Solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ in the Systems H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 and H_2O—$(NH_4)Al(SO_4)_2$—H_3PO_4 at the Temperatures of 20 °C and 30 °C and Vapour Pressure above these Systems

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Influence of concentration of H_2SO_4 and H_3PO_4 on the solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ in aqueous solutions and vapour pressure above saturated solutions of the systems H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 and H_2O—$(NH_4)Al(SO_4)_2$—H_3PO_4 was investigated. The measurements were carried out at the temperatures of 20 °C and 30 °C. It is shown that in the system H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ increases with increasing concentration of H_2SO_4 up to 8 mass % H_2SO_4. When concentration of the acid further increases, solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ decreases. However, from the concentration of *ca.* 35 mass % H_2SO_4 it starts to increase again. At high concentrations of sulfuric acid (> 30 mass %) it is $Al_2(SO_4)_3 \cdot 16H_2O$ and not $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ which is in equilibrium with the solution. Water vapour pressure above the solutions shows how the activity of water changes with composition of the investigated systems.

Leaching of uranium ores by sulfuric acid is one of the technologies used for uranium production. For 1 ton of ore 20—60 kg of H_2SO_4 are used. Acid solutions remaining after separation of uranyl sulfate contain a series of compounds from decomposition of accompanying minerals and subsequent technological operations. In these operations ammonium carbonate or sulfate is used [1]. As a result of that the basic composition of these solutions corresponds to the system H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4. For a rational design of technology for winning of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ and H_2SO_4 from these solutions it is important to know the influence of concentration of sulfuric acid on the solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$. For explanation of obtained data we have found that it might be useful to investigate the influence of H_3PO_4 on the solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ (this acid has no common anions with alum) and to study the influence of composition on the thermodynamic activity of water in the investigated systems. Accordingly also the vapour pressure above these systems was measured.

EXPERIMENTAL

$(NH_4)Al(SO_4)_2 \cdot 12H_2O$ of purity "purum" (Lachema, Brno) was used. H_2SO_4 (Cheman, Poland) was of anal. grade and H_3PO_4 (Germany) was of purity "purum" For measurement of solubility of (NH_4)-$Al(SO_4)_2 \cdot 12H_2O$ the isothermal method was used [2]. The method is based on an optical observation of dis-

appearing of the last crystal of solid phase at a gradual addition of the solvent at constant temperature. Measuring vessel (150 cm^3) was placed in a thermostat. The temperature was kept constant with the precision ± 0.05 °C. Each measurement was repeated 3—5 times. The measurement was done in such a way that water required for dissolution of weighed-in sample of salt was gradually added. The amount of added H_2SO_4 (93 %) or H_3PO_4 (85 %) was determined by weighing. The exact amount of added water was determined after dissolution of the last crystal by weighing of the whole system with the precision of 0.01 g. Actually, at each run the system was heated in water bath until all salt was dissolved. Then the system was cooled down in water or in a mixture of water with ice until the first crystals of solid phase appeared. After that the system was placed into the thermostat and water was added in small amounts until the last crystal was dissolved.

In the next step part of water was evaporated and composition of crystals coexisting in equilibrium with the saturated solution was determined by the X-ray powder diffraction analysis.

Pressure of water vapours above saturated solutions was measured by the method of dew point [3, 4]. Principle of this method consists in determination of the temperature T_b at which water vapours above the solution having temperature T_s condense. Scheme of measuring apparatus and its detailed description are published in paper [3]. Measuring vessel is placed in

thermostat with glycerine bath. Temperature of brass block is maintained constant by water flowing from the second thermostat. Surface of the brass block is coated by a chromium mirror which has been deposited galvanically. Condensation of water vapours is observed on this mirror. Temperatures of the solution and the brass block are measured by thermocouples and corresponding voltages are stored in an on-line computer. Precision of the measurement was checked by measuring vapour pressure of pure water and pressure above solutions of NH_4NO_3. These data were taken from literature [4]. It was found that the error of the measurement did not exceed 4 %. At the measurement of vapour pressure above the solutions containing acids no evaporation of acids was observed.

