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Solid-liquid Phase Equilibria in the Aqueous Ternary System Containing Lithium, Potassium, and Sulfate ions at 288.15 K

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1 Introduction

Salt lakes are widely distributed in the western of China, especially in the area of Qinghai-Xizang (Tibet) Plateau. A series of salt lakes in the Qaidam Basin, located in Qinghai Province, China, is famous for their abundance of lithium, potassium and boron resources (Zheng et al, 1988; Deng et al, 2012). It is well known that the thermodynamic phase equilibrium and phase diagrams play an important role in exploiting the brine resources and describing the geochemical behavior of brine and mineral system. The investigation of the thermodynamics and phase diagram of the system is of theoretical and practical importance (Wang et al, 2008, 2010; Gao et al, 2011; Liu et al, 2011; Deng et al, 2011).

2 Experimental

The equilibrium experiments in this work were conducted by the method of isothermal solution equilibrium. The samples of the ternary system were prepared by adding the second salt gradually to the binary saturation points at 288.15 K. The solid reagents and water are all put into a 100 ml glass bottle. Then all bottles are sealed and placed in the magnetic stirring thermostatic bath (HXC-500-12A). The solid-liquid mixtures in the bottles were stirring for one week to accelerate the establishment of equilibrium states. Experimental results show that the equilibrium states can be attained in 10–15 days under continuous stirring, and the time for the clarification of an aqueous solution is about 1 day. The solutions were taken out periodically for chemical analysis. If the solution composition does not change any more, the system can be considered to reach thermodynamic equilibrium. In this state, the solution

composition should represent that of saturated solution. Wet solid phase are separated from the solution by vacuum filtration using a glass sand core crucible, and dried for X-ray diffraction. Some clarified liquid phases were taken out for quantitative analysis, and some other solutions were used to measure the density and pH value. The solid phase minerals were evaluated with combined chemical analysis and observed with a BX51 digital polarizing microscope and X-ray powder diffraction.

The concentration of the K^+ ion in liquids and their corresponding wet solid phases were analyzed by gravimetric method of sodium tetraphenyl borate with a precision of $\pm 0.05\%$ in mass fraction. The SO_4^{2-} ion concentration was measured by gravimetric method of barium chloride with a precision within $\pm 0.3\%$ in mass fraction. The concentration of Li^+ was calculated by subtraction via charge balance and combined with analytical verified measurement occasionally by ICP-OES with a precision within $\pm 0.5\%$ in mass fraction (Analytical laboratory of Qinghai institute of salt lakes at

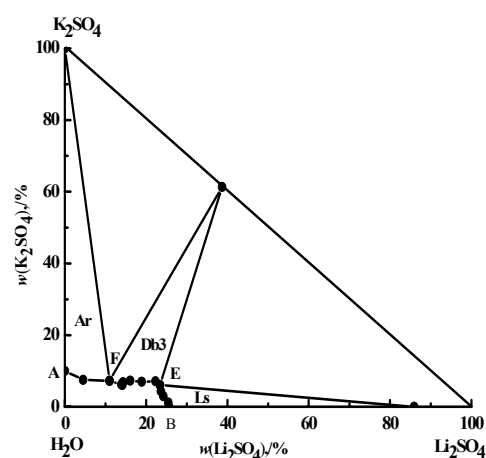


Fig. 1. Phase diagram of the ternary system Li_2SO_4 - K_2SO_4 - H_2O at 288.15 K. Ar- K_2SO_4 ; Db3- $Li_2SO_4 \cdot K_2SO_4$; Ls- $Li_2SO_4 \cdot H_2O$.

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CAS, 1988).

The measurements of the liquid-phase physicochemical properties were corresponding to density and pH value. The densities (ρ) were measured in triplicate using a high precision densimeter (DMA 4500, Anton Paar, Austria) with an uncertainty of $\pm 1.0 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. A PHSJ-5 digital acidometer was used for pH values of equilibrium solutions with an uncertainty of ± 0.01 , and the measurements was maintained at the desired temperature with $\pm 0.01 \text{ K}$ through control of the thermostat (K_2O -cc-NR, Huber, Germany).

The experimental data on the solubilities and the relevant physicochemical properties including density and pH value of the ternary system $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ at 288.15 K were determined experimentally. In the phase diagram of the ternary system at 288.15 K, there are two invariant point of E: $\text{Li}_2\text{SO}_4\text{--H}_2\text{O} + \text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4$, and the compositions of Li_2SO_4 and K_2SO_4 in the liquid phase with mass fraction (100w) are 24.24, 2.31; F: $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4 + \text{K}_2\text{SO}_4$, and the compositions of Li_2SO_4 and K_2SO_4 in the liquid phase with mass fraction (100w) are 10.97, 10.46, respectively. There are three variant curves, and three crystallizing zones corresponding to lithium sulphate monohydrate ($\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$), potassium sulphate (K_2SO_4), and double salts

lithium potassium sulphate ($\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4$). There were no solid solutions formed in this system, and it belongs to the incongruent double salts type.

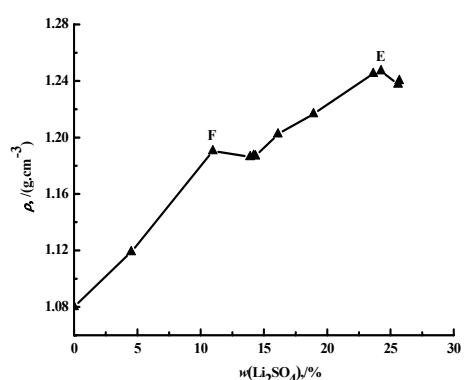
The relationship of the solution physicochemical properties (density and pH value) with the concentration of lithium sulphate in the ternary system $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ at 288.15 K was plotted in Figure 2. It was found that the solution density and pH value in the ternary system at the two temperatures changed regularly with an increase in the mass fraction of lithium sulphate. The solution densities from point A to point E in the phase regions of K_2SO_4 and $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4$ of the ternary system increased with the increasing concentration of lithium sulphate, and reached the maximum value at eutectic point E; and the solution pH value from point A to points F increased slowly, while increased sharply from points F to point B with the increasing concentration of lithium sulphate.

Acknowledgement

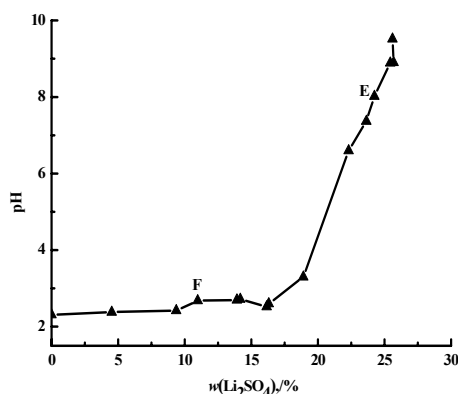
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(a) density vs. composition



(b) pH value vs. composition

Fig. 2. Physicochemical properties versus composition diagram for the ternary system $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ at 288.15 K.