# Co-precipitation of cations of zinc and divalent metals from phosphoric acid solutions

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It has been established that the joint pairwise deposition of cations $Zn^{2+}$ and $M^{2+}$ ($M^{2+}$ = $Mg^{2+}$, $Mn^{2+}$, $CO^{2+}$) in the systems $ZnCl_2$–$M^{II}Cl_2$–($Na_2HPO_4$, $Na_2HPO_4 \cdot Na_3PO_4$, $Na_3PO_4$ or ($NH_4)_2HPO_4$)–$H_2O$ ($M^{II}$ = Mg, Mn, Co) is accompanied by the formation of a phosphate-matrix — $Zn_3(PO_4)_2 \cdot 4H_2O$ — substitutional solid solutions with general formulas $Zn_{3-x}Mg_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$, $0 < x \leq 1.00$. It has been shown that for the use of an alkaline precipitant — $Na_3PO_4$ — the regions of homogeneity of the solid solutions expand, but the time of reaching equilibrium increases. In the case of other precipitants, the duration of crystallization is reduced, the boundaries of solid solution formation are more clearly fixed, but the degree of cation substitution in the phosphate matrix structure is narrowed. For the systems studied, a diagram of residual concentrations, which can be used to predict the formation of solid solutions during co-precipitation of cations in unexplored phosphoric acid systems, has been proposed.

**Keywords**: co-precipitation, solid solution, precipitator, phosphates.

**Спільне осадження катіонів цинку і двовалентних металів із фосфорнокислих розчинів**. *Н.М.Антрапцева, Н.В.Солод, О.Д.Кочкодан, О.О.Кравченко*

Визначено, що спільне попарне осадження катіонів $Zn^{2+}$ і $M^{2+}$ ($M^{2+}$ = $Mg^{2+}$, $Mn^{2+}$, $CO^{2+}$) в системах $ZnCl_2$–$M^{II}Cl_2$–($Na_2HPO_4$, $Na_2HPO_4 \cdot Na_3PO_4$, $Na_3PO_4$ або ($NH_4)_2HPO_4$)–$H_2O$ ($M^{II}$ = Mg, Mn, Co) супроводжується утворенням на основі фосфату-матриці і $Zn_3(PO_4)_2 \cdot 4H_2O$ і твердих розчинів заміщення з загальними формулами $Zn_{3-x}Mg_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$, $0 < x \leq 1.00$. Показано, що за використання лужного осаджувача — $Na_3PO_4$ — розширюються області гомогенності твердих розчинів, але збільшується тривалість досягнення рівноваги. У разі застосування інших осаджувачів тривалість кристалізації скорочується, більш чітко фіксуються межі утворення твердих розчинів, але звужується ступінь заміщення катіонів в структурі фосфату-матриці. Для досліджених систем запропонована діаграма залишкових концентрацій, яка може бути застосована для прогнозування утворення твердих розчинів під час спільного осадження катіонів у невивчених фосфорнокислих системах.

## 1. Introduction

Compounds containing several different cations are used for the synthesis of new multifunctional materials with a specific complex of improved technically valuable properties. These include divalent metal phosphates, which by their chemical nature can be various hydrated solid solutions or double salts. They are known for their efficiency in the production of laser, ceramic and heat-sensitive materials, organic synthesis catalysts, ionic conductors, anti-corrosion pigments, phosphors, ferro- and piezoelectric materials, etc. [1–4]. They are obtained by joint pairwise deposition of divalent metal cations, in particular magnesium, calcium, manganese(II), cobalt(II), and zinc from aqueous solutions.

According to the literature sources [2, 4−9], the main methods to obtain them are as follows:

— homogeneous interaction of aqueous solutions of salts of the corresponding cations (sulfates, chlorides or nitrates) with a precipitant solution — hydrogen phosphate, medium phosphate of alkali metals or ammonium and their mixture;

— heterogeneous interaction of the corresponding hydroxocarbonates with phosphate acid at fixed concentrations of hydrogen ions.

In particular, studies of the conditions for the synthesis of a solid solution of hydrated medium phosphates by precipitation in the $MgCl_2$–$CoCl_2$–$Na_3PO_4$–$H_2O$ system are known [5]. The paper [6] presents the results of studying phosphates formed during the interaction of solutions of calcium and cobalt(II) nitrates with ammonium bicarbonate. The possibilities of synthesis of solid solutions of hydrated phosphates of various degrees of protonization by means of joint pairwise precipitation of Cu(II), Co(II), Ni(II), and Zn cations from aqueous solutions are considered in [7,8].

Heterogeneous interaction is most often used to produce solid solutions of protonated phosphates of divalent metals. An example of the implementation of such synthesis is the deposition of hydrogen- and dihydrogen phosphates of divalent metals $Mn_{1-x}M^{II}_xHPO_4 \cdot 3H_2O$ (M = Mg, Co, Zn) [9] and $Co_{1-x}Zn_x(H_2PO_4)_2 \cdot 2H_2O$ from phosphoric acid solutions [5].

