Crystallization features of solid solutions of hydrated diphosphates in the system ZnSO$_4$–CoSO$_4$–K$_4$P$_2$O$_7$–H$_2$O

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During the interaction in the system ZnSO$_4$–CoSO$_4$–K$_4$P$_2$O$_7$–H$_2$O, due to isomorphic intersubstitution of cations, two solid solutions of hydrated zinc and cobalt(II) diphosphates are formed – Zn$_{2-x}$Co$_x$P$_2$O$_7$·5H$_2$O and Co$_{2-x}$Zn$_x$P$_2$O$_7$·6H$_2$O. The crystal structures and homogeneity ranges of these solid solutions are different: Zn$_{2-x}$Co$_x$P$_2$O$_7$·5H$_2$O crystallizes in the orthorhombic system (space group *Pnma*, Z=4), Co$_{2-x}$Zn$_x$P$_2$O$_7$·6H$_2$O – in the monoclinic system (space group *P2$_1$/n*, Z=4). The homogeneity range of the solid solution Zn$_{2-x}$Co$_x$P$_2$O$_7$·5H$_2$O defined as $0 \leq x \leq 0.69$, is in 1.8 times wider than in the case of isomorphic substitution of Co(II) with Zn in the Co$_2$P$_2$O$_7$·6H$_2$O structure during crystallization of the Co$_{2-x}$Zn$_x$P$_2$O$_7$·6H$_2$O solid solution ($0 \leq x \leq 0.39$). The fact of the existence of different homogeneity ranges is substantiated by applying the main factors of isomorphism, the characteristics of co-precipitating cations and the chemical properties of diphosphate-matrix.

Keywords: hydrated diphosphates, solid solution, crystallization, homogeneity ranges.

Особливості кристалізації твердих розчинів гідратованих дифосфатів в системі ZnSO$_4$–CoSO$_4$–K$_4$P$_2$O$_7$–H$_2$O. *Н.М. Антрапцева, Н.В. Солод, О.О. Кравченко*

Під час взаємодії в системі ZnSO$_4$–CoSO$_4$–K$_4$P$_2$O$_7$–H$_2$O внаслідок ізоморфного взаємозаміщення катіонів утворюються два твердих розчини гідратованих цинку і кобальту(II) дифосфатів– Zn$_{2-x}$Co$_x$P$_2$O$_7$·5H$_2$O і Co$_{2-x}$Zn$_x$P$_2$O$_7$·6H$_2$O. Кристалічні структури і області гомогенності цих твердих розчинів різні: Zn$_{2-x}$Co$_x$P$_2$O$_7$·5H$_2$O кристалізується в орторомбічній сингонії (пр. гр. *Pnma*, Z=4), Co$_{2-x}$Zn$_x$P$_2$O$_7$·6H$_2$O – в моноклінній (пр. гр. *P2$_1$/n*, Z=4). Область гомогенності твердого розчину Zn$_{2-x}$Co$_x$P$_2$O$_7$·5H$_2$O, визначена як $0 \leq x \leq 0.69$, у 1.8 разів ширша, ніж у разі ізоморфного заміщення Co(II) на Zn в структурі Co$_2$P$_2$O$_7$·6H$_2$O під час кристалізації твердого розчину Co$_{2-x}$Zn$_x$P$_2$O$_7$·6H$_2$O ($0 \leq x \leq 0.39$). Факт існування різних меж гомогенності обґрунтований із застосуванням основних факторів ізоморфізму, характеристик катіонів, що співосаджуються, та хімічних властивостей дифосфатів-матриць.

1. Introduction

Polymeric phosphates, particularly diphosphates of divalent metals, which have a polymeric structure of the phosphate anion, are capable of such processes as chelation, ion exchange and complexation. These processes ensure improvement of the physical and chemical properties and performance characteristics of various functional materials based on them.

Solid solutions of diphosphates with two different cations, the content of which can be regulated within wide limits, have a fairly wide range of applications: as effective sorbents, thermosensitive paints, luminescent materials, catalysts, pigments, corrosion inhibitors, etc. [1-3].

Most of the research related to the chemistry of solid solutions of diphosphates is devoted to anhydrous salts [2, 4-7]. Among the crystalline hydrates, the most studied are double salts

of constant cationic composition, in particular diphosphates of alkali and polyvalent metals [8, 9].

Solid solutions of hydrated divalent metal diphosphates were studied in terms of their structure, as well as IR spectroscopic and thermal properties [10-12]. Thus, in [10], electronic structure and atomic structure peculiarities of isomorphic modified zinc diphosphates were investigated. The authors of [11] focused on the study of vibrational spectra and thermal properties of the solid solution of manganese(II)-cobalt(II) diphosphates. Electron structure peculiarities of disordered Mn and Co diphosphates have been studied in [12]. However, there is no information regarding the synthesis of the studied diphosphate solid solutions in these works.

