Formation of barely soluble compounds in the CuSO$_4$–K$_4$P$_2$O$_7$–H$_2$O system

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The article deals with barely soluble compounds formed in the CuSO$_4$–K$_4$P$_2$O$_7$–H$_2$O system. The precipitates were analysed by X-ray diffraction (XRD), chemical analysis and FTIR spectroscopy. The results have shown that the formation of barely soluble compounds occurs in the following steps: semiamorphous voluminous precipitate → Cu$_2$P$_2$O$_7$ · 5H$_2$O → Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (*Dimorph A*) → Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (*Dimorph B*). A double salt may be formed after some time in the reaction mixture as a result of heterogeneous reaction:

$$3Cu_2P_2O_7 \cdot 5H_2O\downarrow + H_2P_2O_7^{2-} + 4K^+ \rightarrow 2Cu_3K_2(P_2O_7)_2 \cdot 3H_2O\downarrow + 2H^+ + 9H_2O.$$
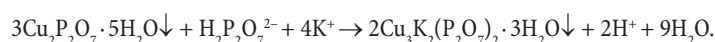
This process has not been described in any previous publications.

Key words: copper, diphosphates, precipitation, heterogeneous reaction, XRD analysis

INTRODUCTION

Diphosphates have been widely investigated not only owing to the fundamental scientific interest, but also because of their importance and use in practical applications. A wide diversity of solid phases is inherent for diphosphates and dependent on reactive cations and conditions of the experiment. Acidic, neutral and basic, single and double salts with a varying crystal water content may be formed [1–6].

Most of the published scientific research deals with the compounds that have been allowed to reach the equilibrium state, and represent the final stage of precipitate formation. In contrast, after a careful observation, Kokhanovskii in some of his articles has suggested that formation of the diphosphate precipitate is a complicated step-wise process. Under certain conditions, a semiamorphous precipitate is formed first, which then dissolves and finally a fine crystalline precipitate is formed [7–9].

Some of the diphosphates are unstable in mother solutions and may undergo a few possible transformations:

a) the content of crystal water may change;

b) the composition of a precipitate may change substantially, for example, in the system Sr(NO$_3$)$_2$–K$_4$P$_2$O$_7$–H$_2$O a successive transformation of barely soluble compounds may occur: K$_{10}$Sr$_7$(P$_2$O$_7$)$_5$(OH)$_4$ · 16H$_2$O → → K$_7$Sr$_7$(P$_2$O$_7$)$_5$OH · 14.5H$_2$O → Sr$_2$P$_2$O$_7$ · 3H$_2$O [10];

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c) polymorphous transformation may occur [11–13].

Christoffersen et al. have investigated the growth of monoclinic Ca$_2$P$_2$O$_7$ · 4H$_2$O, acicular (needlelike) and columnar triclinic Ca$_2$P$_2$O$_7$ · 2H$_2$O from supersaturated solutions on corresponding seed crystals. According to their findings, the rates of crystal growth can be explained using the polynuclear growth mechanism [14, 15]. The authors have also noted an interesting phenomenon in the formation and growth of monoclinic Ca$_2$P$_2$O$_7$ · 4H$_2$O [13]. At pH 5, the crystals grow at a rate increasing with supersaturation, as might be expected. In contrast, at pH 7 the rate of growth is increasingly inhibited by increasing supersaturation. The authors suggested that this autoinhibition was due to chelation of Ca^{2+} and P$_2$O$_7^{4-}$ on the crystal surface, which blocked the normal growth and formation processes.

In this paper, the formation of barely soluble compounds in the CuSO$_4$–K$_4$P$_2$O$_7$–H$_2$O system is thoroughly investigated.

EXPERIMENTAL

All experiments were carried out at 18 ± 2 °C. Stock 1 M CuSO$_4$ and 1 M K$_4$P$_2$O$_7$ solutions were diluted to the appropriate concentrations. The mixing of the solutions was performed by pouring both solutions simultaneously into a beaker under continuous stirring with a magnetic stirrer. The necessary pH was immediately adjusted using concentrated and diluted (1 M and 0.1 M) H$_2$SO$_4$ as appropriate. As the pH

of the mixture increased slowly during the first 2–3 hours of mixing, it was adjusted every 20 min. For reaction times longer than 3 days, the reaction mixture was poured into a conical flask and heat-sealed with a polished glass plug and paraffin to prevent evaporation. The suspensions were filtered using a *Filtrak* filter "a slow filtering for finest deposits", a Buchner funnel and a vacuum jet pump.

The precipitates were washed several times and air-dried to a constant weight. Approximately 0.1 g of the precipitate was accurately weighed and dissolved in 20 cm^3 5% HNO_3.

Cu^{2+} and K^+ concentrations in the solutions were determined by atomic absorption spectrometry using a Perkin–Elmer AAS–603 spectrophotometer with an acetylene-air flame. Standard solutions were prepared from monoelement stock solutions containing 1000 mg/l of Cu^{2+} and K^+. The measurements were carried out using Cu 324.9 nm and K 383.6 nm spectral lines.

X-ray diffraction (XRD) patterns of the precipitates were measured using Cu K_α radiation selected by a secondary graphite monochromator. A continuous scan mode was used in the range of $5° \leq 2\theta \leq 45°$ with a scan rate of $1° \ \text{min}^{-1}$.

