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## The Metastable Phase Equilibria of the MeX - MgCl<sub>2</sub> - H<sub>2</sub>O Systems

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### 1 Introduction

The Pingluoba brine, which characterized as high concentration with sodium, potassium, boron, lithium, and rubidium, possess great development value. The main composition of the brine can be summarized to the complex multi - component system (Li - Na - K - Mg - Rb - Cl - B<sub>4</sub>O<sub>7</sub>). In this system, the carnallite type double salts MeCl·MgCl<sub>2</sub>·H<sub>2</sub>O (Me = K<sup>+</sup>, Rb<sup>+</sup>, Li(H<sub>2</sub>O)<sup>+</sup>) can be easily formed. The investigation of the solubility diagrams of carnallite type double salts system is of practical importance in comprehensive utilization of brine.

Emons studied the mechanism and kinetics of formation and decomposition of carnallite double salts (Emons, 1988). Christov investigated the effect of temperature on the solubility of carnallite type double salts (Christov et al., 1995). However, these work focused on the ternary system MeX - MgX<sub>2</sub> - H<sub>2</sub>O, the phase equilibria about quaternary or quinary carnallite double salts system are less reported. Accordingly, the phase equilibria in the quaternary carnallite type double salt system have been done by our research group.

### 2 Results and Discussion

The isothermal evaporation method was employed for the metastable phase equilibria research. Based on the experimental data, the related metastable phase diagrams were constructed. From the diagrams, we can get the information about crystalloid forms, crystallization path, and crystallization zones of different salts.

There are two carnallite type double salts rubidium carnallite (RbCl·MgCl<sub>2</sub>·6H<sub>2</sub>O), potassium carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O) and a solid solution [(K, Rb)Cl] formed in the metastable phase diagram of quaternary system K<sup>+</sup>, Rb<sup>+</sup>, Mg<sup>2+</sup> // Cl<sup>-</sup> - H<sub>2</sub>O at 323 K (Jiang et al., 2013). The solid solution has the largest crystallization field almost occupies the entire phase region, the salt MgCl<sub>2</sub>·6H<sub>2</sub>O has the smallest crystallization field. The

crystallization zone of rubidium carnallite is larger than that of potassium carnallite.

In the metastable phase diagram of quaternary system Li<sup>+</sup>, Rb<sup>+</sup>, Mg<sup>2+</sup> // Cl<sup>-</sup> - H<sub>2</sub>O at 323 K (Yu et al., 2014), there are two carnallite type double salts lithium carnallite (LiCl·MgCl<sub>2</sub>·7H<sub>2</sub>O) and rubidium carnallite (RbCl·MgCl<sub>2</sub>·6H<sub>2</sub>O) formed. The scope of crystallization areas is in the follow order: RbCl·MgCl<sub>2</sub>·6H<sub>2</sub>O > RbCl > LiCl·H<sub>2</sub>O > MgCl<sub>2</sub>·6H<sub>2</sub>O > LiCl·MgCl<sub>2</sub>·7H<sub>2</sub>O.

There are two carnallite type double salts lithium carnallite (LiCl·MgCl<sub>2</sub>·7H<sub>2</sub>O), potassium carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O) formed in the metastable phase diagram of quaternary system Li<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> // Cl<sup>-</sup> - H<sub>2</sub>O at 323 K (Yu et al., 2014). Salt KCl has the largest crystallization region; it contains almost 95 % of the general crystallization field. The crystallization field of potassium carnallite is larger than that of lithium carnallite.

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### References

- Christov C., Balarew C., 1995. Effect of temperature on the solubility of carnallite type double salts. *J. Solution Chem*, 24: 1171–1181.
- Emons H.H., 1988. Mechanism and kinetics of formation and decomposition of carnallite double salts. *J. Therm. Anal*, 33: 113–120.
- Jiang Dongbo, Zeng Ying and Yu Xudong, 2013. Metastable phase equilibria for the quaternary system containing potassium, magnesium, rubidium and chloride at 323.15 K. *Fluid Phase Equilibria*, 349: 67–70.

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