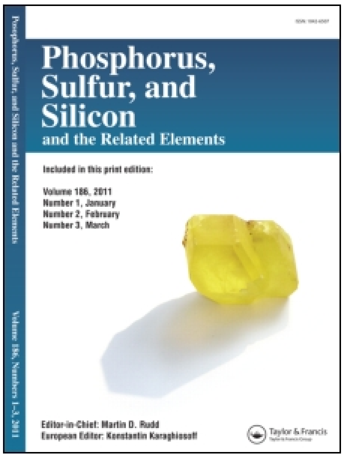

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ION EXCHANGE AND SORPTION PROCESSES AS METHODS OF SYNTHESIS OF DOUBLE PHOSPHATES AND INTERCALATED COMPOUNDS

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Traditional methods of obtaining salts by precipitation from solutions, crystallization from melts and solid-state reactions are often ineffective for the synthesis of double phosphates of mono- and polyvalent metals. The reactions of ion exchange or exchanged interaction are not widely used for this purpose. Only soluble acid salts capable of substituting their protons for cations and having sufficient hydrolytical stability are suitable. Their number is quite limited. Among these are: $M(HPO_4)\cdot H_2O$, M = Ti, Zr, Hf, Ge, Sn, Pb; $UO_2HPO_4\cdot 4H_2O$, $H_2MP_3O_{10}$, M = Al, Ga, V, Cr, Mn, Fe (TPM-I). A distinctive feature of these compounds is that all of them have two-dimensional lamellar lattice which is capable of reversible changing of crystallographic parameters during the ion exchange process. This proceeds quite easily, since the interaction of protons with the lattice is weak. No cases of effective ion exchange are reported in the solutions of anhydrous phosphates with three-dimensional structure. The analysis of the available literature data on the structure and other physico-chemical properties, as well as our own investigations, have permitted to come to the conclusion that the absence of the above-mentioned properties is primarily caused by the firmness of the bond between protons and the phosphate skeleton and by low proton mobilities.

We have supposed that the ion exchange properties of the hydrogen salts with three-dimensional lattice can be enhanced by the partial delocalization of the protons. One of the simplest ways of increasing the thermal vibrations of atoms of any substance is to rise the temperature. Consequently we have studied the interaction of the following hydrogen phosphates of polyvalent metals with the melts of the nitrates of alkaline metals: $MHPO_4$ and $MH_2P_2O_7$, M = Mg, Ca, Sr, Ba; $PbHPO_4$, $Ca_2HP_3O_{10}$; $BaH(PO_3)_3$; β-$FeHP_2O_7$; α-, β-, δ-$MnHP_2O_7$; $MNH_4HP_3O_{10}\cdot H_2O$, M = Al, Cr; TPM-I, M = Al, Ga, V, Cr, Mn, Fe; $GeHP_3O_{10}$. The melt served as the heating medium of the systems and gave possibility to realize the exchange process. With the exception of TPM-I, none of the enumerated compounds shows the ion exchange properties at normal conditions.

The studies were carried out by complex thermal analysis on a MOM OD-103 apparatus and on a METTLER TA-3000 thermoanalyzer. The source compounds and the reaction products were studied by chemical analysis, quantitative thin-layer chromatography, X-ray powder diffraction (HZG-4/A), infrared and Raman spectroscopy (Specord 75 IR, RAMALOG-4).

The study of the interaction of the above-mentioned acid anhydrous phosphates with the nitrates of alkaline metals showed that the exchange reactions take place in the systems with $PbHPO_4$, $MgH_2P_2O_7$, $Ca_2HP_3O_{10}$, β-$FeHP_2O_7$, α-, β-, δ-$MnHP_2O_7$, $GeHP_3O_{10}$ and follow the schemes:

$$PbHPO_4 + MNO_3 \xrightarrow[-HNO_3]{t_m} PbMPO_4 , \qquad M = Li, Na;$$

$$MgH_2P_2O_7 + 2MNO_3 \xrightarrow[-2HNO_3]{t_m} MgM_2P_2O_7, \quad M = Li, Na;$$

$$M(III)H_2P_3O_{10} + 2CsNO_3 \xrightarrow[-2HNO_3]{t_m} M(III)Cs_2P_3O_{10} ,$$

M(III) = Al, Ga, Cr, Mn, Fe (t_m-a temperature of the melting of nitrates).

