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*** PHASE EQUILIBRIUM AND PHASE DIAGRAM FOR
THE QUATERNARY SYSTEM (Li⁺, K⁺//Cl⁻, SO₄²⁻-H₂O) AT 288.15 K**

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The phase and physicochemical properties diagrams of the quaternary system (Li⁺, K⁺//Cl⁻, SO₄²⁻-H₂O) at 288.15 K were constructed using the solubilities, densities, and refractive indices measured. In the phase diagrams of the system there are three invariant points, seven univariant isotherm dissolution curves, and five crystallization regions corresponding to

lithium chloride monohydrate ($\text{LiCl}\cdot\text{H}_2\text{O}$), lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$), potassium chloride (KCl), potassium sulfate (K_2SO_4), and double salt lithium potassium sulfate ($\text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$), where the double salt lithium potassium sulfate ($\text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$) is an incongruent double salt. The crystallization area of potassium sulfate (K_2SO_4) is the largest, and the crystallized zone of lithium chloride monohydrate ($\text{LiCl}\cdot\text{H}_2\text{O}$) is the smallest. These results indicate that potassium sulfate is easy to saturate and crystallize from solution and that lithium chloride has a high solubility during isothermal evaporation. The solution density and refractive index of the quaternary system change regularly with the increase of K^+ concentration.

Keywords: stable phase equilibrium; phase diagram; lithium sulfate double salt; potassium; crystallization; isotherm; refractive index; invariant points.

There are more than seven hundred salt lakes with an area larger than 1 km^2 in the Qinghai-Tibet Plateau. The Salt Lake of Qaidam Basin consists of a series of lakes including the Dong-Xi-Taijinaier Lake, Da-Xiao-Caidan Lake and Yiliping Lake, and is one of the subtypes of magnesium sulfate brines famous for its abundance of lithium, potassium, and boron resources [1-5]. The main components of its brines can be described with the $\text{Li}^+ + \text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Cl}^- + \text{SO}_4^{2-} + \text{borate} + \text{H}_2\text{O}$ system. It is well-known that phase diagrams and phase equilibria play an important role in exploiting brine resources and describing the geochemical behavior of brine mineral. To exploit the valuable brine resources economically, the phase equilibria and phase diagrams of brine systems containing boron at different temperatures are required.

In order to acquire the thermodynamic behaviors and exploit these valuable brine resources, the solid-liquid phase equilibria systems containing lithium have been studied, including three-, four-, and five-component systems ($\text{Li}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$) at (348.15, 323.15, and 308.15) K, ($\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$) at (348.15, 308.15, and 288.15) K, ($\text{LiCl} + \text{NaCl} + \text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$) at 273.15 K, and ($\text{LiCl} + \text{Li}_2\text{SO}_4 + \text{MgCl}_2 + \text{MgSO}_4 + \text{H}_2\text{O}$) at (323.15 and 308.15) K, and ($\text{Li} + \text{Na} + \text{K} + \text{Cl} + \text{SO}_4 + \text{H}_2\text{O}$) at 308.15 K [6-15].

Although the quaternary system ($\text{Li}^+, \text{K}^+//\text{Cl}^-, \text{SO}_4^{2-}-\text{H}_2\text{O}$) over a wide temperature had been previously reported since the 1950s [16], the phase diagram and solution physico-chemical properties are still not sufficient, and both of the systems at 288.15 K haven't been reported yet. The average temperature of the Dong-Xi-Taijinaier Salt Lake region in summer is around 288.15 K, so the phase diagram study of these ternary systems at 288.15 K has significant value for separating and purifying lithium salts from the brines. In this paper, the isothermal solubilities, solution density and refractive index of the quaternary system ($\text{Li}^+, \text{K}^+//\text{Cl}^-, \text{SO}_4^{2-}-\text{H}_2\text{O}$) at 288.15 K were presented by the isothermal dissolution equilibrium method to describe the stable behaviors to separate and purify the lithium-containing mixture salts.