There is little information available in the scientific resources on systematic studies of the conditions for the synthesis of solid solutions of crystalline hydrated diphosphates of divalent metals. For example, the synthesis of a continuous solid solution of hydrated manganese and zinc diphosphates by the interaction of aqueous solutions of manganese(II) and zinc sulfates with potassium diphosphate has been described [13]. The synthesis of a solid solution of hydrated manganese and cobalt diphosphates with a limited homogeneity range is mentioned in [14].

The analysis of the abovementioned studies indicates that the conditions for synthesis of hydrated diphosphates of divalent metals are determined by the structure of the anion and its behavior in aqueous solution. The tendency of diphosphates to hydrolytic destruction, which is influenced by the duration of contact of the solid phase with the mother liquor, the pH of the aqueous solution and the temperature of the interaction, determine the choice of conditions for the synthesis of individual hydrated diphosphate matrices and crystalline solid solutions based on them. In preparative works [15, 16], it was noted that individual hydrated zinc and cobalt diphosphates precipitate during interactions in the systems $M^{II}SO_4$–$K_4P_2O_7$–H_2O (M^{II} = Zn, Co). However, zinc precipitates in the form of crystalline diphosphate, while cobalt(II) diphosphate is amorphous. This behavior significantly complicates the synthesis of solid solutions of crystalline hydrated zinc and cobalt(II) diphosphates by the co-precipitation of cations in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system. There is very little data in the scientific works regarding this process. Systematic studies in this direction have not been conducted yet.

The aim of this work is to study the features of crystallization of solid solutions of hydrated zinc and cobalt(II) diphosphates in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system.

2. Experimental

The crystallization of solid solutions of hydrated diphosphates in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system was investigated by the method of residual concentration according to [17]; zinc sulfate $ZnSO_4 \cdot 7H_2O$, cobalt(II) sulfate $CoSO_4 \cdot 7H_2O$, and potassium diphosphate $K_4P_2O_7$ were used as starting materials.

Unlike the classical application of this method, the ratio of the precipitant to Zn^{2+} and Co^{2+} (n = P/M^{II}) was fixed, varying the ratio between the precipitating cations while maintaining their total concentration constant.

The data were obtained by specifying the conditions of interaction in the $ZnSO_4$–$K_4P_2O_7$–H_2O and $CoSO_4$–$K_4P_2O_7$–H_2O systems; the following parameters were determined that ensure the joint precipitation of Zn^{2+} and Co^{2+} cations: the ratio in the composition of the initial solutions (n = $P_2O_7^{4-}$/ΣZn^{2+}, Co^{2+} = 0.2, K = Zn^{2+}/Co^{2+}, molar, within $0.02 \leq K \leq 9.00$), the initial concentration of the initial solutions is 0.1 mol/L, the temperature range of interaction is 293–298 K, the duration of contact of the solid phase with the mother liquor is until equilibrium is reached.

Since in the case of obtaining solid solutions the duration of reaching equilibrium is different for the precipitation of individual $Zn_2P_2O_7 \times 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$, it was determined for each specific value of K = Zn^{2+}/Co^{2+} by potentiometric studies in a separate series of experiments. Taking into account the property of the diphosphate anion to be destroyed in aqueous solutions, the anionic composition of diphosphate upon contact with the mother solution was studied.