The infrared spectra were obtained with a FTIR Hartmann & Braun spectrometer in the region of 4000 to 500 cm^{-1} using KBr pellets.

The yield of the heterogeneous reaction was calculated as the ratio of Cu^{2+} ions participating in this reaction to the total amount of Cu^{2+} ions present in the reaction mixture. One released H^+ ion corresponds to three Cu^{2+} ions undergoing transformation in the heterogeneous reaction.

The yield was determined in two ways:

1. After titration of the amount of H^+ ions released at the end of the heterogeneous reaction.

2. After summation of the titration of the amount of H^+ ions released after testing the reaction rate.

RESULTS AND DISCUSSION

First, formation of barely soluble compounds at Cu^{2+} and $P_2O_7^{4-}$ concentrations of 0.05 M each in the pH range from 3.5 to 6.5 has been investigated.

Our investigation has shown that three poorly soluble compounds can be formed in the $CuSO_4$–$K_4P_2O_7$–H_2O system: single salt $Ca_2P_2O_7 \cdot 5H_2O$ (later CuDp) and two polymorphs of double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ *Dimorph A* and *Dimorph B* (later CuKDp (A) and CuKDp (B)) [16]. Their X-ray diffractograms are presented in Fig. 1.

In most cases, FTIR absorption spectra of precipitates were recorded and studied. The obtained results coincided with the results obtained by X-ray diffraction and chemical analysis.

As $CuSO_4$ and $K_4P_2O_7$ solutions were mixed and the pH was adjusted, a colloidal solution started to form immediately, which after a few minutes transformed into a voluminous gelatinous precipitate. X-ray diffractograms of the precipitates

obtained after 15 min of reaction mixture preparation show a semiamorphous structure and have a rather similar visual appearance under all the experimental conditions tested. In order to keep a constant pH, during the first 2–3 hours it had to be adjusted (we used H_2SO_4). This indicates a transformation of unstable initial compounds with a release of OH$^-$ or connection of H^+ ions. X-ray diffractograms of precipitate samples taken after 1–4 hours show that a fine crystalline defective $Cu_2P_2O_7 \cdot 5H_2O$ is formed if the pH of the reaction mixture is ≤5.5.

These results demonstrate that the formation of barely soluble compounds essentially depends on pH.

First, the formation of poorly soluble compounds at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M and $n = 1$ was investigated. At pH 5.0, in order to ascertain the reproducibility of the results, six experiments were performed under exactly the same conditions. X-ray diffractograms of precipitates obtained after 1 h of mixing show formation of the fine crystalline defective single salt CuDp. Its crystallinity improves under continuation of mixing without change in the pH of the reaction mixtures. After some time the pH of the reaction mixtures begins to decrease without visible changes in the diffractograms. Afterwards, a gradual formation of a fine crystalline double salt, CuKDp(A), becomes visible in
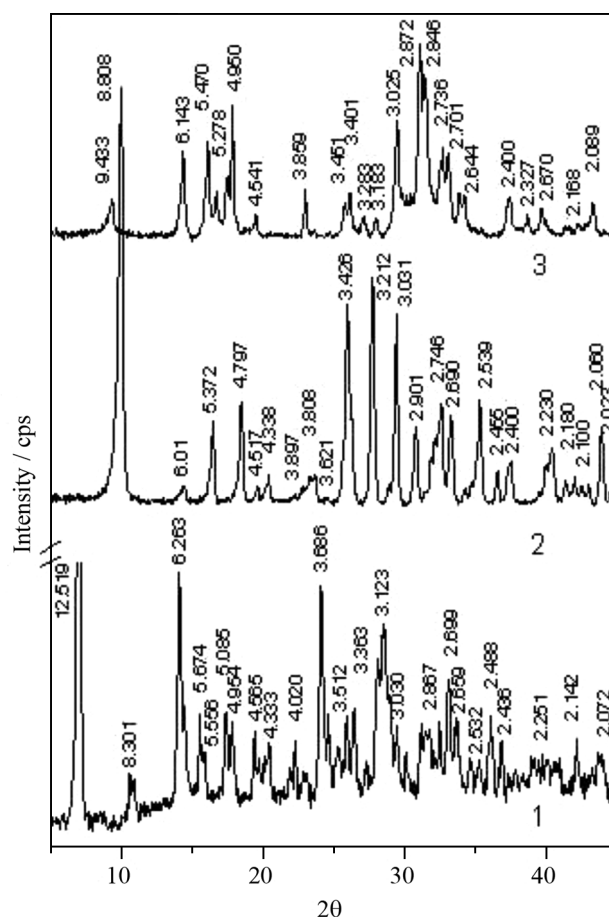

