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Solid-liquid phase equilibria of quaternary system $NH_4^+//C1^-$, SO_4^{2-}, $H_2PO_4^-$–H_2O and its subsystems $NH_4^+//C1^-$, SO_4^{2-}–H_2O, $NH_4^+//C1^-$, $H_2PO_4^-$–H_2O at 313.15 K

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ABSTRACT

Solid–liquid phase equilibrium and physical properties of ternary systems NH_4Cl-$NH_4H_2PO_4$-H_2O, NH_4Cl-$(NH_4)_2SO_4$-H_2O and quaternary system NH_4Cl-$(NH_4)_2SO_4$-$NH_4H_2PO_4$-H_2O at 313.15 K and atmospheric pressure were obtained by means of an isothermal solution method. The solid phases formed in the systems studied were determined by the Schreinemaker wet residue method. Based on the measured data, corresponding phase diagrams and the diagrams of physical properties versus composition were plotted. Neither complex salt nor solid solution is found in these systems at 313.15 K. The ternary phase diagram of $NH_4^+//C1^-$, $H_2PO_4^-$–H_2O contains one invariant point, and three crystallization regions ($NH_4H_2PO_4$, NH_4Cl, and (NH_4Cl + $NH_4H_2PO_4$)). The ternary phase diagram of $NH_4^+//C1^-$, SO_4^{2-}–H_2O is similar to the previous one, also contains one invariant point, three crystallization regions (($(NH_4)_2SO_4$, NH_4Cl, and (NH_4Cl + $(NH_4)_2SO_4$)). The quaternary phase diagram of $NH_4^+//C1^-$, SO_4^{2-}, $H_2PO_4^-$–H_2O contains one quaternary invariant point, three crystallization regions (($(NH_4)_2SO_4$, NH_4Cl, and $NH_4H_2PO_4$), and crystallization field of $NH_4H_2PO_4$ is the largest one of them. All results obtained in this work can be used for the stripping process of solvent extraction in the production of potassium dihydrogen phosphate.

1. Introduction

Potassium dihydrogen phosphate (KDP) has an important value in the current phosphate industry, and it is also applied in many industries, such as industry, agriculture, pharmacy, and foodstuff. KDP also is the efficient nonlinear optical material which is widely used as second harmonic generator for Nd:YAG laster [1]. In addition, it has aroused considerable interest with the advantage of wide frequency conversion, high efficiency, and high damage threshold against high power laser [2].

In recent years, the methods of producing KH_2PO_4 emerge endlessly, including neutralization process, extraction method, ion exchange process, double decomposition, direct method, crystallization, electrolysis method, etc [3,4]. To produce higher-quality KH_2PO_4 with lower cost of raw materials and simpler process is today's need. Among them, extraction technology was considered to be promising because it has the advantages of low energy consumption, mild reaction conditions, and high product purity. To obtain a higher purity of KH_2PO_4 for specific applications, purified wet-process phosphoric acid and KCl as raw materials were used to product KH_2PO_4 with the method of solvent extraction [5–7]. A simple process of solvent extraction was shown in Fig. 1.

The KH_2PO_4 produced with the method of extraction technology often contains three steps, and the main reactions are listed as follows:

$$KC1 + H_3PO_4 \rightarrow KH_2PO_4 + HC1 \quad (1)$$

$$HC1 + M \rightarrow HC1 \cdot M \quad (2)$$

$$HC1 \cdot M + NH_3 \rightarrow NH_4Cl + M \quad (3)$$

M represents the extraction agent. Crystallization process is a crucial step in the production of KH_2PO_4. When it comes to the crystallization process of by-products ammonia chloride and ammonium dihydric phosphate, NH_3 must be added as stripping agent. Thus, NH_4^+, $C1^-$, $H_2PO_4^-$, SO_4^{2-} would be included in the solution of crystallization process [8]. The production of pure KH_2PO_4 and by-products NH_4Cl requires the appropriate ion concentration in the solution, which can be obtained from the phase equilibrium. Therefore, a comprehensive knowledge of phase equilibrium of the quaternary system K^+, $NH_4^+//C1^-$, SO_4^{2-}, $H_2PO_4^-$–H_2O is important.

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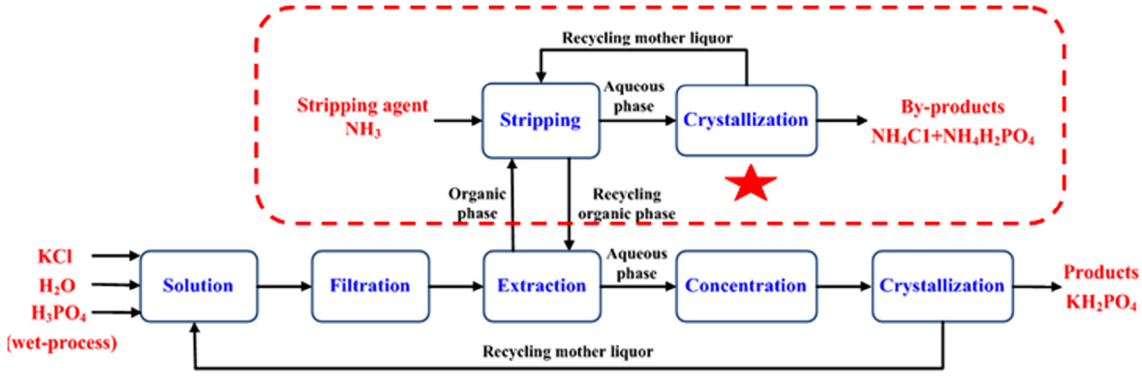

Fig. 1. A schematic diagram of solvent extraction for KH_2PO_4 production.