There are extremely insufficient data in the literature on the synthesis of solid solutions of medium phosphates by joint precipitation of zinc and magnesium, manganese(II), or cobalt(II) cations from phosphoric acid solutions. No systematic research has been conducted in this area.

The aim of this paper is to study the process and products of joint pairwise precipitation from phosphoric acid solutions of zinc and magnesium, manganese(II) or cobalt(II) cations and the conditions for the formation of solid solutions of medium hydrated phosphates.

## 2. Experimental

The generalization of known data and the results of our studies have shown that individual medium phosphates are deposited at different pH values (from 4.9 to 6.5 for $Zn_3(PO_4)_2 \cdot 4H_2O$ up to 7.0−9.0 for $Mg_3(PO_4)_2 \cdot 8H_2O$). Therefore, to create conditions for joint pairwise deposition of the cations of $Zn^{2+}$ and $Mg^{2+}$ ($Mn^{2+}$ or $Co^{2+}$), aqueous solutions of phosphates of various protonations were used as a precipitator. Solutions of $(NH_4)_2HPO_4$, $Na_2HPO_4$, mixtures of $Na_2HPO_4$ and $Na_3PO_4$, taken in various ratios, or $Na_3PO_4$, were chosen as such precipitators. This made it possible to vary the pH of precipitation over a wide range, thereby creating conditions for the deposition of phosphates of a specific anionic composition.

To establish a quantitative ratio between precipitant solutions and salts containing precipitated cations ($n = P/\sum M^{II}$), a separate series of experiments, in which the value of n changed from 0.5 to 3.0, was performed. The results of the analysis of the equilibrium solid phase and mother liquor showed that in the $CoCl_2$–$(NH_4)_2HPO_4$–$H_2O$ system, for example, phosphates precipitate on average in the range of $n = 0.50−1.00$, and double phosphates at $n > 2.5$ with the general formula $M^{II}NH_4PO_4 \cdot nH_2O$ or $M^{II}NaPO_4 \cdot nH_2O$. Based on the data obtained during the synthesis of solid solutions of medium phosphates, the stoichiometrically necessary amounts of the precipitant were selected ($n = 0.67$).

The temperature regime of the process, the concentrations of the initial solutions, the rate and order of their supply to the reaction vessel were established experimentally, taking into account classical methods for obtaining crystalline sediments [2].

The obtained data on co-deposition of $Zn^{2+}$ and $Mg^{2+}$ cations ($Mn^{2+}$ or $Co^{2+}$) were analyzed by the method of residual interaction concentrations in the following systems: $ZnCl_2$–$M^{II}Cl_2$–$(NH_4)_2HPO_4$–$H_2O$ ($M^{II}$ = Mg, Mn, Co), $ZnCl_2$–$M^{II}Cl_2$–$Na_2HPO_4$–$H_2O$, $ZnCl_2$–$M^{II}Cl_2$–$Na_2HPO_4$–$Na_3PO_4$–$H_2O$ ($Na_2HPO_4$:$Na_3PO_4$ in the ratio 2:1, 1:1, 1:2), $ZnCl_2$–$M^{II}Cl_2$–$Na_3PO_4$–$H_2O$, as well as in similar systems with solutions of sulfate or nitrate salts.

Aqueous salt solutions 0.05−0.025 mol/l and a precipitant solution 0.2−0.01 mol/l were used as initial reagents. For each series of experiments, the initial concentration of cations ($C^0$) was recorded in the absence of a chemical reaction, which was 0.025 mole/l. The ratio of cations in the initial solutions varied in the range of $K = Zn^{2+}/M^{2+}$ (molar) $= 50.0−0.11$. The ratio of phosphorus to the sum of deposited cations was $n = P/\sum Zn^{2+}$, $M^{2+} = 0.67$. The deposition temperature was varied in the range of

25–75°C. The equilibrium state in the solid phase-liquid phase system was reached within 3–8 days.

According to the methodological part of the research, a mixture of aqueous solutions of zinc and magnesium salts (manganese or cobalt), taken in a given ratio, and the precipitant were fed in parallel with constant stirring into the reaction vessel. After stabilization of the composition of the system, the precipitate was separated from the mother liquor and analyzed.

The content of phosphorus, cations and water was determined by chemical analysis in the composition of the solid phase according to [9]. The residual concentration of cations of zinc ($C_{Zn}^{resid.}$), magnesium ($C_{Mg}^{resid.}$), manganese ($C_{Mn}^{resid.}$), cobalt ($C_{Co}^{resid.}$) and phosphorus ($C_{P}^{resid.}$) was similarly determined in equilibrium mother liquors; pH, specific electrical conductivity, relative density, relative viscosity, and refractive index were also measured.

To identify the solid phase and study it, a complex of physical and chemical analysis methods was used, as described in [9].