Fig. 1. X-ray diffractograms: *1* – $Cu_2P_2O_7 \cdot 5H_2O$, *2* – $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*), *3* – $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*)
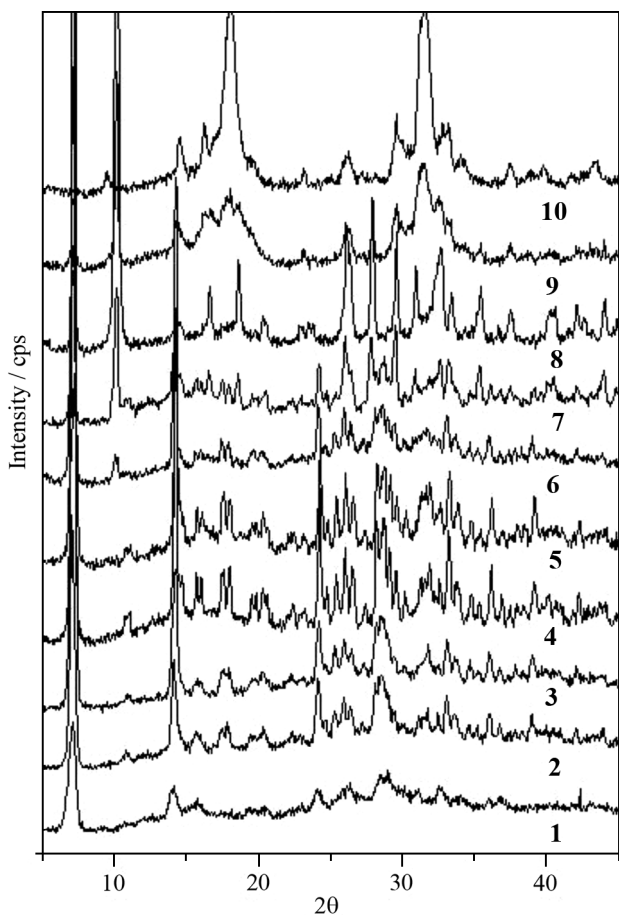
Fig. 2. X-ray diffractograms of precipitates obtained from reaction mixture at [Cu^{2+} + P$_2$O$_7^{4-}$] = 0.1 M, n = 1, initial adjusted pH 5.0. Duration of mixing and pH: *1* – 15 min, 5.0; *2* – 1 h, 5.0; *3* – 2 h, 5.0; *4* – 18 h, 5.00; *5* – 30 h, 3.75; *6* – 40 h, 3.65; *7* – 48 h, 3.50; *8* – 4 days, 2.70; *9* – 10 days, 2.52; *10* – 20 days, 2.44

Table 1. Dependence of reaction mixture pH and [K$^+$] / [Cu^{2+}] ratio in precipitates on duration of mixing the reaction mixture at various initial pH, [CuSO$_4$] = [K$_4$P$_2$O$_7$] = 0.05 M

Initial pH	Duration of interaction	pH	[K$^+$] / [Cu^{2+}]
4.0	15 min	4.0	0.050
	1 h	4.0	0.0085
	20 h	4.00	0.0057
	4 days	4.00	0.0058
	7 days	4.00	0.0039
	10 days	4.00	0.0059
	12 days	3.82	0.019
	16 days	3.22	0.04
	18 days	3.07	0.13
	20 days	2.86	0.225
	22 days	2.65	0.63
	26 days	2.39	0.65
	30 days	2.26	0.67
5.0	15 min	5.0	0.043
	1 h	5.0	0.028
	18 h	5.00	0.025
	28 h	4.26	0.11
	30 h	3.75	0.28
	40 h	3.65	0.34
	48 h	3.51	0.39
	4 days	2.69	0.50
	10 days	2.52	0.64
	20 days	2.44	0.66
5.5	15 min	5.5	0.26
	2 h	5.5	0.17
	12 h	5.50	0.21
	18 h	5.38	0.28
	24 h	4.73	0.43
	2 days	4.50	0.50
	4 days	3.43	0.61
	5 days	3.06	0.66
6.0	15 min	6.0	0.15
	2 h	6.0	0.26
	4 h	6.00	0.30
	18 h	6.00	0.42
	24 h	5.98	0.63
	3 days	5.97	0.65
	10 days	5.96	0.66

the diffractograms. Over time, the intensity of the peaks of double salt increases with decrease in the intensity of peaks of the single salt. Later, the decrease in pH stops, and after some time the transformation of CuKDp(A) into a corresponding *Dimorph B* (CuKDp(B)) occurs. The investigation of this process is described in our earlier publication [16]. Substantial diffractograms of one experiment are shown in Fig. 2.

The time after which a decrease in the pH of the reaction mixtures was detected (induction time) was in the range of 15–24 hours, the duration of this process was in the range of 90–130 hours, the transformation of CuKDp(A) into CuKDp(B) began after 5–11 days and continued for 1–3 days. Also, the reproducibility of the results was moderate.

The dynamics of the ratio [K$^+$] / [Cu^{2+}] in the precipitates of one experiment *versus* the duration of interaction was investigated. Initially, this ratio is low and it diminishes as soon as the pH begins to decrease. The possible reason for a moderate decrease in the [K$^+$] / [Cu^{2+}] ratio is the improvement of CuDp crystals. As a result, the amount of mother solution enclosed in defects of the crystals diminishes. When the pH begins to decrease, the ratio begins to increase and

reaches values close to 0.(6) which is equal to the molar ratio of [K$^+$] / [Cu^{2+}] in the double salt Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (Table 1).

The results show that after the induction time when visibly only an improvement in the crystallinity of CuDp occurs, a heterogeneous reaction begins:

$$3Cu_2P_2O_7 \cdot 5H_2O\downarrow + H_2P_2O_7^{2-} + 4K^+ \Rightarrow$$
$$\Rightarrow 2Cu_3K_2(P_2O_7)_2 \cdot 3H_2O\downarrow + 2H^+ + 9H_2O.$$
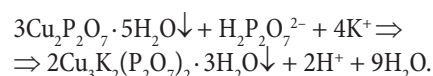
H$_2$P$_2$O$_7^{2-}$ is the main form of diphosphate ion in the pH range 2–6 [17]. It is clear that this reaction may proceed only

through instable intermediate products. The rate of the reaction may be easy controlled by periodically adjusting the pH to its previous value, using a standardized solution of strong alkali. Additionally not to complicate the system, a KOH solution (0.35 N) was used. As the rate of the reaction was moderate, the frequency of the addition of alkali solution was chosen to be hourly, and the addition, as a rule, lasted no longer than one minute.