The results of chromatographic analysis of diphosphates, which were in contact with the mother solution for different periods of time, showed that the quantitative indicators of the destruction process of diphosphate anion remained practically unchanged (at the level of 1.8–2.4% relative to P_2O_5 in the form of monophosphate anion) for 5–15 days. Increasing the duration of contact of diphosphate with the mother solution to 18–20 days was accompanied by a noticeable destruction of P–O–P bonds. The amount of monophosphate anions increased to
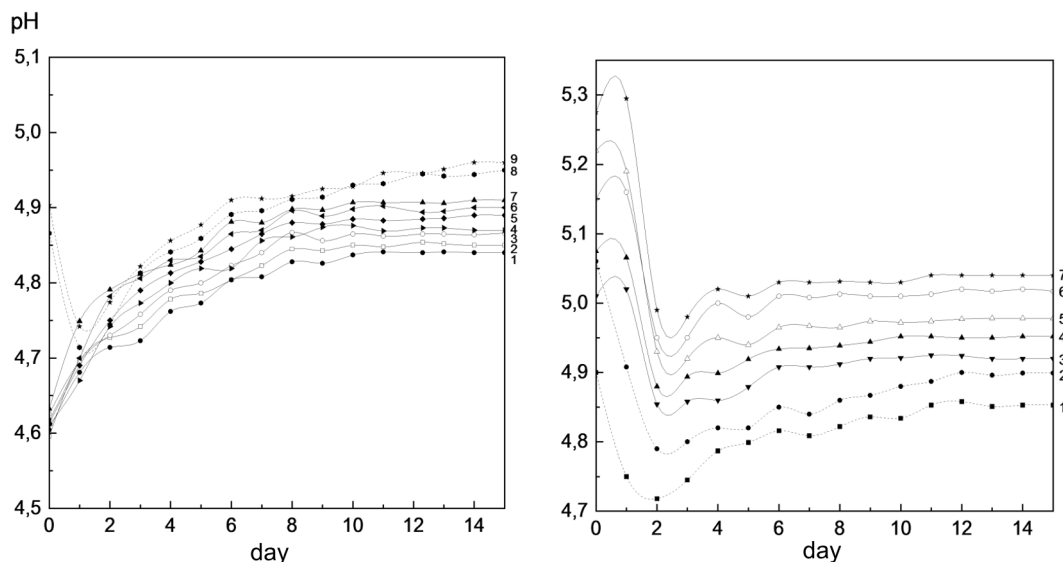
Fig. 1. pH changes of mother solutions during interaction in the system $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O: **a** – in the absence of Co^{2+} (1), for values of K ($K = Zn^{2+}/Co^{2+}$) 9.00 (2); 4.00 (3); 3.00 (4); 1.50 (5); 1.00 (6); 0.67 (7); 0.54 (8); 0.43 (9); **b** – in the absence of Zn^{2+} (7), for values of K 0.02 (6), 0.05 (5), 0.09 (4), 0.11 (3), 0.18 (2), 0.25 (1)

4.0–4.6% relative to P_2O_5, respectively. Therefore, the optimal duration for achieving equilibrium in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system was chosen to be 12 days.

The synthesis of crystalline solid solutions of hydrated diphosphates was carried by the method described in [13].

The phosphorus content in the solid phase was determined by chemical analysis (gravimetric quinoline molybdate method, relative error is 0.2%), water content was estimated by the loss of mass of samples when heated to 1073 K (relative error is 1%) according to [17]. The content of Zn and Co(II) in their combined presence was determined by the complexometric method by the sum of Zn^{2+} and Co^{2+} cations using the back titration method and by the spectrophotometric method of determining the content of Co^{2+} in the form of a complex of surfactants (1-(2-pyridylazo)-resorcinol) (spectrophotometer SF–46, relative error is 0.5%). The experiments showed that the content of diphosphate ions in the solution aliquot at the level of 2.4 µg (recalculated to P) does not affect the analysis results. The zinc content was calculated as the difference between the total cations and the Co^{2+} content.

Similarly, the residual concentrations of zinc cations $C^{resid.}(Zn^{2+})$, cobalt $C^{resid.}(Co^{2+})$, phosphorus $C^{resid.}(P)$ were determined in equilibrium mother solutions; the pH was measured.

For the identification of the solid phase and its investigation, a complex of physicochemical methods was applied: X-ray phase analysis, vibrational spectroscopy methods, electron microscopy, and crystal-optical analysis, as described in [18].

3. Results and discussion

Figure 1 presents the results of potentiometric investigations aimed at determining the time required to achieve equilibrium in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system. Analysis of the pH change in the mother solutions with different Zn^{2+} and Co^{2+} contents during contact with the solid phase indicates that there are three different groups of potentiometric curves. The first group (curves 1–7) refers to solutions with $0.67 \leq K = Zn^{2+}/Co^{2+}$ (molar) ≤ 9.0 that are similar in nature and close in pH values (Fig.1a). The initial pH values of their mother solutions range from 4.59 to 4.63. During the first day of contact with the solid phase, pH increases to 4.70–4.75, continues to increase over the next 8 days, and gradually stabilizes by 12–15 days.

The second group of potentiometric curves (3–7) shows a fundamentally different character of pH change compared to the curves of the first group (Fig. 1b). These curves correspond to solutions with $0.11 \leq K \leq 0.02$. Their initial pH values range from 5.01 to 5.28. With further contact between the solid phase and the mother solutions, the pH sharply decreases to 4.85–4.99 (on the second day). Over days 6–8 of contact, it gradually increases and practically stabilizes by 9 day at pH values of 4.92–5.00.

The potentiometric curves obtained from the solutions with $0.18 \leq K \leq 0.54$ (curves 8, 9 in Fig. 1a and 1, 2 in Fig. 1b) form the third group. In these solutions, the change in pH and the specific pH values have features characteristic of both the first two groups of curves simultaneously. The time to reach equilibrium in the system for these K values increases to 15 days.

The experimentally determined pH values of the equilibrium mother solutions correlate with the stability constants of hydroxo complexes formed during the interaction in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system ($lg\,K_1$ ($ZnOH^+$) = 6.31, $lg\,K_1$ ($CoOH^+$) = 4.40) [19].

