The Study of Phase Equilibria and Superprotonic Crystals in the (NH₄)₂SO₄ – K₂SO₄ – H₂SO₄ – H₂O system

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Abstract. The phase equilibria in the quaternary water-salt system K₂SO₄ – (NH₄)₂SO₄ – H₂SO₄ – H₂O at a temperature of 35 °C were studied for the first time. The areas of crystallization, solubility, and reproducible conditions for obtaining crystals of solid solutions were determined: (K₂(O(NH₄)₂)SO₄, (K₂O(NH₄)₂)H₂SO₄), (K₂O(NH₄)₂)H₂SO₄·H₂O, which are superprotonics. The study of phase equilibria in ternary systems K₂SO₄ – H₂SO₄ – H₂O and (NH₄)₂SO₄ – H₂SO₄ – H₂O was carried out, the solubility values and the solubility character of the compounds (NH₄)₂SO₄, (NH₄)₂H₂SO₄, K₂H₂SO₄·H₂O, NH₄HSO₄ and KHSO₄ were determined.

1. Introduction

Currently, the study of superprotonic crystals is of great interest both for solving fundamental scientific problems and for practical applications.

Compounds of the family with the general formula MnHₙ(AO₄)ₘ(OR)ₙ·yH₂O (M = K, Rb, Cs, NH₄, AO = SO₄, SeO₄, HPO₄), named superprotonics are capable of exhibiting an abnormally high proton conductivity at relatively low temperatures. The high proton conductivity in these compounds is due to the presence of a disordered network of hydrogen bonds, which provides conditions for proton diffusion. The superprotonic conductivity is related to the structural features of these compounds. Conductivity is independent of humidity, real structure (defects), and the presence of dopants [1]. All currently known crystals of this family are water-soluble compounds, therefore, one of the ways to search for new superprotonic crystals and modify the properties of the already known is to study phase equilibria in multicomponent water-salt systems.

This paper presents the results of a study of phase equilibria in a quaternary water-salt system K₂SO₄ – (NH₄)₂SO₄ – H₂SO₄ – H₂O.

2. Experimental Techniques

In this work, the following reagents were used: ammonium sulfate ((NH₄)₂SO₄) reagent grade (technical specifications 6-09-04-198-83); potassium sulfate (K₂SO₄) chemically pure grade (technical specifications 6-09-04-201-82) and sulfuric acid (H₂SO₄) chemically pure grade (GOST 4204-77).

X-ray diffraction (XRD) analysis of a powdered single crystals was carried out at room temperature on a Rigaku Miniflex 600 (Japan) desktop X-ray diffractometer (X-ray copper-anode tube, continuous...
scanning at a rate of 2 deg/min and step of 0.02° in the angular range 2θ = 5°–75°, without sample rotation) in atmosphere.

The phase equilibria were studied by the parallel crystallization method [2]. A series of 90 initial solutions was prepared in identical sealed vessels (crystallizers) with a variable ratio of initial dry components and acid.

The compositions of the mentioned initial solutions in the forming ternary \(\text{K}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4\) system diagram were distributed as follows: 10 sections according to the content of sulfuric acid - 15, 20, 30, 40, 45, 50, 55, 60, 65 and 75 mol %; 9 points were evenly spaced in each section, so that the extreme points belong to the forming ternary systems \(\text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}\) и \((\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}\) respectively (except for the cross section of 15 mol %, (Fig. 1). After which the minimum amount of distilled water (5 ml) was added.

![Figure 1](image)

**Figure 1.** The compositions of the mentioned initial solutions in the forming ternary \(\text{K}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4\) system diagram.

Then, at a temperature of 35° C, the solubility of the weighed portions of the components was determined by repeated addition of water in small portions (1-5 ml) to obtain saturated solutions with a minimum (not more than 3-5 salt crystals) of the precipitate at the bottom of the vessel. Additionally, the amount of salt dissolved in a saturated solution was analyzed by the gravimetric method by precipitation of barium sulfate according to the procedure [3].

After determining the solubility, the initial solutions were additionally aged for two days at the set temperature. Such exposure is necessary to establish dynamic interphase equilibrium between the saturated solution and the precipitate in the crystallizer. After the indicated exposure, the temperature of the crystallizers decreased according to the same program to the required value for several days. The crystals formed by this approach had a size of at least 2-5 mm and were easily decanted from the solution by washing the surface of the samples with 96% ethanol.