In order to ascertain the reproducibility of the results, six experiments were performed under the same conditions (Table 2). An uneven jumpy proceeding is characteristic of the reaction (three curves are given in Fig. 3). The reproducibility of the results is moderate, but the regularities are clearly seen.

The induction time was in the range of 16–26 h, and this process lasted 24–32 h.

The maximal rates ranged within 1.3–1.7 mM/h Cu^{2+}.

The calculated yield of the reaction reached 92–98%. Similar results of the yield (94–100%) were obtained in the previous experiment after titration of the reaction mixture when the reaction was finished.

When the initially adjusted pH was reduced to 4.0, three identical experiments were performed. The results of the investigation markedly differed from the previous ones (Fig. 4). According to the diffractograms, the precipitates obtained after 15 min were highly defective CuDp. Their structure distinctly improved already after 1 hour of mixing. The improvement slowly continued 10–16 days without change in reaction mixture pH. A decrease of the reaction mixture pH (heterogeneous reaction) began after a substantially longer time period as compared with the previous research when the initially adjusted pH was 5.0. Likewise, initially no marked changes were seen in the diffractograms. When the pH further diminished, a substantial disorder in the structure of the precipitate was observed. Afterwards, peaks of fine crystalline CuKDp(B) emerged and later began to dominate in the diffractograms. When the decrease in pH was finished, only peaks of CuKDp(B) were seen.

Also, in this case the phase of CuKDp(A) is invisible in diffractograms. Apparently, at low pH, CuKDp(A) turns

Table 2. **Data on induction time, duration and yield of heterogeneous reaction obtained at the same experimental conditions** $[CuSO_4] = [K_4P_2O_7] = 0.05$ M, pH 5.0

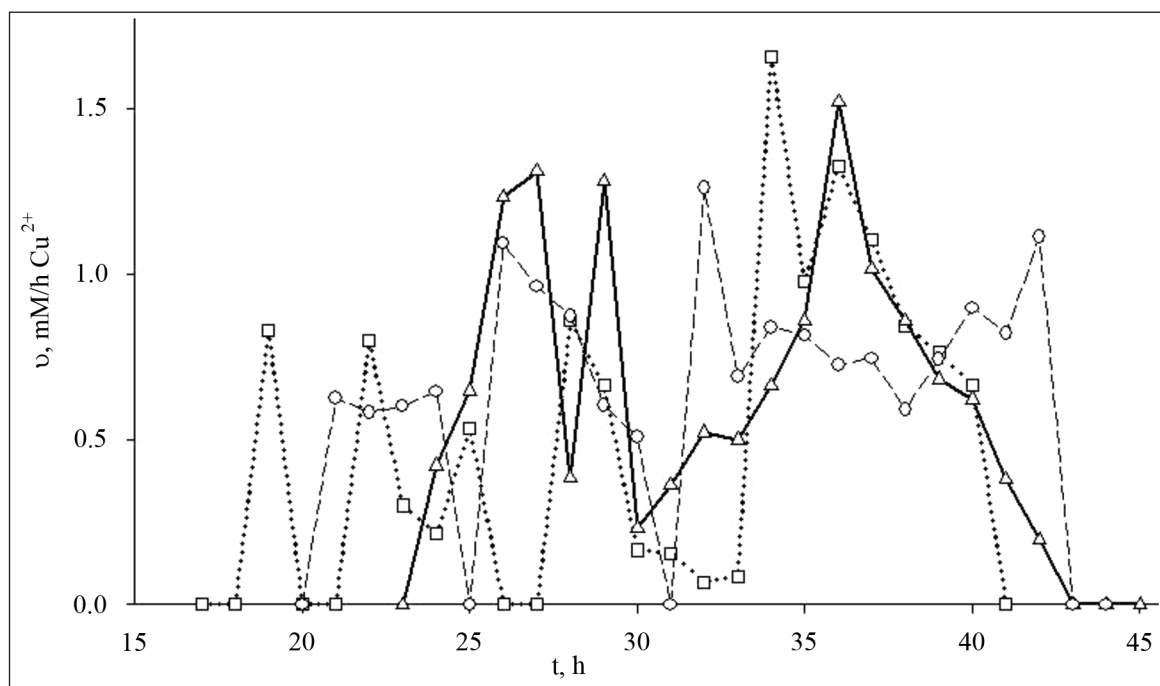| Induction time, h	Duration of heterogeneous reaction, h	Yield of heterogeneous reaction, %
16	21	92
17	23	98
20	23	95
21	26	94
23	20	96
26	25	95

Fig. 3. Dependence of heterogeneous reaction rate on duration of interaction at $[K^+] / [Cu^{2+}] = 0.1$ M, $n = 1$, pH 5.0