The «composition-property» diagram constructed by the results of determining the residual concentrations of zinc $C^{resid.}$(Zn^{2+}), cobalt $C^{resid.}$(Co^{2+}), and phosphorus $C^{resid.}$(P) in the equilibrium mother solutions, indicates that the Zn^{2+} and Co^{2+} contents change adequately to the composition of the original mother solutions with $0.67 \leq K \leq 9.0$; the values of $C^{resid.}$(P) and pH remain practically constant (Fig. 2). This character of the change in residual concentrations is maintained up to $K=0.67$, at which a clear inflection point is observed on all curves (less noticeable for $C^{resid.}$(P), indicating a change in the phase state of the equilibrium precipitate. With further increase in Co^{2+} in the original solutions ($0.43 \leq K < 0.67$), there is a sharp decrease in the pH values of the mother solutions and a violation of the linear dependence in the values of $C^{resid.}$(Zn^{2+}) and $C^{resid.}$(Co^{2+}).

These changes in the mother solutions indicate that the formation of the solid phase at $0.67 \leq K \leq 9.0$ is accompanied by similar processes, and its phase composition is the same. At $K < 0.67$, the composition of the solid phase and the occurring processes are fundamentally different.

On the «composition-property» diagram constructed for the mother solutions with $0.02 \leq K \leq 0.25$, similar changes are registered. On the residual concentration curves, there is an inflection point at $K= 0.11$, indicating the formation of a single-phase precipitate at $0.02 \leq K \leq 0.11$.

The chemical composition of the solid phase is completely consistent with the composition of the mother solutions (Table 1). The results of the chemical analysis showed that the simultaneous precipitation of Zn^{2+} and Co^{2+} for all K values from the range of $0.02 \leq K \leq 9.0$ leads to formation of diphosphates. This is evidenced by the ratio n_1 = P/ΣZn,Co = 1.00 corresponding to the calculated value for diphosphates, the specific composition of which is determined by
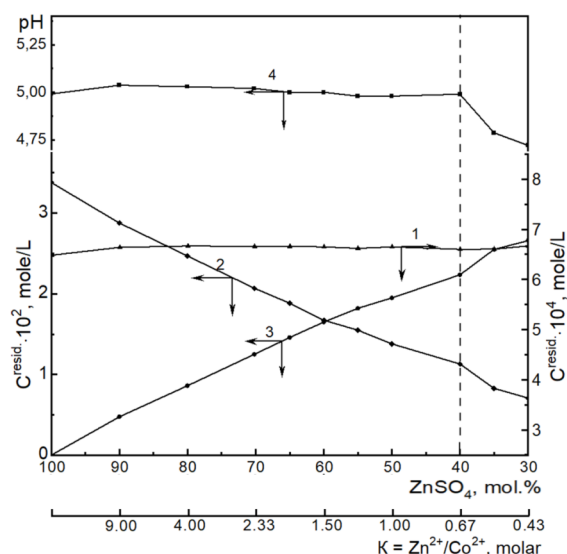

Fig. 2. The change in residual concentrations in the equilibrium mother solutions of the system $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O: 1 – $C^{resid.}$ (P), 2 – $C^{resid.}$ (Zn^{2+}), 3 – $C^{resid.}$ (Co^{2+}), 4 – pH

the composition of the original solutions. This conclusion is also confirmed by the results of quantitative paper chromatography, according to which the anionic composition of the solid phase at all K values is represented by the diphosphate anion (98.6–97.4 % relat.).

The content of all ingredients (Zn, P, H_2O) in the diphosphate precipitated in the absence of Co^{2+} in the initial solutions corresponds to their calculated values for individual zinc diphosphate (Table 1). The X-ray (Fig. 3a) and spectroscopic (Fig. 3b) characteristics correspond to $Zn_2P_2O_7 \cdot 5H_2O$ [20, 10]. In the absence of Zn^{2+} in the initial solutions, the content of Co, P, H_2O in the precipitate corresponds to that calculated for cobalt(II) diphosphate (Table 1). It was identified (Fig. 3a, b) as the known $Co_2P_2O_7 \cdot 6H_2O$ [11, 14, 16]. Diphosphates obtained in the solutions with $0.02 \leq K \leq 9.00$ contain both zinc (from 30.82 to 2.10 wt. %) and cobalt (from 1.63 to 27.38 wt. %), and their content varies depending on the composition of the initial solutions (Table 1).

Based on the specific content values of the ingredients, the crystallized diphosphates are divided into three different groups, similar to those determined by the analysis of equilibrium mother solutions.