## 3. Results and discussion

Analysis of mother solutions of the $ZnCl_2$–$MgCl_2$–$Na_2HPO_4$–$H_2O$ (25°C) system showed that each curve of residual concentrations of zinc ($C_{Zn}^{resid}$), magnesium ($C_{Mg}^{resid}$), phosphorus ($C_{P}^{resid}$) and pH consists of two branches with a cutoff point of 40 mol%. $ZnCl_2$ ($K$ = Zn/Mg = 0.67, molar). Since the residual concentrations characterize the solubility of the equilibrium precipitate, the inflections on the Cresid curves indicate a change in its phase composition.

The compositions of the solid phase, calculated according to the data of $C^{resid}$, show that the precipitation area of the mechanical mixture of hydro- and average phosphate is 0<$K$<0.67. The relative amount of the latter, based on the values of $n_1 = $ P/$\sum$(Zn, Mg) in the sediment, increases when $K$ changes from 0 to 0.67. As a result, the residual concentrations of zinc, phosphorus, and magnesium increase, while the pH decreases (Fig. 1). The results of X-ray phase and chemical analyses showed that under these conditions, a solid phase is deposited, which is a mechanical mixture of two crystalline phases — magnesium hydrogenphosphate and the $Zn_3(PO_4)_2 \cdot 4H_2O$ phase [10, 11].

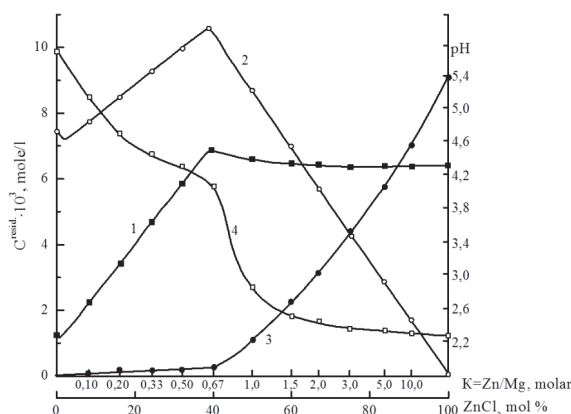When $K$ > 0.67, the residual concentration of phosphorus practically retains their



Fig. 1. Residual concentrations in the $ZnCl_2$–$MgCl_2$–$Na_2HPO_4$–$H_2O$ system at 25°C (*1* — P, *2* — Mg, *3* — Zn, *4* — pH).

value, while the magnesium concentration and pH decreases, the zinc concentration increases. The changes in pH values are due to the changes in the concentrations of $Zn^{2+}$ and $Mg^{2+}$ ions which interact with water to form hydroxocomplexes according to the schemes (1) and (2):

$$M^{2+} + H_2O \longleftrightarrow MOH^+ + H^+, \qquad (1)$$
$$lgK_1(ZnOH^+) = 4.40,$$

$$MOH^+ + H_2O \longleftrightarrow M(OH)_2 + H^+, \qquad (2)$$
$$lgK_1(MgOH^+) = 2.60.$$

Since this interaction is accompanied by the release of free hydrogen ions, the pH of the solution is largely determined by the stability constants of the hydroxocomplexes of cations. Comparison of these values completely characterizes the change in pH of the solution: with an increase in the concentration of $Zn^{2+}$ and by reducing $Mg^{2+}$, the pH of the solution decreases.

The ratio $n_1$ for $K$ > 0.67, acquires a value close to the calculated value for average phosphates, which indicates the presence of one phase of medium phosphate in the sediment (Table 1). Analysis of this phase indicates the simultaneous presence of zinc and magnesium in it, the contents of which correlate with the composition of the initial solutions. Identification of these phosphates by X-ray phase and IR spectroscopic analyses indicates the formation of a solid substitution solution with a phosphate-matrix structure of $Zn_3(PO_4)_2 \cdot 4H_2O$.

In the second series of experiments, codeposition of $Zn^{2+}$ and $Mg^{2+}$ was performed at 75°C. According to the results of analy-

Table 1. Compositions of co-precipitation products in systems $ZnCl_2$–$MgCl_2$–$Na_2HPO_4(Na_2HPO_4 \cdot Na_3PO_4,\ Na_3PO_4)$–$H_2O$ (75°C)

