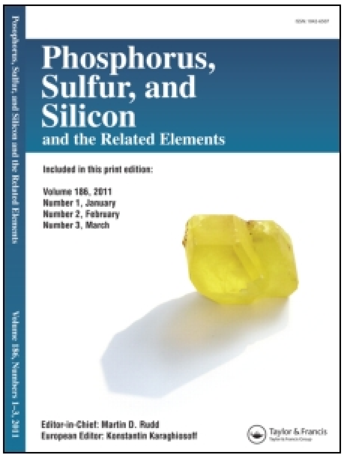

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Chemistry of Double and Individual Phosphates and Polyphosphates of Divalent Metals

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CHEMISTRY OF DOUBLE AND INDIVIDUAL PHOSPHATES AND POLYPHOSPHATES OF DIVALENT METALS

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The problems of formation of double and individual hydrated divalent metal phosphates of different protonization level are presented.

The results of the systematic experimental research on determining the possibility, conditions of obtaining and nature of the double hydrated phosphates Mg - M^{II} (M^{II} = = Mn, Co, Zn) are reviewed. The production conditions and nature of double dihydrophosphates $Mg_{1-x}M^{II}_{x}(H_2PO_4)_2 \cdot 2H_2O$ (0<x<1,00) are studied. It has been determined that they all crystallize in monoclinic system (space group $P\ 2_1/n$, Z = 2) and form continuous series of solid substitution solutions. It is possible to vary in a wide range (from 0,1 to 16% $M^{II}O$) the content of Mg and M^{II} in the double dihydrophosphates by changing the composition of initial chemical reagents during synthesis.

The compositions of synthesized double hydrophosphates can be described by formula $Mg_{1-x}M^{II}_{x}HPO_4 \cdot 3H_2O$. They all crystallize in the orthorombic system (space group Pbca) and are identical in structure with individual hydrophosphates $MgHPO_4 \cdot 3H_2O$. The hydrophosphates of magnesium-manganese form a continuous range of solid substitution solutions. The boundary line compositions of solid solutions of magnesium-cobalt and magnesium-zinc hydrophosphates are determined. The cause of this phenomenon is discussed.

It is shown that the double mediate phosphates Mg - - M^{II} (M = Co, Zn) form limited series of solid substitution solutions based on the individual zinc or cobalt, but not magnesium phosphates structures. For the magnesium-cobalt phosphates these compounds have general formula

$Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ $(0<x\leqslant 1{,}00)$, and for magnesium-zinc $Zn_{3-x}Mg_x(PO_4)_2\cdot 4H_2O$ $(0<x\leqslant 1{,}00)$. The boundary of double phosphate formation is determined by the production of the maximally saturated solid solutions of composition $Co_2Mg(PO_4)_2\cdot 8H_2O$ and $Zn_2Mg(PO_4)_2\cdot 4H_2O$. The existence of the limit in cobalt and zinc atom substitution by magnesium is explained by the peculiarities of the crystal structure of the matrix $Co_3(PO_4)_2\cdot 8H_2O$ and $Zn_3(PO_4)_2\cdot 4H_2O$ and is defined by the conditions of their precipitation (particularly by the pH of the medium).

The conditions of formation and existence, the composition and main characteristics of all produced double phosphates are determined by physical and chemical methods. The isomorphicity of cation substitution into the structure and the homogeneity of the synthesized double dihydro-, hydro- and mediate phosphates were proved by means of linear dependence of elementary cell parametres, volume, density and refraction index on cation content in the whole range. Some properties of double synthesized phosphates were studied. The correlation between their composition and solubility in water or citrate solutions is shown. Special attention is paid to the investigation of thermal behaviour of double phosphates. The chemistry of thermolysis is studied and the physico-chemical schemes of their dehydration are proposed. Thus, for $Mg_{1-x}Mn_x(H_2PO_4)_2\cdot 2H_2O$ $(0<x<1{,}00)$ it is shown that the formation of the final product of heating, cyclotetraphosphate $(Mg_{1-x}Mn_x)_2P_4O_{12}$, is result of two simultaneous parallel processes. The first one results in $(Mg_{1-x}Mn_x)_2P_4O_{12}$ formation in course of dehydration of acidic low-molecular condensed phosphates. The second way of cyclotetraphosphate formation consists of dehydration of the intermediate phosphoric acids and their subsequent interaction with salts produced by partial dehydration. The quantitative relations between these two directions are determined by cation nature. Depending on the composition of double dihydrophosphates the ratios are as follows: for