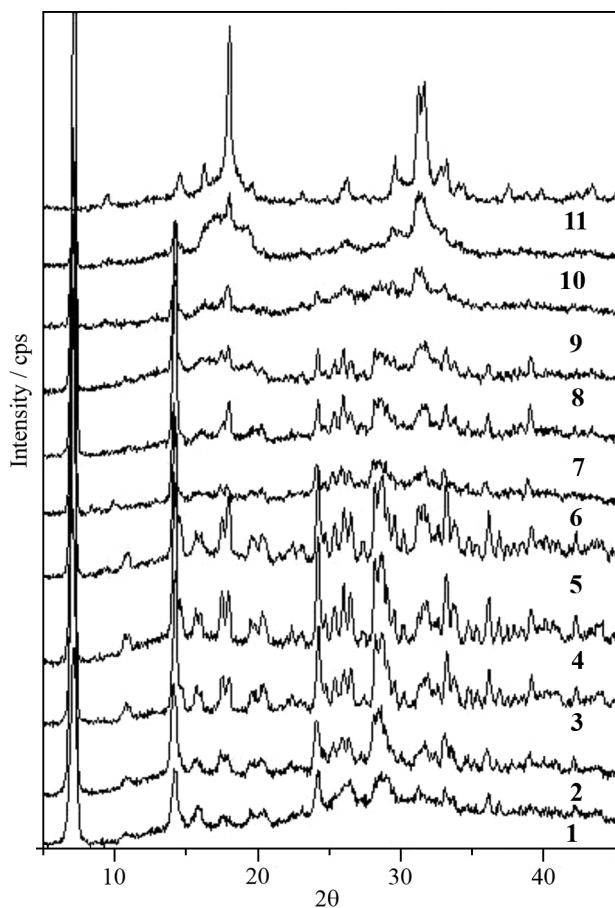**Fig. 4.** X-ray diffractograms of precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$, initial adjusted pH 4.00. Duration of mixing and pH: *1* – 15 min, 4.0; *2* – 1 h, 4.0; *3* – 10 days, 4.00; *4* – 12 days, 3.82; *5* – 15 days, 3.35; *6* – 16 days, 3.22; *7* – 18 days, 3.07; *8* – 20 days, 2.86; *9* – 24 days, 2.55; *10* – 26 days, 2.39; *11* – 30 days, 2.26
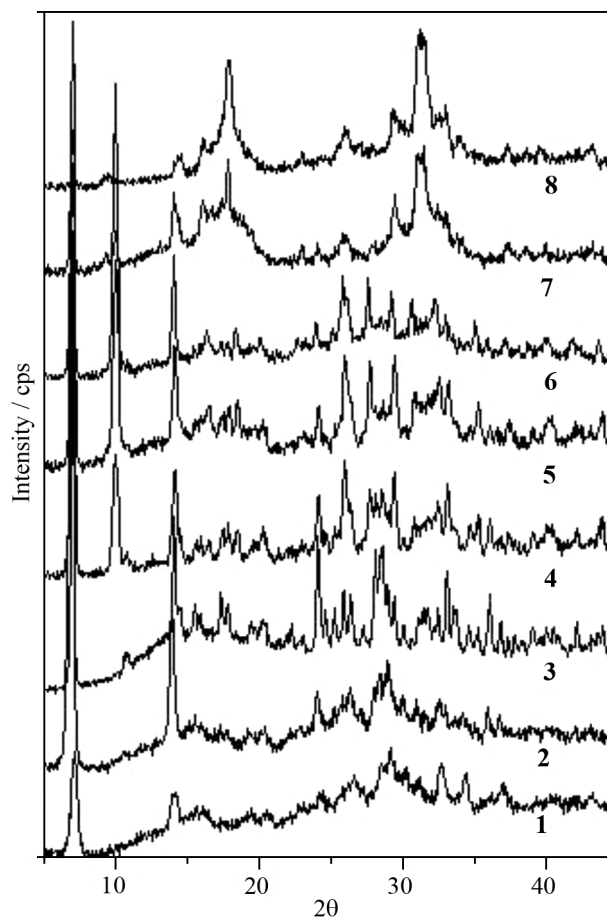
Fig. 5. X-ray diffractograms of precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$, initial adjusted pH 5.5. Duration of mixing and pH: *1* – 15 min, 5.5; *2* – 2 h, 5.5; *3* – 12 h, 5.50; *4* – 18 h, 5.38; *5* – 24 h, 4.73; *6* – 2 days, 4.50; *7* – 3 days, 3.45; *8* – 7 days, 3.06

into CuKDp(B) at a high rate which makes the detection of CuKDp(A) hardly possible.

The calculated yield values of the heterogeneous reaction where 97, 99 and 102%, i. e. slightly higher than those at pH 5.0.

At pH 5.5, three experiments were performed under the same conditions. The transformation from semiamorphous precipitate into finecrystalline CuDp lasted 6–10 hours, i. e. was significantly slower in comparison to our previous experiments. The heterogeneous reaction began after 14–20 hours, and the induction time was similar to that obtained at pH 5.0. This reaction lasted 80–120 hours. Already after 3–6 days the transformation of CuKDp(A) into CuKDp(B) began, and the process lasted no longer than two days. Substantial diffractograms of one experiment are shown in Fig. 5.

Until the heterogeneous reaction begins, the ratio $[K^+]$ / $[Cu^{2+}]$ is significantly higher in comparison to those in our previous experiments (Table 1). When the pH begins to decrease, the ratio begins to increase and reaches the values close to 0.67.