| $K = Zn/Mg$ molar | pH | Chemical composition | | | | | Phase composition |
|---|---|---|---|---|---|---|---|
| | | P, mass% | Mg, mass% | Zn, mass% | $n_1$ | $K_1$ | |
| Precipitant $Na_2HPO_4$ | | | | | | | |
| 10.00 | 2.29 | 14.08 | 0.53 | 43.20 | 0.66 | 32.10 | $Zn_{2.92}Mg_{0.08}(PO_4)_2 \cdot 4H_2O$ |
| 3.00 | 2.36 | 14.17 | 0.80 | 42.41 | 0.67 | 19.00 | $Zn_{2.85}Mg_{0.15}(PO_4)_2 \cdot 4H_2O$ |
| 1.00 | 2.75 | 13.70 | 1.52 | 38.80 | 0.67 | 9.30 | $Zn_{2.71}Mg_{0.29}(PO_4)_2 \cdot 4H_2O$ |
| 0.67 | 4.15 | 14.13 | 2.91 | 36.04 | 0.68 | 4.59 | $Zn_{2.46}Mg_{0.54}(PO_4)_2 \cdot 4H_2O$ |
| 0.50 | 4.34 | 15.78 | 5.90 | 30.46 | 0.72 | 1.93 | Mixture of phases $MgHPO_43H_2O$ and $Zn_{2.46}Mg_{0.54}(PO_4)_2 \cdot 4H_2O$ |
| 0.10 | 5.14 | 17.33 | 12.90 | 6.02 | 0.90 | 0.17 | |
| 0.00 | 5.70 | 17.63 | 14.10 | – | 0.98 | 0.00 | $MgHPO_4 \cdot 3H_2O$ |
| Precipitant $Na_2HPO_4 \cdot Na_3PO_4 = 1{:}1$ | | | | | | | |
| 5.00 | 3.05 | 14.21 | 0.30 | 44.53 | 0.66 | 55.10 | $Zn_{2.95}Mg_{0.05}(PO_4)_2 \cdot 4H_2O$ |
| 3.00 | 3.20 | 14.00 | 0.63 | 42.42 | 0.67 | 26.26 | $Zn_{2.89}Mg_{0.11}(PO_4)_2 \cdot 4H_2O$ |
| 2.00 | 3.90 | 13.85 | 1.22 | 40.54 | 0.66 | 12.20 | $Zn_{2.77}Mg_{0.23}(PO_4)_2 \cdot 4H_2O$ |
| 1.00 | 5.56 | 14.52 | 4.04 | 35.32 | 0.67 | 3.30 | $Zn_{2.30}Mg_{0.70}(PO_4)_2 \cdot 4H_2O$ |
| 0.67 | 5.58 | 15.15 | 6.31 | 28.61 | 0.70 | 1.68 | Mixture of $MgHPO_4 \cdot 3H_2O$ and $Zn_{2.30}Mg_{0.70}(PO_4)_2 \cdot 4H_2O$ |
| 0.50 | 5.70 | 15.52 | 7.72 | 26.50 | 0.74 | 1.28 | |
| Precipitant $Na_3PO_4$ | | | | | | | |
| 10.00 | 8.12 | 13.50 | 1.33 | 40.10 | 0.65 | 11.00 | $Zn_{2.75}Mg_{0.25}(PO_4)2 \cdot 4H_2O$ |
| 3.00 | 8.43 | 14.31 | 4.10 | 34.71 | 0.66 | 3.10 | $Zn_{2.27}Mg_{0.73}(PO_4)_2 \cdot 4H_2O$ |
| 2.00 | 8.61 | 15.00 | 5.94 | 31.84 | 0.67 | 2.01 | $Zn_2Mg(PO_4)_2 \cdot 4H_2O$ |
| 1.00 | 8.80 | 14.81 | 8.83 | 23.63 | 0.67 | 1.00 | Mixture of phases $Mg_3(PO_4)_2 \cdot 8H_2O$ and $Zn_2Mg(PO_4)_2 \cdot 4H_2O$ |
| 0.50 | 9.10 | 15.00 | 11.82 | 16.20 | 0.66 | 0.51 | |
| 0.01 | 9.10 | 15.08 | 17.04 | 1.16 | 0.67 | 0.12 | |
| 0.00 | 9.10 | 15.21 | 17.91 | 0.00 | 0.67 | 0.00 | $Mg_3(PO_4)_2 \cdot 8H_2O$ |

ses of the solid phase formed when using various precipitants, the ratio of $n_1 = P/Mg$ in sediments obtained at $K = 0$ (precipitant $Na_2HPO_4$ or a mixture of $Na_2HPO_4{:}Na_3PO_4 = 1{:}1$), is close to the calculated value for hydrogenphosphates ($n_1 = 1.0$). Only the reflections characteristic of $MgHPO_4 \cdot 3H_2O$, are present on diffraction patterns.

When the value of $K$ increases ($K > 0$), the proportion of hydrogen phosphate in the sediment decreases, as evidenced by a decrease in the pH of the mother solution to 4.34 and 5.58, respectively. On diffraction patterns of sediments obtained under conditions of $0 < K \leq 0.50$ (precipitant $Na_2HPO_4$) and $0 < IK \leq 0.67$ (precipitant $Na_2HPO_4{:}Na_3PO_4 = 1{:}1$), in addition to reflections characteristic of $MgHPO_4 \cdot 3H_2O$, reflections of a

new crystalline phase with the $Zn_3(PO_4)_2 \cdot 4H_2O$ structure are recorded.

