitation of the mixture salts effectively. Comprehensive thermodynamic models that accurately predict lithium aqueous chemistry and the solubility of the lithium mineral as a function of composition and from low to high temperature are critical for understanding many important geochemical processes (Meng et al., 2013). Although BET thermodynamic model of the ternary system LiCl–CaCl₂–H₂O have been studied (Zeng et al., 2008), the Pitzer chemical model for the system are not reported in the literature.

2 Methodology

The isothermal dissolution method was used to determine the solubilities of the aqueous ternary system LiCl–CaCl₂–H₂O at 288.15 K. A thermostatic shaker (model HXC-500-12AE) with an temperature uncertainty ± 0.1 K was used for the measurement of phase equilibrium. The bottles with appropriate quantity of salts and DDW were placed in the thermostatic rotary shaker. When the equilibrium achieved, the composition of the liquid phase and wet residues were determined. Then the phase diagram of the system can be plotted using the solubility data.

The solubility modelling approach based on fundamental Pitzer specific interaction equations was

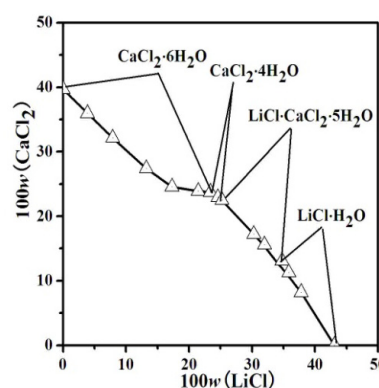


Fig. 1. Comparison of the experimental and calculated phase diagrams of the stable ternary system LiCl–CaCl₂–H₂O at 288.15 K; Δ , experimental data; —, calculated isotherm curve.

employed to fit the Pitzer parameters (Pitzer, 1995). The chemical model, which combined the Pitzer parameters and the equilibrium constants of the equilibrium solid phases, was constructed. The solubilities for the ternary system, the mean activity coefficients of lithium chloride and calcium chloride and the water activities in the solutions at 288.15 and 323.15 K were also calculated to validate the accuracy of the model.

3 Results and discussion

Solubilities of the ternary system LiCl–CaCl₂–H₂O at 288.15 K were investigated as shown in Figure 1. There are three invariant points, four isothermal solubility curves, and four crystallizing zones corresponding to CaCl₂·6H₂O, CaCl₂·4H₂O, LiCl·CaCl₂·4H₂O, LiCl·H₂O. No solid solutions are found in the ternary system.

Combined our experimental results with other experimental data available in the literature at 273.15, 288.15, 298.15, 313.15 and 323.15 K (Zeng, 2008;

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Howard & Silcock, 1979), the single-salt parameters available in the literature (Greenberg & Møller, 1989), the mixed ion-interaction parameters $\theta_{\text{Li,Ca}}$ and $\psi_{\text{Li,Ca,Cl}}$ were fitted by a multiple linear regression procedure or temperature extrapolation method. According to the Pitzer parameters and the experimental solubilities of the ternary system, the equilibrium constants of the equilibrium solid phases were obtained with the method of the activity product constant in each stable solution. Then the temperature-dependent equations for the mixed parameters and equilibrium constants of the solids were built into the model by adjusting selected constants in the following equation 1. Figure 2 shows the mixed parameters $\theta_{\text{Li,Ca}}$ and $\psi_{\text{Li,Ca,Cl}}$ versus temperature.

$$P(T) = a_1 + a_2/T/K + a_3(T/K)^2 + a_4(T/K)^3 \quad (1)$$

The solubilities for the ternary system $\text{LiCl}-\text{CaCl}_2-\text{H}_2\text{O}$ were calculated using the Pitzer model to validate the accuracy of the model. The calculated phase diagram and the experimental phase diagram at 288.15 K in Figure 1 are found to be in good agreement, which indicates that the model obtained in this work is reliable.

To check the reliability of the model, the water activities were also calculated using the experimental concentration data in the literature (Filippov & Mihelbson, 1977) at 298.15 K. The calculated and the experimental water activities agree well, which also validate the accuracy of the model.