The yield of the heterogeneous reaction reaches only 47, 55 and 59%. The yield was determined when the reaction was finished. The obtained results can be explained as follows: part of Cu^{2+} ions precipitate as an amorphous double salt at this pH as soon as in the first minutes of the interaction (according to the data of chemical and XRD analysis). Because part of Cu^{2+} ions is already precipitated, the yield of the heterogeneous reaction is low (about 50%).

At pH maxima (6.0 and 6.5), the reduction of pH was imperceptible. When the pH was adjusted to 6.0, the precipitates obtained after 15 min and 4 hours were semiamorphous (Fig. 6). The peaks in the diffractogram of the precipitate obtained after 4 hours of mixing are slightly sharper and clearly defined, but it is impossible to obtain information about its composition. The diffractogram of the precipitate obtained after 8 hours of mixing is complicated, however, a mixture of CuDp and CuKDp(A) may be seen. After 18 hours of interaction, the peaks of CuKDp(A) dominated. After 24 hours, only peaks of CuKDp(A) were seen in the diffractograms. After a long time (45 and 75 days), only a slight improvement in the CuKDp(A) structure and
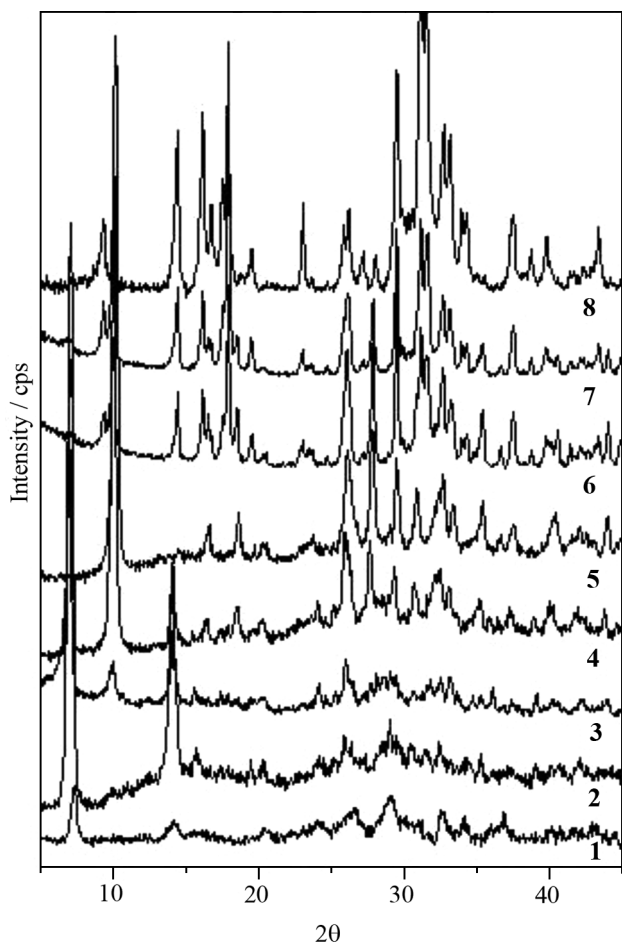
Fig. 6. X-ray diffractograms of precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$, initial adjusted pH 6.0. Duration of mixing and pH: *1* – 15 min, 6.0; *2* – 4 h, 6.00; *3* – 8 h, 6.00; *4* – 18 h, 6.00; *5* – 24 h, 5.98; *6* – 50 days, 5.96; *7* – 55 days, 5.95; *8* – 70 days, 5.95

and 20 days. The calculated yield of the heterogeneous reaction was 92 and 95%.

When $[Cu^{2+} + P_2O_7^{4-}]$ at $n = 1$ was increased to 0.25 M, the heterogeneous reaction began as soon as after 2–3 hours and continued no longer than two days in the initial pH range of 4.0–5.5.

The rates of the heterogeneous reaction were investigated. Three experiments were performed for all investigated pH.

The reproducibility of the results was good in this case, in contrast to the medium reproducibility of the results obtained when $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$. The duration of the heterogeneous reaction substantially decreased with increasing the initial pH (Fig. 8). The maximal rate was obtained at pH 5: 5.5, 5.6 and 6.0 mM/h Cu^{2+}. At pH 5.5, the heterogeneous reaction was not observed; however, the reaction had not been observed at a higher pH in the previous experimental series when $[Cu^{2+} + P_2O_7^{4-}]$ was 0.1 M. The calculated yield of the heterogeneous reaction at the initial pH 4.0 was 80, 85 and 88%, at pH 4.5–73, 74 and 77%, at pH 5.0–35, 37 and 40%, at pH 5.2–7.1, 7.4 and 7.5%, at pH 5.5 and 6.0–0.0 and 0.0%.

At $[Cu^{2+} + P_2O_7^{4-}] = 0.25$ M, n was reduced from 1 to 0.67. The induction time of the heterogeneous reaction substantially prolonged – from 2–3 h to 8–26 h in the investigated pH range 4.0–6.0. The duration of this reaction increased several times (for example, from 8 h to ~60 h at the initial pH 4.5). The rate of the heterogeneous reaction distinctly decreased and achieved at the initial pH 5.5 the maximum 1.8–2.1 mM/h Cu^{2+}, whereas the maximal rate at $n = 1$ was 5.5–6.0 mM/h Cu^{2+} at the initial pH 5.0. The maximum yield of this reaction was obtained at pH 4.0 and reached only ~ 55%.

an insignificant decrease in pH (~0.2) occurred; then the transition of CuKDp(A) to CuKDp(B) began and lasted 15 and 30 days.