Starting with $K = 0.67$ and 1.0, respectively, the ratio n1 in sediments stabilizes, taking a value close to the calculated value for medium phosphates. On diffraction patterns of sediments obtained at $K \geq 0.67$ and $K \geq 1.0$, only one crystalline phase with a medium zinc phosphate tetra-hydrate structure is fixed. According to the results of chemical analysis, the precipitated phosphates contain two cations — zinc and magnesium, and the latter is present in amounts that adequately compensate for the lack of a cation in the composition of medium zinc phosphate. This indicates an isomorphic substitution of the zinc fraction for magnesium in the $Zn_3(PO_4)_2 \cdot 4H_2O$ structure with the formation of a solid solution of the gen-

Table 2. The composition of the solid phase in the system $ZnSO_4$–$MnSO_4$–$Na_3PO_4$–$H_2O$ ($n = 0.67$; 75°C; $\tau = 24$ hours)

| $K$ = Zn/Mg, molar | The solid phase composition, mas.% | | | | Chemical composition | Phase composition |
|---|---|---|---|---|---|---|
| | Zn | Mn | P | $H_2O$ | | |
| – | 42.70/ 42.61* | – | 13.59/ 13.52 | 15.72/ 15.70 | $Zn_3(PO_4)_2 \cdot 4H_2O$ | $Zn_3(PO_4)_2 \cdot 4H_2O$ Solid solution $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$ $0 < x \leq 1.00$ (orthorhombic crystal system, sp.gr. Pnma, Z=4) |
| 50.00 | 42.00 | 0.93 | 13.62 | 15.53 | $Zn_{2.92}Mn_{0.08}(PO_4)_2 \cdot 4H_2O$ | |
| 10.00 | 38.33 | 3.67 | 13.57 | 15.82 | $Zn_{2.68}Mn_{0.32}(PO_4)_2 \cdot 4H_2O$ | |
| 5.00 | 35.74 | 5.99 | 13.66 | 15.95 | $Zn_{2.48}Mn_{0.52}(PO_4)_2 \cdot 4H_2O$ | |
| 2.00 | 29.37 | 11.83 | 13.85 | 16.07 | $Zn_{2.00}Mn_{1.00}(PO_4)_2 \cdot 4H_2O$ | |
| 1.75 | 28.81 | 12.57 | 13.89 | 16.01 | Mixture of $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ and $Mn_3(PO_4)_2 \cdot 3H_2O$ | Mixture of phases $Zn_3(PO_4)_2 \cdot 4H_2O$ and $Mn_3(PO_4)_2 \cdot 3H_2O$ |
| 1.00 | 23.36 | 17.71 | 14.06 | 15.62 | | |
| 0.10 | 4.58 | 35.35 | 14.75 | 14.45 | Mixture of $Mn_3(PO_4)_2 \cdot 3H_2O$ and $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ | |
| 0.005 | 0.42 | 39.34 | 14.96 | 13.93 | | |
| 0.00 | 0.00 | 39.85/ 39.90* | 14.89/ 14.78 | 13.10/ 13.14 | $Mn_3(PO_4)_2 \cdot 3H_2O$ | $Mn_3(PO_4)_2 \cdot 3H_2O$ |

eral formula $Zn_{3-x}Mg_x(PO_4)_2 \cdot 4H_2O$. The saturated solid solution in the case of co-precipitation of $Zn^{2+}$ and $Mg^{2+}$ cations with the $Na_2HPO_4$ solution is a phosphate, the $x$ value of which is 0.54 (Table 1). The magnesium content in phosphates increases with increasing pH of the medium. During precipitation with a more alkaline precipitant ($Na_2HPO_4$:$Na_3PO_4$ = 1:1) the degree of substitution of zinc with magnesium increases to 0.7, corresponding to the composition of the saturated solid solution $Zn_{2.3}Mg_{0.7}(PO_4)_2 \cdot 4H_2O$.

The region of homogeneity of the solid solution reaches its maximum possible value in phosphate $Zn_2Mg(PO_4)_2 \cdot 4H_2O$, obtained at pH 8.61 ($Na_3PO_4$ precipitant). There is no further increase in the degree of substitution of magnesium by zinc in the crystal structure of $Zn_3(PO_4)_2 \cdot 4H_2O$ (Table 1). This is also evidenced by the spectrum of nuclear magnetic resonance on ^{31}P nuclei, in which one absorption peak is recorded, which corresponds to a chemical shift of 4.14 ppm. For solid solution phosphates of various cationic composition ($0 < x \leq 1.00$), the value of the chemical shift within the measurement error remains constant, which indicates the presence of a single-crystal phase and the absence of amorphous phosphates.

Pycnometric density of precipitated phosphates decreases linearly with increasing degree of substitution ($x$). The same relationship is established for refractive indices, the values of which are in good agreement with those known for $Zn_3(PO_4)_2 \cdot 4H_2O$.

The use of aqueous solutions of chlorides, sulfates or nitrates as starting salts does not make fundamental differences either in the chemistry of precipitation processes or in the composition of the solid phase.

Taking into account the obtained results, the joint deposition of zinc and manganese cations in the form of medium phosphates was performed in an alkaline medium, which provides the maximum possible degree of substitution in the structure of zinc phosphate.

According to the results of solid phase analysis, in the system $ZnSO_4$–$MnSO_4$–$Na_3PO_4$–$H_2O$, in the entire studied range of values $0 \leq K$ = Zn/Mn (molar)$\leq 50.0$, phosphates are precipitated with $n_1 = (P/\sum Zn,Mn)$ = 0.67 (Table 2).