The first group includes diphosphates obtained in the range $0.67 \leq K \leq 9.00$. They contain almost the same amount of phosphorus and water (Table 1). The change in K_1 (K_1 = Zn/Co, atomic), which characterizes the zinc and cobalt(II) content in these diphos-

Table 1. Characteristics of diphosphates crystallizing in the system $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O (n = $P_2O_7^{4-}/\Sigma Zn^{2+}$, Co^{2+} = 0.2, C^0 = 0.1 mole/L, 298 K)

$K = Zn^{2+}/Co^{2+}$, molar	The solid phase composition					
	Content of ingredients, wt. %				Chemical composition	Phase composition
	Zn	Co	P	H_2O		
-	$\dfrac{33.08}{33.12}$**	-	$\dfrac{15.58}{15.69}$	$\dfrac{22.93}{22.82}$	$Zn_2P_2O_7 \cdot 5H_2O$	$Zn_2P_2O_7 \cdot 5H_2O$
9.00	30.82	1.63	15.45	23.03	$Zn_{1.89}Co_{0.11}P_2O_7 \cdot 5H_2O$	Solid solution $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0<x\leq0.69$) orthorhombic system, sp. gr. *Pnma* (D_{2h}^{16}), *Z=4*
4.00	29.71	2.60	15.47	23.10	$Zn_{1.82}Co_{0.18}P_2O_7 \cdot 5H_2O$	
1.50	24.31	7.50	15.46	23.30	$Zn_{1.49}Co_{0.51}P_2O_7 \cdot 5H_2O$	
1.00	22.04	9.57	15.47	23.43	$Zn_{1.35}Co_{0.65}P_2O_7 \cdot 5H_2O$	
0.67	21.38	10.13	15.47	23.51	$Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$	
0.54	19.56	10.64	15.45	24.93	$Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O +$ $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$	Mechanical mixture of phases with structures $Zn_2P_2O_7 \cdot 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$
0.43	13,17	15.36	15,43	25,78		
0.25	11,96	18.70	15.50	25,71		
0.18	8.13	22.25	15.54	25.98		
0.11	6.04	23.48	15.44	27.25	$Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$	Solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0.39$) monoclinic system, pr. gr. $P2_1/n$, Z=4
0.05	4.53	25.08	15.39	27.30	$Co_{1.72}Zn_{0.28}P_2O_7 \cdot 6H_2O$	
0.02	2.10	27.38	15.37	27.38	$Co_{1.87}Zn_{0.13}P_2O_7 \cdot 6H_2O$	
-	-	$\dfrac{29.51}{29.47}$**	$\dfrac{15.37}{15.49}$	$\dfrac{27.41}{27.03}$	$Co_2P_2O_7 \cdot 6H_2O$	$Co_2P_2O_7 \cdot 6H_2O$

** Calculated values

phates, follows a linear dependency but varies inadequately with the K value in the initial solutions. For $K = 1.00$, for example, the K_1 value is 2.08, emphasizing the predominant precipitation of Zn^{2+}, whose diphosphate complexes are more stable compared to similar cobalt complexes (stability constants $lgK_1 (CoP_2O_7)^2 = 6.1$; lg $K_1 (ZnP_2O_7)^{2-} = 8.7$) [19].

In diphosphates obtained in the range $0.02\leq K\leq0.11$ (the second group), the zinc and cobalt contents change systematically with an increase in the cobalt content in the initial solutions. The P and H_2O contents remain practically unchanged and are close to the values determined for $Co_2P_2O_7 \cdot 6H_2O$ (considering partial substitution of Co by Zn). The H_2O content in this group of diphosphates is 3.8–4.2 wt. % higher compared to the first group (Table 1).

The phase composition of these two groups of diphosphates differs. The results of X-ray phase analysis of diphosphates formed at $0.67 \leq K \leq 9.00$ showed the presence of only one crystalline phase, all of whose reflections are characteristic of a phase with the $Zn_2P_2O_7 \cdot 5H_2O$ structure (Fig. 3a). Diphosphates formed in the range $0.02 \leq K \leq 0.11$ also precipitate as one crystalline phase, but its structure differs from the previous one. They are identified as diphosphates with a structure similar to that of individual $Co_2P_2O_7 \cdot 6H_2O$ (Fig. 3a).