The microcalorimetric study on the ion exchange reactions in melts showed that such processes take place in the open systems only. The values of ΔH of reaction were experimentally determined for some of them, and the thermodynamic analysis for the determination of the $\Delta H^o_{f,298}$ and S^o_{298} was carried out.

In the systems with lithium nitrate the realization of another type of the exchange reaction is observed, if both cations and protons of the phosphates are substituted by the univalent cations:

$$M(II)H_2P_2O_7 + 4LiNO_3 \xrightarrow[-2HNO_3]{t_m} M(II)(NO_3)_2 + Li_4P_2O_7 ,$$

M = Ca, Sr, Ba.

We have also studied the interaction of two types of acid triphosphates of trivalent metals which have a two-dimensional lattice with melts of the nitrates of alkaline metals: α-$MNH_4HP_3O_{10}\cdot H_2O$, M = Al, Cr, and TPM-I, M = Al, Ca, Cr, Mn, Fe. There is no literature data about ion exchange properties of the former, but the latter is a typical ion exchanger in aqueous solutions. The results of the investigation indicate that the reactions with the chromium salts proceed in the same way:

$$CrNH_4HP_3O_{10} + 2MNO_3 \xrightarrow[-HNO_3,\ NH_3]{t_m} M_2CrP_3O_{10} ,$$

$$H_2CrP_3O_{10} + 2MNO_3 \xrightarrow[-2HNO_3]{t_m} M_2CrP_3O_{10}, \quad M = Li, Na, K, Rb,$$

and the formation of the half-substituted $CrMHP_3O_{10}$ may occur in the melts of potassium and rubidium nitrates. In the systems with other TPM-I the reactions are completed by the formation of the half-substituted salts $M(III)M(I)HP_3O_{10}$. The exchange processes with the participation of both types of salts proceed in the same way in the melts of $CsNO_3$, resulting in the substitution of two protons and restructuring of the lattice from the lamellar to the three-dimensional one.

The analysis of the obtained results allows us to draw the following conclusions: (1) the reactions of exchanged interaction with the participation of acid anhydrous phosphates of polyvalent metals, which do not possess ion exchange properties at normal conditions, are possible at heightened temperatures in the melts of mineral salts; (2) depending on the peculiarities of phosphates structure and the nature of polyvalent (in the phosphates) and monovalent (in melts) cations, the interaction between reagents may proceed either by ion exchange mechanism, with the formation partially or fully substituted double salts, or by the mechanism of forming unstable substituted compounds which then undergo disproportioning, or by the way of substitution both the protons and cations of the phosphates for monovalent cations. The available data made it possible to propose some new ways of synthesis of double phosphates. Using this new approach about 50 compounds were obtained, including more than 30 not described earlier.

As it was mentioned above, a number of acid phosphates have lamellar structure. The advantages provided by such a structure, high acidity of the surfaces and high concentration of acid centers both on the surface and inside the volume of crystals, show promise for using salts of this type for the synthesis of intercalated compounds. The chemical modification of the lamellar compounds by creating the "host-quest" type structures allows to obtain materials with new functional properties, including selective sorbents, catalysts, solid electrolytes etc.

We have studied the possibility of preparing the intercalated compounds on the basis of TPM-I, M = Al, Cr, by sorption from gaseous phase and from solutions of the following basic compounds: ammonia, methyl-, ethyl-, dimethyl-, diethylamine, hydrazine, ethyl-, phenylhydrazine, benzylamine, hydroxylamine.