The chemical analysis of the precipitates shows a gradual increase in the $[K^+] / [Cu^{2+}]$ ratio from 0.15 (after 15 min of mixing) to 0.66 (after 10 days of mixing) (Table 1).

Data of FTIR spectra of the precipitates coincide with the results of chemical and XRD analysis. A mixture of CuDp and CuKDp(A) may be seen in the FTIR spectra of the precipitate obtained after a minimal duration of the interaction (15 min). The FTIR spectra show that with prolonging the interaction, the share of CuDp in the precipitate substantially diminishes and CuKDp(A) begins to dominate (Fig. 7).

The reason why the heterogeneous reaction was not observed is not clear.

When the concentrations of $CuSO_4$ and $K_4P_2O_7$ at $n = 1$ in the reaction mixture had been reduced twice, the formation of the double salt was substantially suppressed. When pH 5.0 had been adjusted, CuDp was formed, and only after 12 and 17 days the heterogeneous reaction began and lasted for 16

CONCLUSIONS

A thorough investigation of the formation of barely soluble compounds in the $CuSO_4$–$K_4P_2O_7$–H_2O system was performed. The formation of the compounds substantially depended on the conditions of experiment. As a rule, their formation occurred in the following steps: semiamorphous voluminous precipitate $\rightarrow$ $Cu_2P_2O_7 \cdot 5H_2O$ $\rightarrow$ $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) $\rightarrow$ $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*).

It has been found that after some time a heterogeneous reaction (induction time) may proceed in most cases:

$$3Cu_2P_2O_7 \cdot 5H_2O\downarrow + H_2P_2O_7^{2-} + 4K^+ \rightarrow$$
$$\rightarrow 2Cu_3K_2(P_2O_7)_2 \cdot 3H_2O\downarrow + 2H^+ + 9H_2O.$$
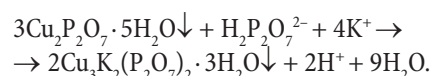
The rate, duration and yield of the heterogeneous reaction substantially depended on the reaction mixture pH, $[Cu^{2+} + P_2O_7^{4-}]$ and n ($[P_2O_7^{4-}] / [Cu^{2+}]$). At a relatively low pH, the induction time was long, the rate of this reaction was low, its duration was long, and the yield of this reaction was maximal (close to 100% when $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M).

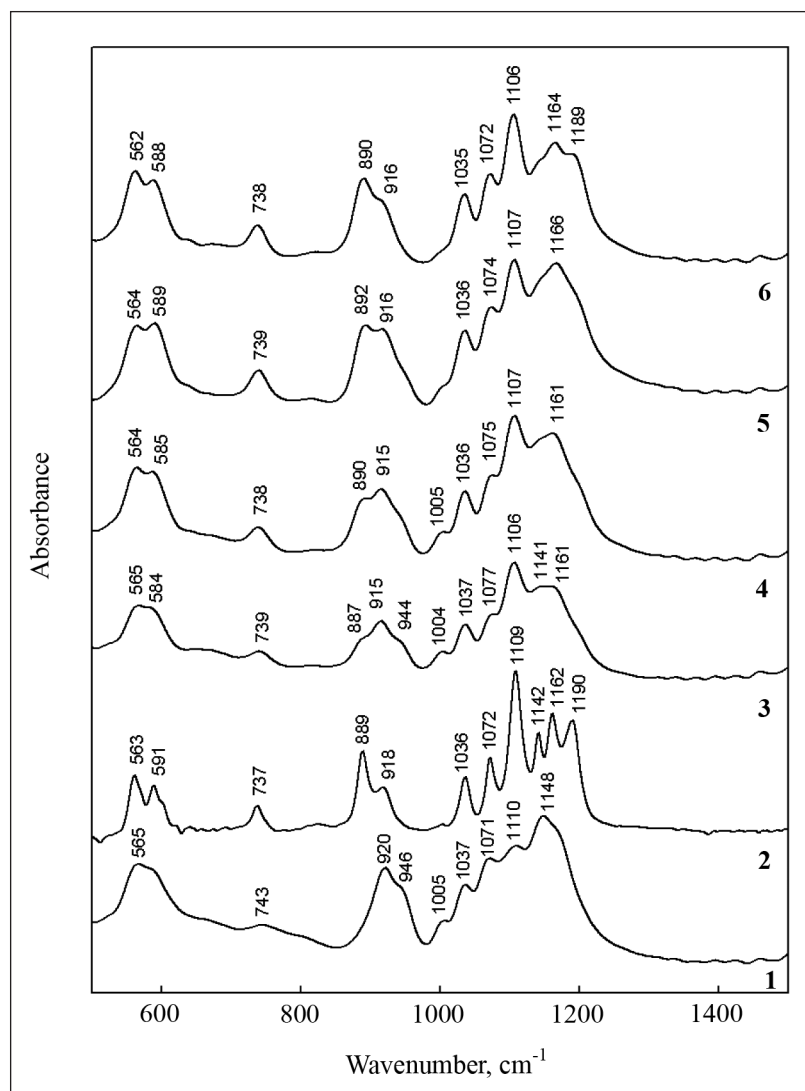**Fig. 7.** FTIR spectra of $1 - Cu_2P_2O_7 \cdot 5H_2O$, $2 - Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) and precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$, initial adjusted pH 6.0. Duration of mixing: $3 - 15$ min, $4 - 4$ h, $5 - 18$ h, $6 - 24$ h