The chemical and phase composition of diphosphates obtained in the range $0.18 \leq K \leq 0.54$ (the third group) simultaneously contains features of diphosphates of the first two groups. X-ray diffraction patterns of these diphosphates clearly indicate a mechanical mixture of diphosphates with $Zn_2P_2O_7 \cdot 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$
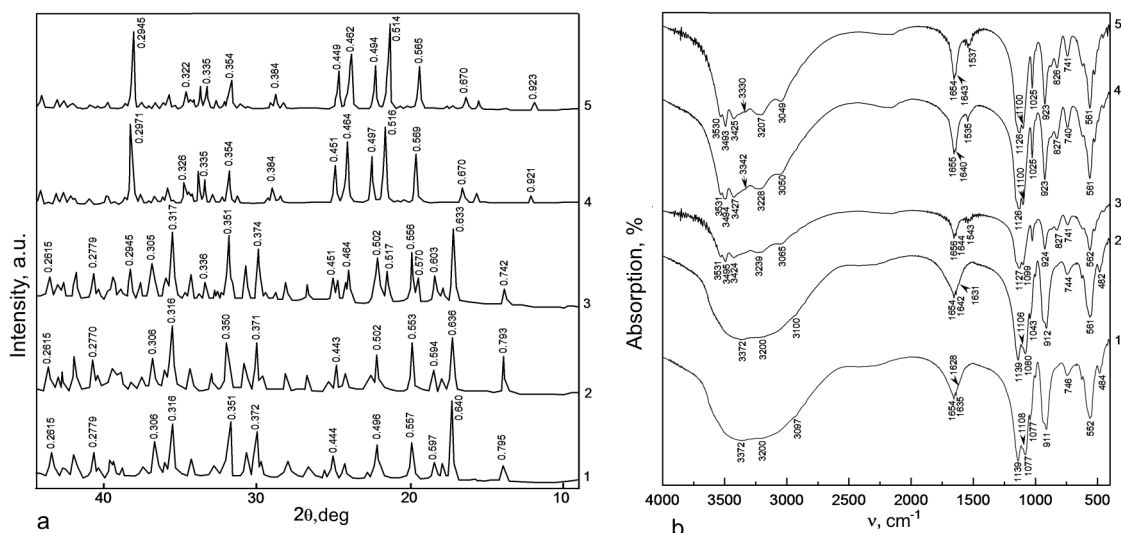
Fig. 3. X-ray diffraction patterns (**a**) and IR absorption spectra (**b**): $Zn_2P_2O_7 \cdot 5H_2O$ (1), $Co_2P_2O_7 \cdot 6H_2O$ (5), limited solid solutions of composition $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ (2), $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ (4) and diphosphates obtained in the range $0.18 \leq K \leq 0.54$ (3)

structures (Fig. 3a). The chemical composition of these diphosphates (Table 1) also differs from that of the first two groups, especially in water content, which changes sharply for $K <$ 0.67 (from 23.51 to 24.93 wt.%) and $K > 0.11$ (from 27.25 to 25.98 wt.%).

The results of chemical and X-ray phase analyses indicate that obtained crystalline diphosphates in the range $0.67 \leq K \leq 9.00$ form a limited substitution solid solution with the general formula $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ and the structure $Zn_2P_2O_7 \cdot 5H_2O$. The homogeneous range determined by chemical analysis is $0 \leq x \leq 0.69$. The saturated solid solution is a diphosphate with the composition $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$. With increasing cobalt content in the initial solutions ($0.02 \leq K \leq 0.11$), diphosphates crystallize to form a limited substitution solid solution with the general formula $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0 < x \leq 0.39$) and the $Co_2P_2O_7 \cdot 6H_2O$ structure. The composition of the saturated solid solution corresponds to diphosphate $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ obtained at $K = 0.11$. For $0.18 \leq K \leq 0.54$, a mechanical mixture of diphosphates with $Zn_2P_2O_7 \cdot 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$ structures is formed.

This is also confirmed by IR spectroscopy studies of diphosphates of these two solid solutions with different crystalline structures (Fig. 3b). A broad intense absorption band with two maxima and a shoulder is observed in the IR spectrum of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ in the v(OH) range. In the case of forming a mechanical mixture of two crystalline phases ($0.18 \leq K$

≤ 0.54), the v(OH) band becomes more complex, with maxima characteristic of the hexahydrate $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ (3531, 3495, 3424, 3239, 3065 cm^{-1}). Its shape corresponds to the cumulative envelope for diphosphates of different hydrations.

Differences are also observed in the range of deformation vibrations of water molecules, where two bands and one shoulder are registered in the spectrum of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$. In the spectra of diphosphates obtained at $0.18 \leq K \leq 0.54$, an additional band at 1543 cm^{-1}, is fixed, characteristic of diphosphates with the $Co_2P_2O_7 \cdot 6H_2O$ structure (Fig. 3b). Three components of the $\delta(H_2O)$ band indicate the presence of three crystallographically non-identical types of water molecules in the diphosphates of the solid solution $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ structure. Analysis of the shape and spectral positions of the v(OH) bands indicates the inequality of their energy state and participation in the formation of hydrogen bonds of different strengths. Estimative calculations of the hydrogen bond energy, performed on the basis of the v(OH) band shift to the low-frequency spectrum range, showed that their values vary within the range of 21.7–40.2 kJ/mol depending on the diphosphate composition.