Experimental

Apparatus and reagents. A magnetic stirring thermostatic water bath (HXC-500-6A, Beijing Fortunejoy Sci. Technol. Co. Ltd.) was used to control the temperature with a precision of 0.01 K. The application of the polarizing microscope (BX51, Olympus Co., Japan) and X-ray powder diffractometer (MSAL XD-3, Beijing Purkinje Instrument Co. Ltd., China) was to identify the crystal structures of solid phases. An

inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leman Co., USA) was employed to determine the concentrations of Li^+ in solution.

The chemicals of analytical grade were obtained from either the Sinopharm Chemical Reagent Co., Ltd: lithium chloride monohydrate ($\text{LiCl}\cdot\text{H}_2\text{O}$, 0.990 in mass fraction), lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$, 0.992 in mass fraction), potassium chloride (KCl , 0.995 in mass fraction), potassium sulfate (K_2SO_4 , 0.995 in mass fraction), and were re-crystallized with doubly deionized water (DDW) before use. Doubly deionized water (DDW) with conductivity less than $1\times 10^{-4} \text{ S}\cdot\text{m}^{-1}$ was used to prepare the series of the artificial synthesized brines and chemical analysis.

Method. The isothermal dissolution method was used in this study, and more details of the experimental method are available in our previous works. In brief, the series of artificial synthesized complexes are sealed in hard polyethylene bottles and placed in the magnetic stirring thermostatic bath (HXC-500-6A). The temperatures of the baths were set at $288 \pm 0.01 \text{ K}$ with 150 rpm stirring speed in order to accelerate the establishment of equilibrium states. After these artificial synthesized complexes had been stirred for about 3 to 5 days, it could be found that the equilibrium was reached when the compositions of the liquid phase had been determined and became constant state. Before taking sampling, it took about 1 h for the clarification of an aqueous solution. Two samples were taken out from the bottles. One was used for determining physicochemical properties including density and refractive index of the liquid phase of the quaternary system. The other was applied to quantitative analysis. In addition, the solid phase minerals were identified X-ray powder diffraction.

The concentration of SO_4^{2-} in liquid phase was obtained by the gravimetric method of barium chloride; the uncertainty for the analytical results in triplicate was within ± 0.003 in mass fraction. The Cl^- ion titrimetric analysis with AgNO_3 standard solution using potassium chromate as indicator, the precision in triplicate could be less than 0.3%. The K^+ ion concentration was measured in triplicate by the gravimetric method of sodium tetraphenylborate, the uncertainty was within ± 0.003 in mass fraction. The Li^+ concentration was measured with ICP-OES (Prodigy, Leman Corporation, USA), and the uncertainty was within ± 0.005 .

The measurements of the liquid-phase physicochemical properties were corresponded to density and refractive index. The densities (ρ) were measured using a digital vibrating-tube densimeter (DMA 4500, Anton Paar Co. Ltd., Austria) with an uncertainty of $\pm 0.00001 \text{ g}\cdot\text{cm}^{-3}$. An Abbe refractometer (WZS-1, Shanghai Yuguang Instrument Co. Ltd., China) was used to measure the refractive index (n_D) with an accuracy of ± 0.0001 . All the measurements were maintained at the desired temperature with $\pm 0.01 \text{ K}$ through control of the thermostat (K20-cc-NR, Huber, Germany).

Results and discussion

Solubilities of the quaternary system (Li^+ , $\text{K}^+//\text{Cl}^-$, $\text{SO}_4^{2-}-\text{H}_2\text{O}$) at 288.15 K. The experimental data on the solubilities and the relevant physicochemical properties including density and refractive index of the quaternary system (Li^+ , $\text{K}^+//\text{Cl}^-$, $\text{SO}_4^{2-}-\text{H}_2\text{O}$) at 288.15 K were determined. According to the experimental data, the stable

phase diagrams of the quaternary system at 288.15 K were plotted, as shown in Fig. 1 and 2.

