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Solid-liquid Phase Equilibria of the Aqueous Systems Containing Lithium, Magnesium and Borate Ions

Yun Song¹, Dong Zhao¹, Xuemin Du¹, Shiqiang Wang^{1, 2, *}, Yafei Guo^{1, 2} and Tianlong Deng^{1, 2}

 ¹College of Chemical Engineering and Materials Science, Tianjin University of Science and Technology, Tianjin 300457, P. R. China
²Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin 300457, P. R. China

*Corresponding author e-mail: wangshiqiang@tust.edu.cn

Abstract. It is well known that the phase chemistry is of great importance in the fields of chemistry, chemical engineering, and the separation and purification of minerals from brine. To effectively employ the resources containing lithium, magnesium and borate, the study on phase equilibrium is essential to the comprehensive utilization of the Salt Lake resources. In this paper, progresses on phase equilibria of salt-water systems containing lithium, magnesium and borate were presented.

1. Introduction

The Qaidam Basin located in the Qinghai-Tibet Plateau in China, is famous for its high concentrations of lithium, magnesium, and borate resources in Salt Lake brine. Therefore, research on metastable phase equilibrium and stable phase equilibrium containing lithium, magnesium and borate is indispensable basic work for exploiting salt lake resources, working out schemes for comprehensive utilization of bittern, and revealing the geochemical behavior of the salt lake brine.

2. Phase equilibria of systems containing lithium, magnesium and borate

2.1. The ternary systems

To effectively utilize and exploit the Salt Lake brine, some related salt-water systems had been studied. Stable phase equilibrium in the aqueous ternary system Li⁺, $Mg^{2+}//borate-H_2O$ at 323 K had been researched by Li et al. [1], and the experimental results showed that the phase diagram consists of one invariant point, two univariate curves, and two crystallization regions which corresponding to single salts hungchaoite (MgB₄O₇·9H₂O) and lithium tetraborate trihydrate (Li₂B₄O₇·3H₂O), respectively. The crystallization region of MgB₄O₇·9H₂O is larger than that of Li₂B₄O₇·3H₂O. Isopiestic studies of thermodynamic properties and representation with ion-interaction model for Li₂B₄O₇-MgCl₂-H₂O system at 298.15 K had been studied by Zhang et al. [2]. The isopiestic molalities and the water activities have been measured by isopiestic method, the water vapor pressures and the osmotic coefficients have been calculated from the measurements in the ion-strength range from 0.0581 mol·kg⁻¹ to 0.6320 mol·kg⁻¹ at 298.15 K for the system Li-Mg-Cl-borate-H₂O. Phase equilibrium of the quaternary systems containing lithium, magnesium and borate ions at 298.15 K had been discussed

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by Jing et al. [3]. This system belongs to simple eutectic type, and neither double salt nor solid solution was generated. There was one invariant point, two univariate curves, two crystallization regions corresponding to $Li_2B_4O_7 \cdot 3H_2O$ and $Mg_2B_6O_{11} \cdot 15H_2O$. The concentration of MgB_4O_7 decreased with the increasing concentration of $Li_2B_4O_7$, which means that $Li_2B_4O_7$ had a strong salting-out effect on MgB_4O_7 . It can be found that $MgB_4O_7 \cdot 9H_2O$ is unstable and easily converts into $Mg_2B_6O_{11} \cdot 15H_2O$. Phase equilibrium in the ternary system $Li_2B_4O_7$ - MgB_4O_7 - H_2O at 273 K and 298.15 K had been considered by the isothermal dissolution equilibrium method [4, 5]. Based on the experimental data, the phase diagram and physicochemical properties versus composition diagrams were depicted. The system belongs to the simple eutectic type, and neither complex salt nor solid solution is formed. It were composed of one invariant point, two univariate solubility curves and two crystallization regions corresponding to $Li_2B_4O_7 \cdot 3H_2O$ and $MgB_4O_7 \cdot 9H_2O$, respectively. And the crystallization regions are larger at 298.15 K than those at 273 K, because the solubilities of these salts in water increase with the rising of temperature.