The solubility diagram corresponding to a stable state with absolute minimum free energy of the system, is also known as phase equilibrium diagram. Beginning with van't Hoff, then studied by D'Ans, Autenrieth, and the Russian school of Kurnakov, Lepeshkov, and Zdanovskii et al. (Solid – liquid) phase equilibrium (SLE) data and phase diagrams are essential for the development, design and control of process. Some SLE of K^+, $NH_4^+//C1^-$, SO_4^{2-}, $H_2PO_4^-$–H_2O -containing systems have been studied, for example,

Wei Shen: ($K_2SO_4 + KH_2PO_4 + H_2O$), ($K_2SO_4 + KC1 + H_2O$) at 313.15 K [9].
Pan Wang: ($K_2SO_4 + KH_2PO_4 + H_2O$) at 298.15, 333.15 K [10].
Z.D. Niu: ($K_2SO_4 + KC1 + H_2O$) at T = (273.15, 298.15, 323.15, 348.15) K [11].
Wei Shen: Na^+ (K^+)//$H_2PO_4^-$, $C1^-$, SO_4^{2-}–H_2O at 313.15 K [12].
Wei Shen : ($KC1 + KH_2PO_4 + H_2O$) at 298.15, 313.15 K [13].

However, information of the SLE for $NH_4^+//C1^-$, SO_4^{2-} $H_2PO_4^-$–H_2O system and its subsystems are scant, and it is an essential research to study the reverse extraction process. In this study, we focus on the (solid + liquid) equilibrium of $NH_4^+//C1^-$, SO_4^{2-} $H_2PO_4^-$–H_2O contained ternary system of $NH_4^+//C1^-$, SO_4^{2-}–H_2O and $NH_4^+//SO_4^{2-}$, $H_2PO_4^-$–H_2O by the isothermal solution saturation method. At the same time, our paper will supply the solid-liquid equilibrium solubility data and physical properties (n_D, ρ, η) of these systems, which can be used to guide the development of processes.

2. Experimental

2.1. Materials and instruments

2.1.1. Chemicals

The experimental materials of NH_4Cl, $(NH_4)_2SO_4$, $NH_4H_2PO_4$ were of a purity (not less than 99.0%). The sources, purity and CAS numbers are listed in Table 1. High-purity Milli-Q water, with a resistivity of above 18.2 MΩ·cm at ambient temperature, was used to prepare the series of supersaturated solutions and chemical analysis.

2.1.2. Apparatus

A constant temperature bath oscillator (SHZ-C, Shanghai Langgan Laboratory Equipment Co. Ltd. China) with a temperature range from 293.15 to 373.15 K was employed for equilibrating samples. An XMTD-4000 type super constant-temperature water bath (Zhengzhou YingYu Yuhua Instrument Co., Ltd., China) was used to keep constant temperature of 313.15 K. In the experiment, the temperature of this oscillator and constant-temperature water bath could be controlled to 0.05 K.

2.2. Experimental methods

The solid-liquid equilibrium experiments for the quaternary system NH_4Cl-$(NH_4)_2SO_4$-$NH_4H_2PO_4$-H_2O and its subsystem was determined by isothermal method. For example, the initial solid liquid mixtures of $NH_4H_2PO_4$ + water, and NH_4Cl + water were used to determine the $NH_4H_2PO_4$ and NH_4Cl saturation curves, respectively. Therefore, we determined the solubility data and composition of them in water. To future study the $NH_4H_2PO_4$ (NH_4Cl) saturated (solid + liquid) equilibrium of the NH_4Cl-$NH_4H_2PO_4$-H_2O system, an initial (solid + liquid) mixture with water and $NH_4H_2PO_4$ (NH_4Cl) was added in a conical flask with doubly deionized water. Then, the conical flask was sealed and placed in the constant temperature bath oscillator. The oscillator vibrated continuously with temperature controlled at around 313.15 K, and the actual temperature of the complex was monitored by a mercury thermometer (uncertainty = ± 0.05 K). A certain amount of NH_4Cl ($NH_4H_2PO_4$) was added into the mixture at different stages until the invariant point was found. During the entire experimental procedure, the mixture was maintained at a temperature of 313.15 K. At each stage, the mixture was stirred for 4 h until it has reached phase equilibrium. And then, it was allowed to settle for 15 h until the liquid phase became completely clear. After the system reached equilibrium, the saturated solution was removed into a beaker at 313.15 K. The liquid phase was added into two volumetric flasks and diluted with deionized water immediately after weighting accurately. Then the remainder of the solution was used to measure the relative physical properties (n_D, ρ, η) of the liquid

Table 1
The purities and suppliers of chemicals.

Chemical	Mass fraction purity (%)	CAS No.	Source	Purification method	Analytical Method[a]
NH_4Cl	≥99.5	12125-02-9	Tianjin Kermel Chemical Reagent Co., Ltd., China	Recrystallization	Volhard method
$(NH_4)_2SO_4$	≥99.0	7783-20-2	Tianjin Kermel Chemical Reagent Co., Ltd., China	Recrystallization	Barium sulfate turbidimetry
$NH_4H_2PO_4$	≥99.0	7722-76-1	Tianjin Kermel Chemical Reagent Co., Ltd., China	Recrystallization	Quinoline phosphomolybdate gravimetric method

[a] Relative standard uncertainties u_r are u_r (NH_4Cl) = 0.05, u_r ($(NH_4)_2SO_4$) = 0.02, u_r ($NH_4H_2PO_4$) = 0.01.