In the absence of manganese(II) in the system, the sediment is represented only by $Zn_3(PO_4)_2 \cdot 4H_2O$, identified by known features [10, 11]. The introduction of a manganese ion into the initial solutions ($K$ = 50.0) leads to its co-precipitation with zinc in the same crystal lattice of the phosphate matrix — $Zn_3(PO_4)_2 \cdot 4H_2O$. The formation of other crystal phases was not recorded (Table 2).

Identification of phosphates obtained under conditions of $0.005 \leq K \leq 50.0$ allows us

Table 3. Characteristics of the equilibrium solid phase in the system $ZnSO_4$–$CoSO_4$–$(NH_4)_2HPO_4$–$H_2O$ (25°C)

| $K$ = Zn/Mg, molar | The solid phase composition, mas.% | | | | Chemical composition | Phase composition |
|---|---|---|---|---|---|---|
| | Zn | Co | P | $H_2O$ | | |
| 20.00 | 42.74/ 42.81* | – | 13.59/ 13.53 | 15.72/ 15.72 | $Zn_3(PO_4)_2 \cdot 4H_2O$ | $Zn_3(PO_4)_2 \cdot 4H2O$ |
| 10.00 | 37.74 | 4.78 | 13.60 | 15.80 | $Zn_{2.63}Co_{0.37}(PO_4)_2 \cdot 4H_2O$ | Solid solution $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $0<x\leq1.00$ (orthorhombic crystal system, sp.gr. Prima, z=4) |
| 4.00 | 35.00 | 7.40 | 13.65 | 15.86 | $Zn_{2.41}Co_{0.59}(PO_4)_2 \cdot 4H_2O$ | |
| 2.00 | 30.35 | 11.73 | 13.70 | 15.92 | $Zn_{2.10}Co_{0.90}(PO_4)_2 \cdot 4H_2O$ | |
| 1.00 | 28.95 | 13.05 | 13.74 | 15.94 | $Zn_{2.00}Co_{1.00}(PO_4)_2 \cdot 4H_2O$ | |
| 0.67 | 26.46 | 14.66 | 14.01 | 16.74 | Mixture of $Zn_2Co(PO_4)_2 \cdot 4H_2O$ and $CoHPO_4 \cdot 1.5H_2O$ | Mixture of phase structure $Zn_3(PO_4)_2 \cdot 4H_2O$ and $CoHPO_4 1.5 \cdot H_2O$ |
| 0.50 | 24.64 | 17.98 | 14.67 | 17.57 | | |
| 0.25 | 20.59 | 23.51 | 15.67 | 17.87 | Mixture of $CoHPO_4 \cdot 1.5H_2O$ and $Zn_2Co(PO_4)_2 \cdot 4H_2O$ | |
| 0.11 | 12.65 | 29.28 | 17.08 | 19.32 | | |
| 0.00 | – | 32.26/ 32.23* | 17.09/ 17.10 | 19.84/ 19.86 | $CoHPO_4 \cdot 1.5H_2O$ | $CoHPO_4 \cdot 1.5H_2O$ |

to distinguish two main ranges of values $K$, in which the formation of medium phosphates differing in phase composition occurs. On diffraction patterns of phosphates formed under conditions of $2.0 \leq K \leq 50.0$, the positions and intensity of diffraction reflections indicate the presence of one crystalline phase $Zn_3(PO_4)_2 \cdot 4H_2O$. The characteristic shift of reflections indicates the formation of a compound of variable composition — a solid solution of the general formula $Zn_{1-x}Mn_x(PO_4)_2 \cdot 4H_2O$. Based on the results of chemical analysis, the values $x$ change from 0 to 1.00 indicating the regions of homogeneity. In the case of formation of a solid solution, the limiting value is $K = 2.0$. Under these conditions, phosphate is deposited with the maximum possible manganese content (11.83 mass %) and the value $x = 1.00$. When $K = 1.75$, manganese (II) in the sediment composition is fixed by only 0.74 mass % more (12.57 mass %). At the same time, on the diffraction patterns, along with phosphate of the composition $Zn_2Mn(PO_4)_2 \cdot 4H_2O$, a second crystalline phase is clearly observed. Phosphate, at $x$ more than 1.00, is not formed.

Under conditions of $0.005 \leq K \leq 2.00$, a heterophase precipitate containing two crystalline phases is formed. One of them is phosphate of the composition $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ with the structure $Zn_3(PO_4)_2 \cdot 4H_2O$, the other is the phosphate with structure $Mn_3(PO_4)_2 \cdot 3H_2O$. The X-ray diffraction and IR spectroscopic characteristics of the latter fully correspond to those known for $Mn_3(PO_4)_2 \cdot 3H_2O$ [11, 12].