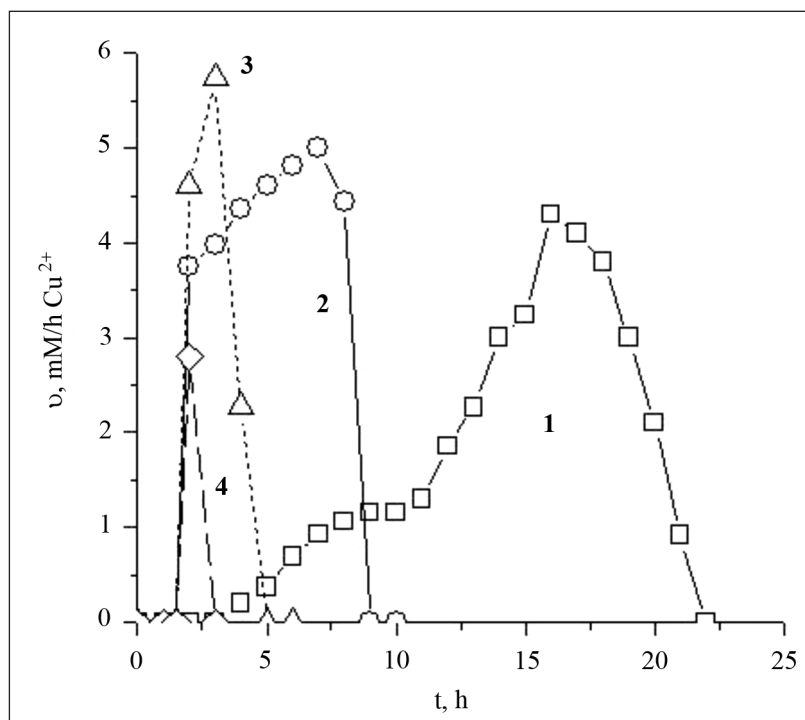**Fig. 8.** Dependence of heterogeneous reaction rate on duration of interaction at $[Cu^{2+} + P_2O_7^{4-}] = 0.25$ M, $n = 1$. Initial adjusted pH: $1 - 4.0$, $2 - 4.5$, $3 - 5.0$, $4 - 5.2$

At increased pH values, the induction time, the yield and duration of the heterogeneous reaction decreased. At an increased $[Cu^{2+} + P_2O_7^{4-}]$, the induction time and duration of the heterogeneous reaction also decreased. After reducing *n* from 1 to 0.67, the induction time and duration of this reaction substantially increased, while the yield notably decreased.

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MAŽAI TIRPIŲ JUNGINIŲ SUSIDARYMO SISTEMOJE $CuSO_4$–$K_4P_2O_7$–H_2O TYRIMAS

S a n t r a u k a

Rentgeno spindulių difrakcijos, cheminės analizės ir FTIR spektroskopijos metodais sistemoje $CuSO_4$–$K_4P_2O_7$–H_2O tirtas mažai tirpių junginių susidarymas. Tyrimas parodė, kad mažai tirpūs junginiai formuojasi palaipsniui: pusiau amorfinės tūriškos nuosėdos → paprastoji druska $Cu_2P_2O_7$ $5H_2O$ → dviguboji druska $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorfas A*) → dviguboji druska $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorfas B*). Po tam tikro laiko, kai reakcijos mišinyje pradeda mažėti pH ir stebimas dvigubos druskos $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ susidarymas, vyksta heterogeninė reakcija:

$$3Cu_2P_2O_7 \cdot 5H_2O\downarrow + H_2P_2O_7^{2-} +$$
$$+ 4K^+ \rightarrow 2Cu_3K_2(P_2O_7)_2 \cdot 3H_2O\downarrow + 2H^+ + 9H_2O.$$
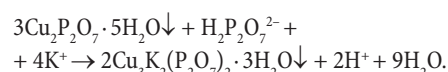
Heterogeninės reakcijos tyrimas parodė, kad reaguojančių medžiagų sąveika sudėtinga. Procesų greičiai, jų trukmė ir heterogeninės reakcijos išeiga labai priklauso nuo reakcijos mišinių pH, $[Cu^{2+} + P_2O_7^{4-}]$ ir *n* ($[P_2O_7^{4-}]$ / $[Cu^{2+}]$). Kai pH reikšmės sąlyginai mažos, heterogeninės reakcijos indukcijos laikai – dideli, greičiai – maži, jos trukmė – ilga, reakcijos išeiga maksimali (artima 100 %, kai $[Cu^{2+} + P_2O_7^{4-}] = 0,1$ M). Didinant reakcijos mišinių pH, reakcijos indukcijos laikas, jos trukmė ir išeiga mažėja. Didinant $[Cu^{2+} + P_2O_7^{4-}]$, indukcijos laikas ir trukmė mažėja. Sumažinus *n* nuo 1 iki 0,67 reakcijos indukcijos laikas ir trukmė gerokai padidėja, o išeiga – sumažėja.