Absorption bands typical for diphosphates which correspond to the stretching vibrations of PO_3-groups (1170–980 cm^{-1}), bridge P–O–P bond (930–720 cm^{-1}), and bending vibrations of P–O groups (630–550 cm^{-1}) are registered in the range of anion sublattice vibrations of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$. The presence of a band

Table 2. Parameters of the unit cell of diphosphates of solid solution $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$, $0 \le x \le 0.69$, (orthorhombic system, Pnma space group)

Diphosphate	a, nm	b, nm	c, nm	V, nm^3
$Zn_2P_2O_7 \cdot 5H_2O$	2.5581	0.9164	0.8368	1.9614
$Zn_{1.82}Co_{0.18}P_2O_7 \cdot 5H_2O$	2.5580	0.9130	0.8361	1.9525
$Zn_{1.68}Co_{0.32}P_2O_7 \cdot 5H_2O$	2.5571	0.9123	0.8358	1.9497
$Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$	2.5562	0.9116	0.8327	1.9403

with a maximum at 744 cm^{-1} indicates the low symmetry of the diphosphate anion, which has a non-centrosymmetric configuration (POP angle $\neq$ 180°).

The IR spectrum of the saturated solid solution $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$, in terms of the absorption nature, the set of absorption bands, their frequencies, and intensities across the entire spectral range, is generally similar to the IR spectrum of the individual $Co_2P_2O_7 \cdot 6H_2O$ (Fig. 3b). This indicates the identity of their structures and simultaneously the structural difference from the diphosphates of the solid solution $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$. This is particularly clearly observed in the spectra of the diphosphates of the solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ in the range of OH-group valence vibrations of water molecules: a broad band with five distinct maxima and a shoulder is observed, which are also present in the spectrum of the diphosphate matrix $Co_2P_2O_7 \cdot 6H_2O$. For the saturated solid solution $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$, the v(OH) values are 3531, 3494, 3427, 3342 (shoulder), 3228, cm^{-1} and 3050 cm^{-1} (Fig. 3b). In the range of water molecules deformation vibrations three components of the $\delta(H_2O)$ band are registered – 1655 cm^{-1}, 1640 cm^{-1}, and 1535 cm^{-1}, which indicate the presence of three crystallographically non-identical types of crystallohydrate water molecules in the diphosphate structure. The broadening of the v(OH) band and the shift of frequencies to the low-frequency range of the spectrum (compared to the vibrations of a free water molecule v_0 = 3700 cm^{-1}) indicate the existence of a system of fairly strong hydrogen bonds in the diphosphate structure, differing in energy and direction. According to the estimation of their energy, the high-frequency maximum in the spectrum of $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ corresponds to the vibrations of OH groups of water molecules involved in the formation of relatively weak intermolecular hydrogen bonds, with an energy not exceeding 11.3 kJ/mol. The low-frequency absorption band (maxi-

mum 3050 cm^{-1}) corresponds to the existence of a rather strong hydrogen bond (energy up to 43.3 kJ/mol) between the OH groups of water molecules and the diphosphate anion.

The differences in the IR spectra of diphosphates of different structures $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ and $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ are less noticeable in the range of diphosphate anion vibrations (Fig. 3b). The number of absorption bands in the range of the $P_2O_7^{4-}$ anion vibrations of $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ indicates its low symmetry, characterized by a bent P-O-P bridge configuration. Considering the high intensity and frequency of the v_s(P-O-P) band, the P-O-P angle does not exceed 160° and practically does not change in diphosphates of the solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0 < x \le 0.39$) of different compositions.

The diphosphates of the solid solution $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ crystallize in the orthorhombic system (*Pnma* space group). The calculated unit cell parameters change in accordance with the ionic radii of Zn^{2+} (r_{ionic} = 0.089 nm) and Co^{2+} (r_{ionic} = 0.088 nm), consistent with Vegard's law, indicating the solid solution formation (Table 2).

The diphosphates of the solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0 < x \le 0.39$) crystallize in the monoclinic system ($P2_1/n$ space group) with unit cell parameters having similar values regardless of the cation composition. This is due to the similar ionic radii of Zn^{2+} and Co^{2+} and the relatively low degree of Co(II) substitution. For the diphosphate $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ with the maximum zinc content, the unit cell parameters are (in nm): a = 0.7199, b = 1.8356, c = 0.7680, V = 1.0410 nm^3, β = 92.25°.