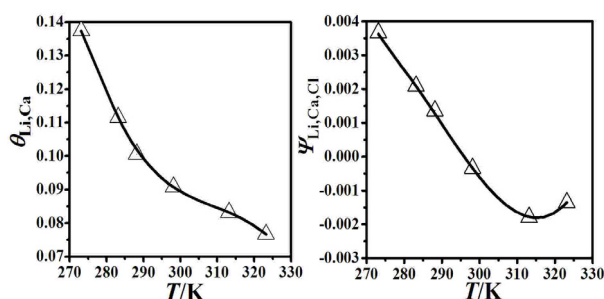


Fig. 2. The mixed parameters $\theta_{\text{Li,Ca}}$ and $\psi_{\text{Li,Ca,Cl}}$ versus temperature diagrams from 273.15 K to 323.15 K. Δ , calculated data; —, calculated curve.

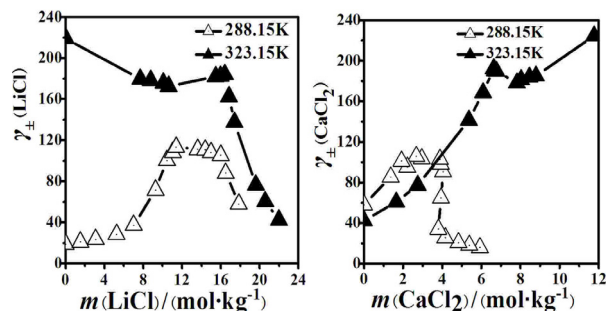


Fig. 3. Mean activity ($\gamma_{\pm}$) calculated from the model of lithium chloride and calcium chloride in the $\text{LiCl}-\text{CaCl}_2-\text{H}_2\text{O}$ system at 288.15 and 323.15 K

The mean activity coefficients of lithium chloride and calcium chloride and the water activities in the solutions up to the saturation molality at 288.15 and 323.15 K were also calculated, and shown in Figures 3 and 4. The curve trends of mean activity coefficients of lithium chloride and calcium chloride at 288.15 and 323.15 K are similar. However, the mean activity coefficients in the system at 323.15 K are larger than those in the system at 288.15 K in Figure 3, while the water activities at 323.15 K is smaller than that at 288.15 K in Figure 4.

4 Summary and Conclusions

Solubilities of the ternary system $\text{LiCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 288.15 K were investigated experimentally. Based on fundamental Pitzer specific interaction equations, the temperature-dependent for the mixed ion-interaction parameters $\theta_{\text{Li,Ca}}$, $\psi_{\text{Li,Ca,Cl}}$ and the equilibrium constants of the solids were obtained. Then the chemical model for the system $\text{LiCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at $T = (273.15 \text{ to } 323.15 \text{ K})$, which contains the Pitzer parameters and the equilibrium constant equations was constructed. The solubility modelling approach achieved a very good agreement with lithium and calcium salts equilibrium solubility data at 288.15 K. The mean activity coefficients of lithium chloride and calcium chloride and the water activities in the solutions up to the saturation molality at 288.15 and 323.15 K were also calculated using the model. This model expands the solubility calculation in the system by evaluating lithium-calcium mixed ion-interaction parameters.

Key words: Lithium chloride, Calcium chloride, Thermodynamic model, Pitzer model.

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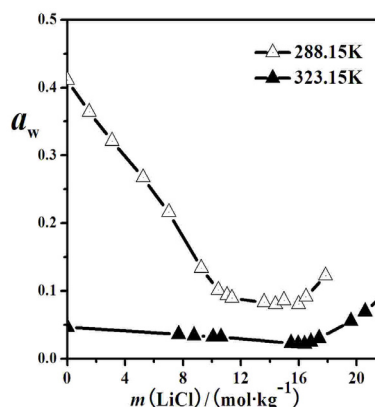


Fig. 4. Water activity (a_w) calculated from the model of the $\text{LiCl}-\text{CaCl}_2-\text{H}_2\text{O}$ system at 288.15 and 323.15 K

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