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THERMAL ANALYSIS OF FREEZE-DRYED FROZEN AQUEOUS SOLUTIONS.

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ABSTRACT

A classification of freeze-dried frozen aqueous solutions of $Me'SO_4$-$Me''SO_4$ is proposed. There are three main types of products : X-ray amorphous mixture of hydrates ; crystalline solid solution based on one of the components ; crystalline mixture of hydrates of initial salts or solid solutions based on their structures.

INTRODUCTION

The ability of cryochemical synthesis to provide different oxide materials with minimal changes in technological scheme opens wide perspectives in the field of multipurpose technology of inorganic materials /1/. The development of this technique needs the investigation of unit stages, such as freeze-drying , of the process. In this work we have studied freeze-drying products of $Me'SO_4$ - $Me''SO_4$ frozen aqueous solutions (Me', Me'' = Zn, Co, Ni, Fe, Mg) and proposed a classification of observed phases.

EXPERIMENTAL AND MEASURING METHODS

In the process of cryochemical synthesis a solution of appropriate sulfates was frozen by dropping in liquid nitrogen. Main part of water was removed in preparative freeze-drier under a pressure about 2 Pa and temperatures of heater 250÷300 K . The obtained product was completely dehydrated in a plate sample holder of a Derivatograph (OD-102) in air with a heating rate of 10 K/min and sample masses 0,08 - 0,1 g . X-ray analysis of samples was also performed.

RESULTS AND DISCUSSION

The systematization of thermal analysis data showed three main classes of freeze-drying products depending on the P_{H_2O} during the process and the type of system $Me'SO_4$ - $Me''SO_4$.

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1/ X-ray amorphous mixture of hydrates.
In this case there are no any reflexes of crystalline phases in the diffractogrammes of products. Thermal dehydration of amorphous hydrates is rather specific and characterized by a single wide peak of water removal in the interval of 300÷550 K. Curves of dehydration obtained for amorphous products of different composition are practically identical. These phases contain 2-2,5 mole H_2O per mole of salt. In any cases (Me = Co,Mg) the dehydration is followed by significant exoeffect resulting from the crystallization of the product. Freeze-drying under sufficiently low P_{H_2O} is a necessary condition for the formation of amorphous products. Ability of a multicomponent composition to crystallize is determined by the properties of its components. The more readily salt component crystallizes, the lower P_{H_2O} is necessary for obtaining the system in the amorphous state. In the studied series of sulfates a maximum affinity to crystallization was found for the $ZnSO_4$, a minimum - for $MgSO_4$ and $NiSO_4$. A little increase of P_{H_2O} during a freeze-drying in comparison with observed case leads to the formation of products of type 2.

2/ Crystalline solid solution based on one of the components.
The mentioned non-equilibrium state of forming phases and large structural similarity of corresponding hydrates make difficult to prove unambiguously the formation of solid solutions by X-ray technique. Their formation is suggested by the fact that dehydration curves of binary products are similar to those of one-component samples and systematically shifting on the temperature scale with the composition of system. The situation observed in the system ($MgSO_4$-$FeSO_4$) · X H_2O is typical, the "crossing" of homogeneity regions in the central part of composition scale being observed. The type of formed solid solution depends on slight variations of experimental conditions. This effect occurs only in systems not forming continuous range of solid solutions during equilibrium crystallization. Dependence of the systematic shift of initial curves on the system composition is specific for every case. In the system ($CoSO_4$-$FeSO_4$) · X H_2O considerable shift of $CoSO_4$·X H_2O dehydration curve appears when the amount of $CoSO_4$ is less than 30 mole %. Further increase of P_{H_2O} under freeze-drying leads to the phase separation of the system and yields products of type 3.

3/ Crystalline mixture of salt component hydrates or solid solutions based on their structures.

The dehydration curves of one-component products are similar to those of crystalline salts; difference of peak intensities reflects different amounts of water. In two- or multi-component salt systems a superposition of curves of corresponding hydrates is observed. It indicates a phase separation during freeze-drying or subsequent thermal dehydration. The first possibility seems more plausible : the degree of a system separation depends on freeze-drying conditions and is less sensitive for thermal dehydration parameters. The ability of systems to separate spontaneously is determined not only by structural features but also by the mobility of components. For example, the system $NiSO_4 \cdot 7H_2O$ - $ZnSO_4 \cdot 7H_2O$ forms continuous range of solid solutions , the system $MgSO_4 \cdot 7H_2O$-$FeSO_4 \cdot 7H_2O$ - doesn't form /2/ ; but the phase separation of these systems during freeze-drying takes place under approximately the same conditions reflecting a high mobility of $ZnSO_4$.

CONCLUSIONS

In the study of complex multicomponent systems such as freeze-drying products a thermoanalytic technique was found to be more informative than diffraction methods. According to given data it is possible to describe these products in therms of thermal analysis.

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