The formation of limited substitution solid solutions based on the structures of both isodimorphic diphosphate matrices $Zn_2P_2O_7 \cdot 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$ is a consequence of the differences in their crystal structures [21, 10, 16]. The homogeneity range $0 \le x \le 0.69$ of the solid
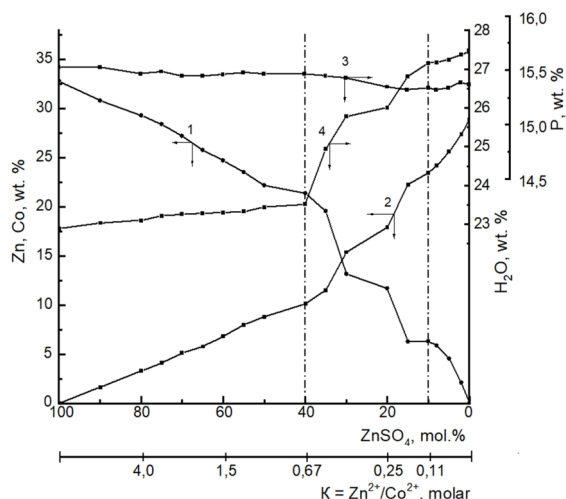
Fig. 4. The homogeneity range of the diphosphate solid solutions crystallizing in the system $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O, and the limits of variation in their composition content of Zn – *1*, Co – *2*, P – *3*, H_2O – *4*

solution $Zn_2P_2O_7 \cdot 5H_2O$ – $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ is 1.8 times wider than the range $0 \leq x \leq 0.39$ of the solid solution $Co_2P_2O_7 \cdot 6H_2O$ – $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ (Fig. 4).

The experimental fact of the presence of such differences in the homogeneity ranges of these solid solutions cannot be unambiguously explained using two main factors of isomorphism – size (Δr) and the proximity of chemical bonds ($\Delta\chi$). The comparison of ionic radii (r_{ionic} Zn^{2+} = 0.089 nm; r_{ionic} Co^{2+} = 0.088 nm; Δr = 1.1%) and electronegativities (x_{Zn} = 1.6, x_{Co} = 1.8; Δx = 0.2) indicates wide isomorphic possibilities for this pair of cations and, consequently, similar homogeneity ranges for their solid solutions.

Significant differences in the manifestation of isomorphic cation substitutions during the crystallization of $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ and $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ solid solutions were explained by comparing the chemical properties of the diphosphate matrices – a factor that, along with other isomorphism factors, has priority significance for solid solutions of hydrated salts.

The dominant role of this factor during the crystallization of solid solutions of hydrated diphosphates in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system is indicated by the preferential precipitation of Zn^{2+} cations, as evidenced by the value K_1 = Zn/Co (atomic) in the composition of the precipitated diphosphates (Table 1), as well as the stability constants of diphosphate complexes (lg K_1 (ZnP_2O_7)$^{2-}$ = 8.7; lg K_1 (CoP_2O_7)$^{2-}$ = 6.1) [19].

Consequently, the homogeneity range of the solid solution $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$)

based on the $Zn_2P_2O_7 \cdot 5H_2O$ diphosphate matrix is wider than in the case of isomorphic substitution of Co(II) with Zn in the $Co_2P_2O_7 \cdot 6H_2O$ structure during crystallization of the solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0 \leq x \leq 0.39$).

Thus, as a result of the interaction in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system, two limited solid solutions of hydrated zinc and cobalt(II) diphosphates are formed, which have different crystal structures and homogeneity ranges.

A comprehensive analysis of the obtained experimental data using modern theories of isomorphic substitutions and the main characteristics of cations made it possible to establish some features of the crystallization of solid solutions of hydrated Zn and Co(II) diphosphates.

4. Conclusions

As a result of the interaction in the $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O system, two solid solutions of hydrated zinc and cobalt(II) diphosphates $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$) and $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0 \leq x \leq 0.39$) are formed due to isomorphic cation substitution.

The crystal structures of these solid solutions are different: $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ crystallizes in the orthorhombic system (*Pnma* space group, Z=4), and $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ – in the monoclinic system (*P2_1/n* space group, Z=4).

The homogeneity range of the $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ solid solution, defined as $0 \leq x \leq 0.69$, is 1.8 times wider than in the case of the $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ solid solution with $0 \leq x \leq 0.39$.

The explanation of this experimentally determined fact, based on a comparison of the chemical properties of the diphosphate matrices, indicates that the isomorphism factor (in addition to the dimensional and chemical bond proximity factors) significantly influences the homogeneity ranges of the hydrated diphosphate solid solutions.

The priority significance of this isomorphism factor during the crystallization of solid solutions of hydrated diphosphates in the system $ZnSO_4$–$CoSO_4$–$K_4P_2O_7$–H_2O is indicated by the preferential precipitation of Zn^{2+} cations, as evidenced by K_1 = Zn/Co (atomic) in the composition of the precipitated diphosphates, as well as the stability constants of diphosphate complexes (lg K_1 (Zn_2O_7)$^{2-}$ = 8.7; lg K_1 (CoP_2O_7)$^{2-}$ = 6.1).

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