In Fig. 1, the dry-salt phase diagram consists of five crystallization zones corresponding to lithium chloride monohydrate (Lc, $\text{LiCl}\cdot\text{H}_2\text{O}$), lithium sulfate monohydrate (Ls, $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$), potassium chloride (Sy, KCl), potassium sulfate (Ar, K_2SO_4), and the double salt lithium potassium sulfate (Db, $\text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$), where the double salt lithium potassium sulfate ($\text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$) is an incongruent double salt. The crystallization area of potassium sulfate (K_2SO_4) is the largest, and the crystallized zone of lithium chloride monohydrate ($\text{LiCl}\cdot\text{H}_2\text{O}$) is the smallest. These results indicate that potassium sulfate is easy to saturate and crystallize from solution and that lithium chloride has a high solubility during isothermal evaporation.

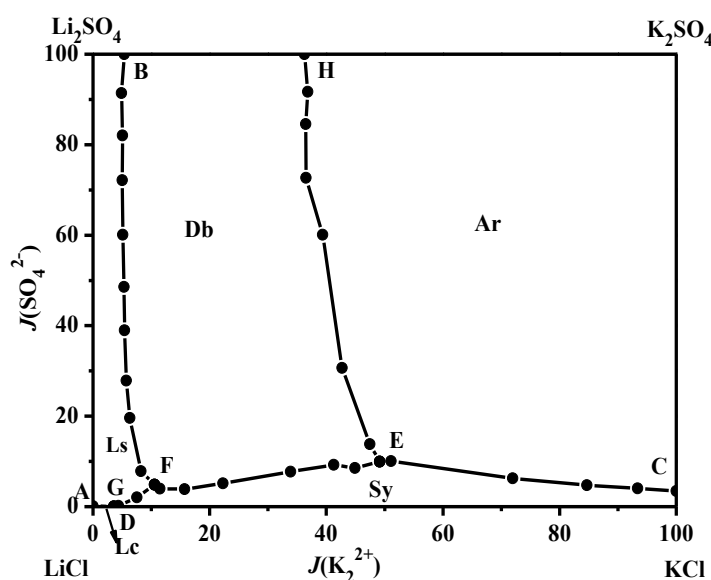


Fig. 1. Phase diagram of the quaternary system (Li^+ , $\text{K}^+//\text{Cl}^-$, $\text{SO}_4^{2-}\cdot\text{H}_2\text{O}$) at 288.15 K

There are three invariant points E, F and G, E saturated with salts $\text{K}_2\text{SO}_4 + \text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4 + \text{KCl}$, F saturated with salts $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O} + \text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4 + \text{KCl}$, G saturated with salts $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O} + \text{LiCl}\cdot\text{H}_2\text{O} + \text{KCl}$. There are seven univariant isothermal dissolution curves of AG, BF, HE, CE, EF, FG, DG, indicating the cosaturation of two salts. Due to the high solubilities of lithium chloride, there is a strong salting-out effect to potassium chloride and lithium sulfate.

Fig. 2 is the water-phase diagram of the quaternary system at 288.15 K, and it shows that the Jänecke index values of $J(\text{H}_2\text{O})$ gradually change with increasing $J(\text{Li}_2\text{B}_4\text{O}_7)$.