The crystals obtained by this method were used to determine the phase composition of equilibrium with the mother liquor of solid phases by powder X-ray phase analysis (XRD).

3. Results and Discussion
For the convenience of presenting the results, it is first necessary to listing the phases crystallizing in the initial ternary \(\text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}\) and \((\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}\) systems.
In the initial ternary K₂SO₄ – H₂SO₄ – H₂O system, in studied range of sulfuric acid content at 35°C belongs to the region of crystallization of four phases: K₂SO₄, K₂H(SO₄)₂, K₂H₂(SO₄)₃·H₂O and KHSO₄.

In the initial ternary (NH₄)₂SO₄ – H₂SO₄ – H₂O system, in similar conditions, the crystallization regions of the three phases are delimited (NH₄)₂SO₄, (NH₄)₂H(SO₄)₂ and NH₄HSO₄.

The initial ratios of K₂SO₄, (NH₄)₂SO₄ and H₂SO₄ in crystallizers, the solubility of the formed equilibrium solid phases for the K₂SO₄ – H₂SO₄ – H₂O and (NH₄)₂SO₄ – H₂SO₄ – H₂O systems are shown in the Table 1.

**Table 1.** The molar ratios of the components in the initial solutions, solubility and equilibrium solid phases in the forming systems K₂SO₄ – H₂SO₄ – H₂O and (NH₄)₂SO₄ – H₂SO₄ – H₂O.

| K₂SO₄ | H₂SO₄ | solubility mol % | solid phases | (NH₄)₂SO₄ | H₂SO₄ | solubility mol % | solid phases |
|-------|-------|------------------|-------------|-----------|-------|------------------|-------------|
| -     | -     | -                | -           | 85        | 15    | 17.9             | (NH₄)₂SO₄   |
| 80    | 20    | 4.7              | K₂SO₄       | 80        | 20    | 19.4             | (NH₄)₂SO₄   |
| 70    | 30    | 6.2              | K₂SO₄       | 70        | 30    | 19.8             | (NH₄)₂H(SO₄)₂ |
| 60    | 40    | 10.6             | K₂H(SO₄)₂   | 60        | 40    | 20.2             | (NH₄)₂H(SO₄)₂ |
| 55    | 45    | 11.5             | K₂H(SO₄)₂   | 55        | 45    | 22.7             | (NH₄)₂H(SO₄)₂ |
| 50    | 50    | 11.7             | K₂H(SO₄)₂   | 50        | 50    | 23.9             | (NH₄)₂H(SO₄)₂ |
| 45    | 55    | 12.2             | K₂H(SO₄)₂ + K₂H₂(SO₄)₃·H₂O | 45 | 55 | 34.9 | NH₄HSO₄ |
| 40    | 60    | 12.9             | K₂H₂(SO₄)₃·H₂O | 40 | 60 | 35.3 | NH₄HSO₄ |
| 35    | 65    | 13.2             | KHSO₄       | 35        | 65    | 36.3             | NH₄HSO₄     |
| 25    | 75    | 13.8             | KHSO₄       | 25        | 75    | 37.1             | NH₄HSO₄     |

The essential difference in the solubilities of the equilibria solid phases, are forming in the ternary system K₂SO₄ – H₂SO₄ – H₂O and (NH₄)₂SO₄ – H₂SO₄ – H₂O are identified. In this case, the solubility of the formed solid phases increases with increasing content of sulfuric acid in the solution due to the in solution interaction effect, which is more pronounced for the (NH₄)₂SO₄ – H₂SO₄ – H₂O system.

In the quaternary system K₂SO₄ – (NH₄)₂SO₄ – H₂SO₄ – H₂O area besides those already listed crystallization phases belonging forming triple systems, was demarcated regions of crystallization of solid solutions (Kᵢ₋₁(NH₄)ᵢ)₂SO₄, (Kᵢ₋₁(NH₄)ᵢ)H(SO₄)₂, (Kᵢ₋₁(NH₄)ᵢ)H₂(SO₄)₃·H₂O and compound KₙHₙHₙHₙ(SO₄)₄, (Fig. 2).