Quantitative ratios of components of the heterophase precipitate depend on the content of the cations $Zn^{2+}$ and $Mn^{2+}$ in the initial solutions. At $1.00 \leq K \leq 2.00$, the phosphate of $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ is mainly precipitated. $Mn_3(PO_4)_2 \cdot 3H_2O$ is present in amounts characterizing it as an impurity phase. At $0.005 \leq K \leq 1.00$, phosphate $Mn_3(PO_4)_2 \cdot 3H_2O$ is formed as the main phase; while only the most intense $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ reflections are observed in the diffraction patterns.

Co-precipitation of cations of $Zn^{2+}$ and $Co^{2+}$ was studied by analyzing the equilibrium mother solutions and the composition of phosphates formed during interaction in the system $ZnSO_4$–$CoSO_4$–$(NH_4)_2HPO_4$–$H_2O$.

The data of the chemical analysis of phosphate are in full accordance with the results of a comprehensive study of the mother solutions. They indicate that the composition of the precipitate formed under conditions of $1.0 \leq K \leq 20.0$ is characterized by close values of the phosphorus content (Table 3).

The results of X-ray diffraction and IR spectroscopic studies of these phosphates showed the presence of only one crystalline phase, free from impurities of other solid phases. It was identified on the basis of

Table 4. Crystallographic characteristics of phosphates of solid solutions with general formula $Zn_{3-x}M^{II}_x(PO_4)_2 \cdot 4H_2O$ ($M^{II}$ = Mg, Mn, Co), $0 < x \le 1.00$ (orthorhombic crystal system, sp.gr. $P_{nma}$, $Z = 4$)

| Phosphate composition | Parameters of the unit cell, nm | | | |
|---|---|---|---|---|
| | $a$ | $b$ | $c$ | $V$, nm³ |
| $Zn_3(PO_4)_2 \cdot 4H_2O$ | 1.0612(4) | 1.8309(4) | 0.5028(3) | 0.9769(2) |
| $Zn_{2.50}Mg_{0.50}(PO_4)_2 \cdot 4H_2O$ | 1.0606(2) | 1.8274(3) | 0.5026(2) | 0.9728(6) |
| $Zn_{2.0}Mg_{1.0}(PO_4)_2 \cdot 4H_2O$ | 1.0600(1) | 1.8260(2) | 0.5023(3) | 0.9722(8) |
| $Zn_{2.75}Mn_{0.25}(PO_4)_2 \cdot 4H_2O$ | 1.0613(4) | 1.8341(5) | 0.5031(3) | 0.9793(12) |
| $Zn_{2.50}Mn_{0.50}(PO_4)_2 \cdot 4H_2O$ | 1.0623(3) | 1.8378(3) | 0.5038(2) | 0.9836(2) |
| $Zn_{2.25}Mn_{0.75}(PO_4)_2 \cdot 4H_2O$ | 1.0632(2) | 1.8414(2) | 0.5044(2) | 0.9875(7) |
| $Zn_{2.0}Mn_{1.0}(PO_4)_2 \cdot 4H_2O$ | 1.0639(3) | 1.8449(3) | 0.5049(1) | 0.9910(6) |
| $Zn_{2.0}Co_{1.0}(PO_4)_2 \cdot 4H_2O$ | 1.0612(2) | 1.8304(2) | 0.5026(2) | 0.9763(11) |

data known for $Zn_3(PO_4)_2 \cdot 4H_2O$ [10, 11], which indicates the similarity of their structure. Chemical analysis of the obtained phosphates revealed the simultaneous presence of both zinc and cobalt(II) in their composition, which indicates the formation of a limited solid substitutions solution of the general formula $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $(0 < x \le 1.00)$.

Phosphates obtained under conditions of $0.11 \le K \le 0.67$ are heterophase. They are a mechanical mixture of two crystal phases — $Zn_3(PO_4)_2 \cdot 4H_2O$ and $CoHPO_4 \cdot 1.5H_2O$, the quantitative ratios between which are determined by the composition of the initial reagents. The saturated solid solution formed during co-deposition of $Zn^{2+}$ and $Co^{2+}$ cations, is a phosphate consisting of $Zn_2Co(PO_4)_2 \cdot 4H_2O$. Attempts to replace more than one zinc atom in the structure $Zn_3(PO_4)_2 \cdot 4H_2O$, (precipitation under conditions $0.11 \le K \le 0.67$) lead to the appearance of an impurity of the second crystalline phase, $CoPO_4 \cdot 1.5H_2O$, in the precipitate (Table 3).

The established correlations between the phosphate composition of solid solutions of $Zn_{3-x}Mg_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$ $(0 < x \le 1.00)$, and the parameters of their crystal lattices (Table 4), retain a linear dependence over the entire region of homogeneity. This fully corresponds to Vegard's law and characterizes the formation of substitutional solid solutions.

For phosphates consisting of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $(0 < x \le 1.00)$ no noticeable changes in the values of the crystal lattice parameters were found even for a saturated solid solution. The explanation

for this phenomenon follows from the closeness of the values of the real ion radii of zinc $r(Zn^{2+}) = 0.089$ and cobalt $r(Co^{2+}) = 0.088$ nm, which mainly determine the parameters of the unit cell of the crystal.