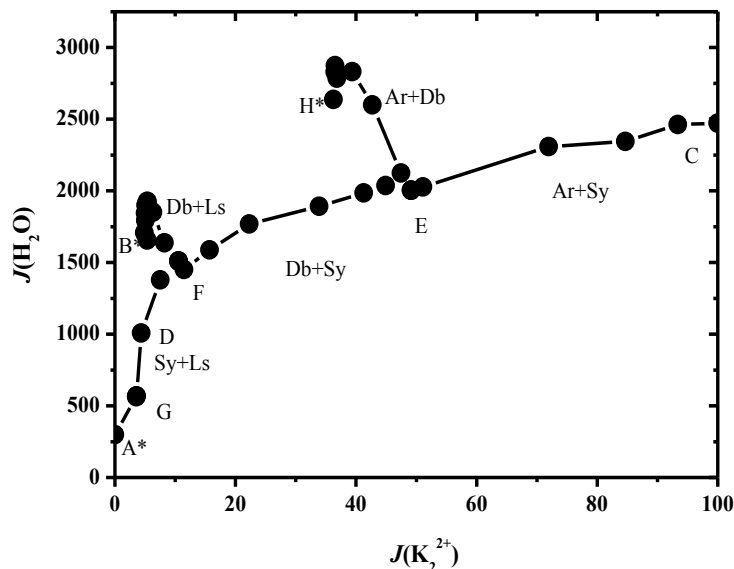


Fig. 2. Water-phase diagram of the quaternary system (Li⁺, K⁺//Cl⁻, SO₄²⁻-H₂O) at 288.15 K

The solution physicochemical properties of the quaternary system. On the basis of experimental data, relationship of the solution density and refractive index with the concentration of K⁺ in the quaternary system (Li⁺, K⁺// Cl⁻, SO₄²⁻-H₂O) at 288.15 K was plotted in Fig. 3. It was found that the solution density and refractive index in the quaternary system changed regularly with the increasing of $J(2K^+)$ concentration.

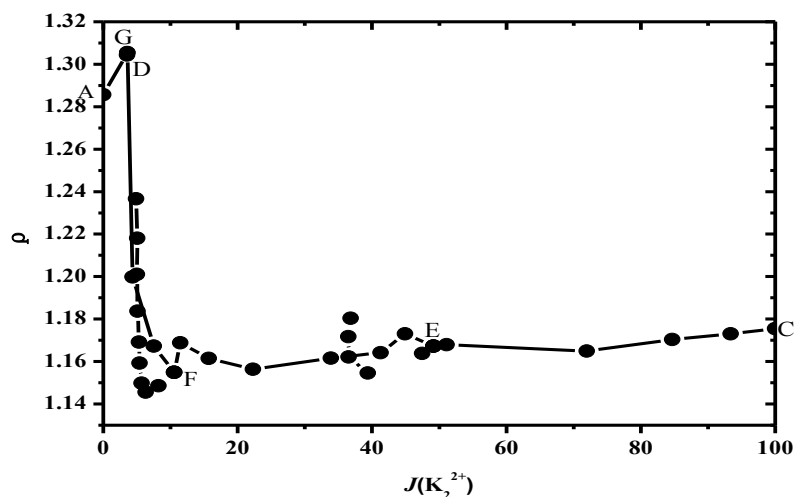
In Fig. 3(a), the density curves of the equilibrium liquid phase decreased sharply with the increasing concentration of $J(2K^+)$ (curve AG and GF), and then the solution densities was decreased slowly with the increasing concentration of $J(2K^+)$ (curve FC), and reached the minimum value of at the point C.

Fig. 3(b) shows the refractive index value versus composition of $J(2K^+)$ in the solution. Similarly as the density in the solution, the refractive index value was decreased sharply from point A to points F, while decreased slowly from points F to point C with the increasing concentration of $J(2K^+)$, and the minimum value at the point C.