The vast crystallization region of the (Kᵢ₋₁(NH₄)ᵢ)₂SO₄ (I, red) solid solution lies between the crystallization branches of the K₂SO₄ and (NH₄)₂SO₄ phases, in the range of sulfuric acid in the initial solutions (hereinafter, excluding water) 0 ÷ (25-30) mol %. In this case, the parameter x takes values in the entire interval from 0 to 1.

The crystallization region of the (Kᵢ₋₁(NH₄)ᵢ)H(SO₄)₂ (II, green) solid solution lies between the crystallization branches of the K₂H(SO₄)₂ and (NH₄)₂H(SO₄)₂ phases, in the range of sulfuric acid in initial solutions (25-30) ÷ (50-55) mol %. The parameter x also takes values in the entire interval from 0 to 1.

The crystallization region of the solid solution (Kᵢ₋₁(NH₄)ᵢ)H₂(SO₄)₃·H₂O (VI, deep blue) is much smaller in sulfuric acid content, 55÷60 mol %. Moreover, the range of the ratio of cations is also very limited. Indeed, as noted in [4], the parameter x in this solid solution lies in the range from 0 to 0.04.

With a further increase in the sulfuric acid content in the initial solutions over 60 mol % crystallization of simple acid sulfates occurs: NH₄HSO₄ (III, light blue), KHSO₄ (VI, orange) and the compound K₋₁₂(NH₄)₋₁₂HSO₄ or KNH₄H₂(SO₄)₄ previously mentioned in the literature (V, turquoise) [5].
Figure 2. a) The projection of the phase diagram of the $K_2SO_4 - (NH_4)_2SO_4 - H_2SO_4 - H_2O$ system onto the plane of the generatrix of the $K_2SO_4 - (NH_4)_2SO_4 - H_2SO_4$. The crystallization regions of the following phases are indicated: I - ($K_{1-x}(NH_4)_x)_2SO_4$, II - ($K_{1-x}(NH_4)_x)_3H_2(SO_4)_2$, III - NH$_4$HSO$_4$, IV - ($K_{1-x}(NH_4)_x)_9H_7(SO_4)_8 \cdot H_2O$, V - KNH$_4$H$_2(SO_4)_2$) n IV - KHSO$_4$

b) Isometric projection of the phase diagram of the system $K_2SO_4 - (NH_4)_2SO_4 - H_2SO_4 - H_2O$; shows the appearance and characteristic sizes of the obtained crystals.
It should be noted that the crystallization regions of the NH₄HSO₄, KHSO₄ and KNH₂H₃(SO₄)₂ phases are not limited to the studied interval for the sulfuric acid content of –75 mol%. However, with a further increase in its amount during the preparation of the initial solutions to values greater than 80 mol%, the weighed portion of the dry initial reagents (K₂SO₄ и (NH₄)₂SO₄) begins to completely dissolve in acid even without the addition of water.

4. Conclusions
A study was made of the phase equilibria in the four-component water-salt system K₂SO₄ – (NH₄)₂SO₄ – H₂SO₄ – H₂O.

The crystallization regions of phases belonging to the forming triple systems K₂SO₄ – H₂SO₄ – H₂O and (NH₄)₂SO₄ – H₂SO₄ – H₂O: K₆SO₄ and (NH₄)₆SO₄, K₅H(SO₄)₂ and (NH₄)₅H(SO₄)₂, K₄H₂(SO₄)₃·H₂O, KHSO₄ and NH₄HSO₄.

The regions of phase crystallization and the regions of solid solutions formed in the four-component system K₂SO₄ – (NH₄)₂SO₄ – H₂SO₄ – H₂O are determined: (K₁₋ₓ(NH₄)ₓ)₂SO₄ (0≤x≤1), (K₁₋ₓ(NH₄)ₓ)₃H(SO₄)₂ (0≤x≤1), (K₁₋ₓ(NH₄)ₓ)₅H(SO₄)₃·H₂O (0≤x≤0.04) [4] and KNH₂H₃(SO₄)₂.

The crystals (K₁₋ₓ(NH₄)ₓ)₅H(SO₄)₃·H₂O [6,7], K₅H(SO₄)₃·H₂O [8] and (K₁₋ₓ(NH₄)ₓ)₅H(SO₄)₃·H₂O [4] undergo superprotonic phase transitions, which makes these objects interesting for study by various physicochemical methods, for which large single-crystal samples are also needed. The obtained research results allow one to reproducibly obtain these compounds for further more detailed study of their physicochemical properties.

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