RESULTS AND DISCUSSION

Dependence of solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ in the system H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 on concentration of H_2SO_4 at the temperatures of 20 °C and 30 °C is shown in Fig. 1. X-Ray powder diffraction analysis of the crystals which are in equilibrium with saturated solution has shown that the solid phase corresponds to $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ up to concentration of ca. 30 mass % H_2SO_4. In this concentration region the results of this work are in good agreement with literature data [5]. At higher concentrations of H_2SO_4 the equilibrium phase is $Al_2(SO_4)_3 \cdot 16H_2O$. (This compound and not $Al_2(SO_4)_3 \cdot 18H_2O$ which coexists with saturated solution of $Al_2(SO_4)_3$ at the temperatures of 20 °C and 30 °C [6] has been determined from the X-ray pattern [7].)
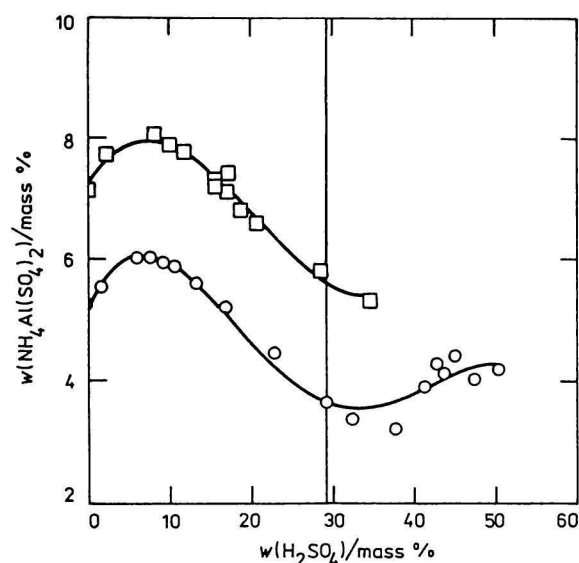
From Fig. 1 it follows that at low concentrations

of H_2SO_4 the solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ increases with increasing concentration of the acid. As the sulfuric acid brings into the solution sulfate anions which are also the product of electrolytic dissociation of $(NH_4)Al(SO_4)_2$ one would expect that the addition of H_2SO_4 would decrease solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$. (This assumption was proved by investigation of the influence of the addition of $(NH_4)_2SO_4$ on dissolution of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$. At the temperature of 20 °C the addition of 2.21 mass % $(NH_4)_2SO_4$ decreases solubility of $(NH_4)Al(SO_4)_2$ from 5.28 mass % in pure water to 2.70 mass %.) Thus when sulfate anions lower solubility of $(NH_4)Al(SO_4)_2$ (NH_4 cations have similar influence) the increase of solubility with increasing concentration of H_2SO_4 can be qualitatively explained by the effect of hydrogen cations which are hydrated in aqueous solution, which causes a decrease in activity of H_2O. This assumption was verified by investigation of the influence of H_3PO_4 on the solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$. The results are presented in Fig. 2. It follows that the addition of H_3PO_4 increases solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ in the whole investigated concentration range. X-Ray powder diffraction analysis of equilibrium solid phase has shown that in the system H_2O—$(NH_4)Al(SO_4)_2$—H_3PO_4 alum $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ coexists with saturated solution up to 15 mass % H_3PO_4. At higher concentrations of acid we were not able to prepare any solid phase even at high supercooling as the undercooled system became a highly viscous mixture.