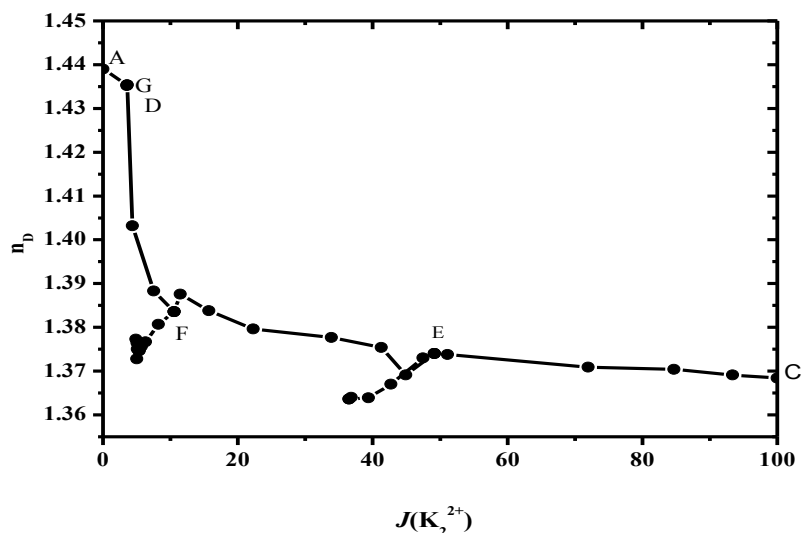
Conclusions

The solubility, solution density and refractive index of the quaternary system (Li⁺, K⁺//Cl⁻, SO₄²⁻-H₂O) were determined using the isothermal dissolution method at 288.15 K, respectively. According to experimental data, the equilibrium phase diagrams and the diagrams of physicochemical properties versus concentration of $J(2K^+)$ were constructed. Phase diagram of the quaternary system consist of three invariant points (E saturated with (E saturated with salts K₂SO₄ + Li₂SO₄·K₂SO₄ + KCl, F saturated with salts Li₂SO₄·H₂O + Li₂SO₄·K₂SO₄ + KCl, G saturated with salts Li₂SO₄·H₂O +

LiCl·H₂O + KCl), and five crystallization regions, which correspond to LiCl·H₂O, Li₂SO₄·H₂O, KCl, K₂SO₄, and the double salt Li₂SO₄·K₂SO₄, where the double salt lithium potassium sulfate (Li₂SO₄·K₂SO₄) is an incongruent double salt. The solution density and refractive index in the ternary system changed regularly with increasing of $J(2K^+)$ concentration in the solution.



(a) Density versus composition



(b) Refractive index versus composition

Fig. 3. Physicochemical properties versus composition diagram of the quaternary system (Li⁺, K⁺//Cl⁻, SO₄²⁻-H₂O) at 288.15 K:

(a) density versus composition; (b) refractive index versus composition.

Acknowledgments

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ФАЗОВОЕ РАВНОВЕСИЕ И ФАЗОВАЯ ДИАГРАММА
ДЛЯ ЧЕТВЕРТИЧНОЙ СИСТЕМЫ (Li⁺, K⁺//Cl⁻, SO₄²⁻-H₂O) ПРИ 288.15 К

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Построены фазовые и физико-химические диаграммы четвертичной системы (Li^+ , K^+/Cl^- , SO_4^{2-} - H_2O) при 288,15 К с использованием измеренных показателей растворимости, плотности и преломления. В фазовых схемах в системах присутствуют три инвариантные точки, семь однородных кривых растворения, изотермы и пять областей кристаллизации, соответствующих моногидрату хлорида лития ($\text{LiCl}\cdot\text{H}_2\text{O}$), моногидрату сульфата лития ($\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$), хлористому калию (KCl), сульфату калия (K_2SO_4), двойной соли сульфата лития и калия ($\text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$), где двойная соль сернокислого калия и лития ($\text{Li}_2\text{SO}_4\cdot\text{K}_2\text{SO}_4$) является неконгруэнтной двойной солью. Области кристаллизации сульфата калия (K_2SO_4) являются большими, а зона кристаллизации моногидрата хлористого лития ($\text{LiCl}\cdot\text{H}_2\text{O}$) являются самыми маленькими. Эти результаты свидетельствуют о том, что сульфат калия легко насыщается и кристаллизуется из раствора и, что хлорид лития обладает высокой растворимостью при изотермическом испарении. Плотность раствора и показатель преломления четвертичной системы меняются регулярно с увеличением концентрации K^+ .

Ключевые слова: стабильное фазовое равновесие; фазовая диаграмма; двойная соль сульфата лития и калия; кристаллизация; изотерма; показатель преломления; инвариантные точки.