2.2. The quaternary systems

Metastable phase equilibrium of the quaternary system MgB4O7-Na2B4O7-Li2B4O7-H2O at 288 K had been studied by the method of isothermal evaporation [6]. Solubilities and densities of the metastable equilibrium solution were determined. The results showed that the system was simple eutectic type and no double salt formed. There were one invariant point, three univariate curves and three crystallization regions corresponding to MgB₄O₇·9H₂O, Li₂B₄O₇·3H₂O and Na₂B₄O₇·10H₂O. The results show that $Na_2B_4O_7$ had the salting-out effect on $Li_2B_4O_7$ but salting-in effect on MgB₄O₇. The density increased with increasing solution concentration, and reached the maximum at the invariant point. The system Li⁺, Mg²⁺//SO4²⁻, B4O7²⁻-H2O at 288 K, 298 K, 308 K and 323 K were researched [7-10]. The results showed that there were no double salt or solid solution at different temperatures. And it had two invariant points, five univariate curves and four regions of crystallization corresponding to Li₂B₄O₇·3H₂O, Li₂SO₄·H₂O, MgB₄O₇·9H₂O and MgSO₄·7H₂O, respectively. The crystallization region of MgB₄ O_7 ·9H₂O is the largest because of its minimum solubility, while the sulfate which had greater solubility and the smallest crystallization region. The crystallization region of magnesium sulfate is MgSO₄·7H₂O at 288 K, 298 K and 308 K but is MgSO₄·6H₂O at 323 K. The crystallization region of Li₂SO₄·H₂O was larger and Li₂B₄O₇·3H₂O was smaller at 323 K. The solubilities and densities of the quaternary system K₂B₄O₇-Li₂B₄O₇-MgB₄O₇-H₂O at 288 K and 348 K had been researched by the isothermal dissolution [11, 12]. This system belongs to a simple eutectic type, and no double salt or solid solution was formed. This system had one invariant point, three univariate curves and three regions of crystallization corresponding to Li₂B₄O₇·3H₂O, K₂B₄O₇·4H₂O and MgB₄O₇·9H₂O. In these crystallization regions, K₂B₄O₇·4H₂O is the smallest, corresponding to the maximum solubility. While $MgB_4O_7 \cdot 9H_2O$ is the largest, corresponding to the minimum solubility. Comparisons on the stable phase diagrams at 288 K and 348 K show that the crystallization regions of MgB₄O₇·9H₂O was decreased at 348 K, but K₂B₄O₇·4H₂O and Li₂B₄O₇·3H₂O enlarged at 348 K. Solid-liquid equilibrium for the quaternary system Li⁺, Mg²⁺//Cl⁻, B₄O₇²⁻-H₂O at 298.15 K had been researched by Wang et al. [13]. According to the experimental results, there are three co-saturated invariant points, seven univariate solubility isotherm curves, and five crystallization regions, which correspond to lithium chloride monohydrate, lithium tetraborate, hungchaoite, bischofite and lithium carnallite. In this system, MgB₄O₇·9H₂O is stable and cannot convert. Compared the crystallization regions at 288.15 K. Li₂B₄O₇·3H₂O decreases sharply, while MgB₄O₇·9H₂O increases obviously, MgCl₂·6H₂O increases slightly, and the others change seldom.

The quaternary system Li^+ , Rb^+ , $Mg^{2+//borate-H_2O}$ at 348 K had been studied by the isothermal dissolution [14]. The phase diagram consists of one invariant point, three univariant curves and three crystallization regions which correspond to $MgB_4O_7 \cdot 9H_2O$, $RbB_5O_8 \cdot 4H_2O$, and $Li_2B_4O_7 \cdot 3H_2O$. The $Li_2B_4O_7 \cdot 3H_2O$ has the smallest crystallization region, but $RbB_5O_8 \cdot 4H_2O$ has the largest, so rubidium pentaborate can be more easily separated from solution than other salts of this system at 348 K.

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2.3. The quinary systems

Study on equilibrium in quinary system Li⁺, K⁺, Mg²⁺//SO₄²⁻, B₄O₇²⁻-H2O at 288 K had been studied by the isothermal dissolution [15]. And this system have double salt. According to the experimental results, there are six co-saturated invariant points, nine univariate solubility isotherm curves, and seven crystallization regions, which correspond to K₂B₄O₇·4H₂O, Li₂SO₄·H₂O, Li₂B₄O₇·3H₂O, K₂SO₄, MgSO₄·7H₂O, K₂SO₄·MgSO₄·6H₂O and KLiSO₄. In this system, the solubility of Li₂SO₄ is the largest, and it has strong salting-out effect on other salts. Wei studied on the metastable phase equilibrium of Li⁺, K⁺, Mg²⁺, Na⁺//B₄O₇²⁻-H₂O at 288.15 K by isothermal evaporation method [16]. According to the experimental results, this system have no double salt or solid solution. And it has one co-saturated invariant point, three univariate solubility isotherm curves and three crystallization regions, which correspond to K₂B₄O₇·4H₂O, LiBO₂·8H₂O and MgB₄O₇·9H₂O. The results show that the interface stability phenomenon of magnesium borate is easily affected by the ions in the solution, while the lithium borate is easy to dissolve into LiBO₂·8H₂O in the metastable equilibrium.