As we have shown above at concentrations higher than 30 mass % H_2SO_4 the solid phase consists of $Al_2(SO_4)_3 \cdot 16H_2O$. However, in the system $Al_2(SO_4)_3$—H_2O the equilibrium solid phase at 20 °C and 30 °C

Fig. 1. Dependence of solubility of $(NH_4)Al(SO_4)_2$ in the system H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 on the content of H_2SO_4. ○ 20 °C; □ 30 °C.
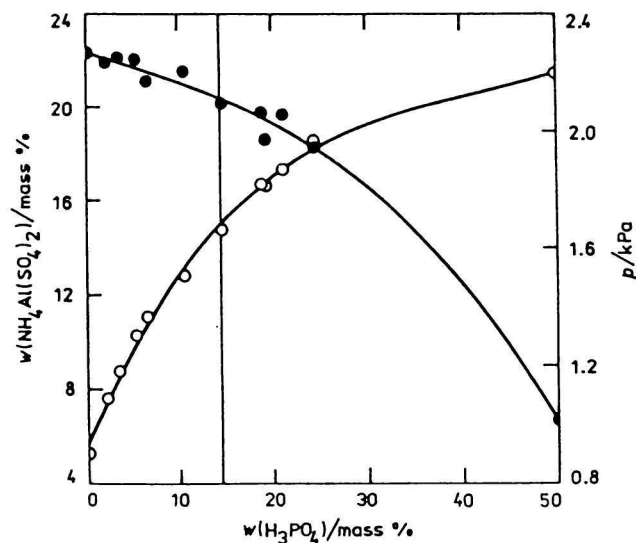
Fig. 2. Solubility of $(NH_4)Al(SO_4)_2$ (○) and water vapour pressure (●) for the system H_2O—$(NH_4)Al(SO_4)_2$—H_3PO_4 saturated with $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ at the temperature of 20 °C.
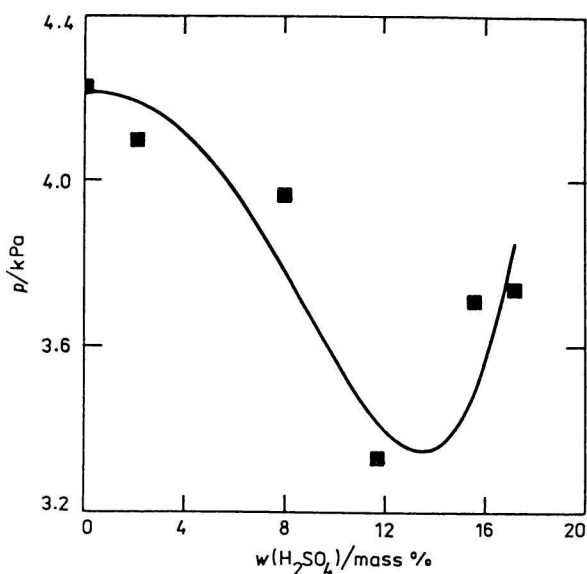
Fig. 3. Water vapour pressure above the system H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 saturated with $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ at the temperature of 30 °C.

consists of $Al_2(SO_4)_3 \cdot 18H_2O$ [6]. This again supports the hypothesis that increasing concentration of acids decreases the activity of water. This assumption has been proved by vapours pressure measurements in the investigated systems. The results are given in Figs. 2 and 3. It follows that in the system H_2O—$(NH_4)Al(SO_4)_2$—H_3PO_4 the pressure of water vapours decreases monotonously with increasing concentration of acid. On the other hand, in the system H_2O—$(NH_4)Al(SO_4)_2$—H_2SO_4 (Fig. 3) vapour pressure decreases only to 13 mass % H_2SO_4. At higher concentrations of H_2SO_4 the pressure of water vapours grows. Change in the pressure of water vapours is directly related to the chemical potential of water in solution. When the solution is saturated it holds that the chemical potential of coexisting equilibrium solid phase equals the chemical potential of this phase in the solution. As the solid phase consists of hydrate, the chemical potential of water is a part of it. This explains why the dependences of the pressure of water vapours above saturated solutions and of solubility of $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ show qualitatively similar behaviour.

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