$Mg_{0,25}Mn_{0,75}(H_2PO_4)_2 \cdot 2H_2O$ 70%, $Mg_{0,5}Mn_{0,5}(H_2PO_4)_2 \cdot 2H_2O$ 75% and for $Mg_{0,75}Mn_{0,25}(H_2PO_4)_2 \cdot 2H_2O$ about 94% of magnesium-manganese cyclotetraphosphate is formed via first pathway and 30, 25 and 6% according to the second one. The thermal dehydration of double mediate phosphate is a less complicated process. Dehydration of $Co_{3-x}Mg_x(PO_4)_2 \cdot 8H_2O$ $(0<x\leqslant 1,00)$ is similar to dehydration of $Co_3(PO_4)_2 \cdot 8H_2O$. Dehydration proceeds in two stages and is accompanied with the formation of insignificant quantities of oligophosphates (up to 6% of di- and triphosphates). Phosphates of the composition $Co_{3-x}Mg_x(PO_4)_2$ $(0<x\leqslant 1,00)$ are the final products of crystallohydrate dehydration.

Conditions of divalent metal individual phosphates formation are examined on the example of scantly investigated hydrated copper phosphates of different protonization level. The peculiarities of $Cu_2OHPO_4 \cdot 0,2H_2O$, $CuHPO_4 \cdot H_2O$, $Cu_3(PO_4)_2 \cdot 2H_2O$ and $Cu(H_2PO_4)_2 \cdot H_2O$ separation are described. These compounds were obtained starting from phosphoric acid and hydroxocarbonate copper.

It is shown that dehydration of $Cu_2OHPO_4 \cdot 0,2H_2O$ begins at temperature above 100°C. Minima of endothermic effects corresponding to the detachment of 0,2 mole H_2O occur at the temperatures of 280 and 315°C. This stage of dehydration is extremely slow and continues up to the temperature of 500°C. When the temperature is 510°C the second stage of dehydration begins which completes the dehydration of Cu_2OHPO_4 at 610-615°C with the formation of $Cu_3(PO_4)_2 \cdot 2CuO$.

Dehydration of $Cu_3(PO_4)_2 \cdot 2H_2O$ proceeds through four principal stages which are accompanied by endothermic effects with minima at 110, 170, 270 and 570°C. Removal of first 0,8 moles of water from crystallohydrate up to 220°C does not affect the monophosphate anion. Removal of the rest 1,2 moles of H_2O, finishing at 610°C, is accompanied by diphosphate groups formation. The raise of temperature to 670°C and over leads to the simplification of anion composition and unhydrous monophosphate copper formation.

Dehydration of $CuHPO_4 \cdot H_2O$ is accompanied by four endothermic effects. In the interval 125-195°C crystallohydrated water is completely removed from $CuHPO_4 \cdot H_2O$ without change in monophosphate anion composition. The removal of structural water from $CuHPO_4 \cdot H_2O$ (200-490°C) is accompanied by diphosphate anion formation.

On the basis of the physico-chemical investigation we came to the conclusion that the dehydration mechanism of $Cu_3(PO_4)_2 \cdot 2H_2O$ is identical to the dehydration mechanism of $CuHPO_4 \cdot H_2O$. It may be explained by the circumstance that $Cu_3(PO_4)_2 \cdot 2H_2O$ has aquacomplex structure in which water oxygen interacts with metal ion in accordance with electrostatic or donor-acceptor mechanism. Such polarization of water molecules promotes the reverse proton transfer towards monophosphate anion across the linear H-bond and formation of hydrophosphate anion type structure. Crystallohydrated water in $CuHPO_4 \cdot H_2O$ is in a non-coordinated state and is connected with hydrophosphate anion by hydrogen bonds.

Further studies in the field of production conditions, composition, formation peculiarities, nature and properties of individual and double phosphates of divalent metals are to be continued.