Li studied on phase equilibrium of quinary system Li⁺, Mg²⁺//SO₄²⁻, Cl⁻, B₄O₇²⁻H2O at 288.15 K by isothermal dissolution equilibrium method [17]. This system have double salt which is LiCl·MgCl₂·7H₂O. According to the experimental results, this system have four co-saturated invariant point, four univariate solubility isotherm curves and six crystallization regions, which correspond to LiCl·H₂O, Li₂SO₄·H₂O, Li₂B₄O₇·3H₂O, MgCl₂·6H₂O, MgSO₄·7H₂O and LiCl·MgCl₂·7H₂O. Among them, the solubility of LiCl was the largest, which had a strong salting out effect on other salts. Because of the common ion effect, it had a strong salting out effect on Li₂SO₄. The phase equilibrium in the quinary system Li⁺, Mg²⁺//SO₄²⁻, Cl⁻, B₄O₇²⁻-H₂O at 298.15 K and 323.15 K had been reported by Sun and Meng et al. [18, 19], respectively. This system at 323.15 K have eight crystallization correspond to LiCl·H₂O, Li₂B₄O₇·3H₂O, MgCl₂·6H₂O, regions, which MgSO₄· $6H_2O_2$ LiCl·MgCl₂·7H₂O, MgSO₄·4H₂O, MgSO₄·H₂O and magnesium borate crystals. Because of the polymerization and depolymerization of boron oxygen anion, the crystalline form of magnesium borate is more complex. When the concentration of MgCl₂ in the liquid phase is low, MgB₄O₇·9H₂O has the tendency to convert $Mg_2B_6O_{11}$ 15H₂O with polymerization, and when the concentration of MgCl₂ in the liquid phase is high, MgB₄O₇·9H₂O has the tendency to convert MgB₆O₁₀·7.5H₂O with polymerization. But there are still some complex solid phase for the unknown borate crystals. At the same time, the metastable phase equilibrium of the system was studied. The results showed that $Li_2B_4O_7$ and MgB₄O₇ could not be precipitated in the form of crystals, and finally the colloidal liquid was obtained. Comparing the stability of the system at different temperatures, with the increase of temperature, the degree of conversion of magnesium borate gradually complicated.

Studies on the stable equilibrium of the quinary system Li⁺, Rb⁺, Mg²⁺//Cl⁻, borate-H₂O at 323 K had been researched by isothermal dissolution [20]. And it has double salts which correspond to LiCl·MgCl₂·7H₂O and RbCl·MgCl₂·6H₂O. The space diagram consists of seven invariant points, twenty univariant curves and eight crystallization regions. In this paper, the crystallization regions of borate are five clustering structure and four clustering structure which correspond to RbB₅O₈·4H₂O and Li₂B₄O₇·3H₂O, MgB₄O₇·9H₂O, respectively. And the crystallization region of the borate is larger because of its smaller solubility and it is more complex. The quinary system Li⁺, K⁺, Rb⁺, Mg²⁺//borate-H₂O at 348.15 K had been discussed by isothermal dissolution [21]. The phase diagram consists of one invariant point, four univariant curves, and four crystallization regions which correspond to Li₂B₄O₇·3H₂O, K₂B₄O₇·4H₂O, RbB₅O₈·4H₂O, and MgB₄O₇·9H₂O.

3. Conclusion

There are a lot of lithium, magnesium and boron resources in Qinghai Saline Lake in China. It is urgent to develop the phase equilibrium at the different temperature as the theoretical guidance for the further extraction and extraction of inorganic mineral resources in Saline Lake. The results of references can be concluded as follows: (1) the temperatures reported on the stable phase equilibria containing lithium, magnesium and borate were focused on 288 K to 323 K while the metastable phase equilibria were relatively less. (2) the study of phase diagram has little social demand, and it is lack of

corresponding thermodynamic data, meanwhile the equilibrium solid phase lack of the use of polarizing microscope. (3) the crystallization region of magnesium-borate tends to be MgB₄O₇·9H₂O in the stable phase equilibria, and it was difficult to combine with other ions to form double salts. But in metastable system, the crystallization region of borate was $B_4O_7^{-2}$ and BO_2^{-2} .

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