Hence, the pairwise precipitation of the cations of $Zn^{2+}$ and $M^{2+}$ ($M^{2+}$ = $Mg^{2+}$, $Mn^{2+}$, $Co^{2+}$) from aqueous solutions of their salts is accompanied by the formation of a phosphate-based matrix — $Zn_3(PO_4)_2 \cdot 4H_2O$ — substitutional solid solutions with the general formulas $Zn_{3-x}Mg_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$ and $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$. The homogeneity domain of each of them corresponds to $0 < x \le 1.00$.

Summarizing the experimental data, it has been established that by the nature of the interactions accompanying the joint precipitation of two cations from phosphate solutions, by their chemical nature and the composition of the interaction products, the systems under study can be represented as a general diagram of the residual concentrations (Fig. 2).

A characteristic feature of the diagram of systems with the formation of a solid solution is the presence of an inflection in the course of the curves of residual concentrations of cations and phosphorus. This inflection separates the compositional regions of the initial salt solutions, in which a solid solution is formed ($ZnCl_2 > A$), from the compositions of salts, the interaction of which is accompanied by the deposition of a heterophase mixture of phosphates ($ZnCl_2 < A$). The curves of the initial $C^0(Zn^{2+})$ and residual $C^{resid}(Zn^{2+})$ of cation concentrations show the clearly visible discrepancy. The difference $C^0(M^{II}) - C^{resid}(M^{II})$ in the $ZnCl_2 > A$ region monotonically de-
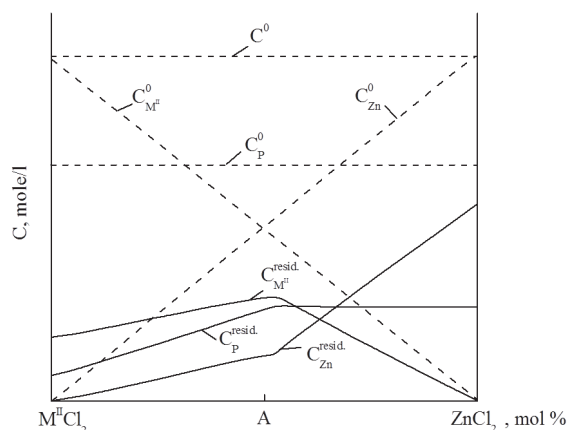
Fig.2. Diagram of residual concentrations of systems with solid solution formation

creases, which indicates a decrease in the cation content of a more soluble individual phosphate in the solid solution.

This type of residual concentration diagram describes interactions not only in the systems of the type $ZnCl_2$–$M^{II}Cl_2$–($Na_2HPO_4$, $Na_2HPO_4$:$Na_3PO_4$, $Na_3PO_4$ or $(NH_4)_2HPO_4$)–$H_2O$ ($M^{II}$ = Mg, Mn, Co), but other systems with divalent metal cations; this can be used to predict the formation of solid solutions during co-precipitation of cations in unexplored phosphoric acid systems.

## 4. Conclusions

It has been established that the pairwise deposition of $Zn^{2+}$ and $M^{2+}$ ($M^{2+}$ = $Mg^{2+}$, $Mn^{2+}$, $Co^{2+}$) cations from phosphoric acid solutions is accompanied by the formation of $Zn_3(PO_4)_2 \cdot 4H_2O$ substitutional solid solutions based on a phosphate-matrix with general formulas $Zn_{3-x}Mg_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$, $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$, $0 < x \le 1.00$. The homogeneity regions of the hydrated solid solutions are determined by the deposition conditions, first of all, by pH values of the medium and the temperature. The effect of these parameters on specific solid solutions varies.

There is no universal precipitant for obtaining solid solutions of various cationic compositions. Each of the precipitants — $Na_2HPO_4$, $Na_3PO_4$, mixture $Na_2HPO_4$ and $Na_3PO_4$ in various ratios, or $(NH_4)_2HPO_4$ — has its advantages and disadvantages.

The alkaline precipitant, $Na_3PO_4$, expands the homogeneity ranges of hydrated solid solutions, but significantly (2–3 times) increases the time of achieving equilibrium; this is especially important for systems with $Mn^{2+}$ and $Co^{2+}$, whose phosphates are initially precipitated as an X-ray amorphous phase. The solutions $(NH_4)_2HPO_4$, $Na_2HPO_4$, mixture $Na_2HPO_4$ and $Na_3PO_4$ reduce the duration of crystallization, make it possible to more clearly fix the boundaries of the formation of solid solutions; but in the case of their use, the degree of substitution of cations in the structure of the phosphate matrix narrows.

The proposed diagram of residual concentrations for the types of systems $ZnCl_2$–$M^{II}Cl_2$–($Na_2HPO_4$, $Na_2HPO_4$:$Na_3PO_4$, $Na_3PO_4$ or $(NH_4)_2HPO_4$)–$H_2O$ ($M^{II}$ = Mg, Mn, Co) can be used to predict the formation of solid solutions during co-precipitation of cations in insufficiently studied phosphate systems.

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