VILNIUS UNIVERSITY
INSTITUTE OF CHEMISTRY

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FORMATION OF BARELY SOLUBLE COMPOUNDS IN THE $CuSO_4$ – $K_4P_2O_7$ – H_2O AND $CuSO_4$ – $(NH_4)_4P_2O_7$ – H_2O SYSTEMS

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VILNIAUS UNIVERSITETAS
CHEMIJOS INSTITUTAS

Oksana Timofejeva

NUOSĖDŲ FORMAVIMOSI SISTEMOSE $CuSO_4$ – $K_4P_2O_7$ – H_2O IR $CuSO_4$ – $(NH_4)_4P_2O_7$ – H_2O MECHANIZMO TYRIMAS

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INTRODUCTION

Various diphosphates have wide applications as fertilizers, food additives, catalysts , corrosion inhibitors and electrode materials for batteries. They are also used in metal finishing processes, chemical analysis, fluorescent lamp production, piezoelectrics, ceramic and etc. Diphosphates have been widely investigated because of their practical and fundamental purposes. While the optimal conditions of the production and the properties of diphosphates have been extensively investigated, there are relatively few published studies on the mechanisms of their formation.

Most of metal ions with diphosphate ions form various barely soluble salt and soluble complex compounds. Main factors, that affect formation of the compounds and their chemical composition, are the molar ratio of diphosphate ions to metal ions (*n*), their concentrations in the initial solution mixture and pH of reaction mixture.

Previously unpublished and unexpected results were obtained while investigating the precipitates formed in the $CuSO_4 – K_4P_2O_7 – (NH_4)_4P_2O_7 – H_2O$ system. It indicated, that previously little-investigated systems $CuSO_4 – K_4P_2O_7 – H_2O$ and $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$ system more interesting properties and the research into the topic should yield novel results, that would wider the understanding of diphosphate chemistry.

The objective:

To investigate the composition and structure of barely soluble compounds forming in the $CuSO_4 – K_4P_2O_7 – H_2O$ and $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$ systems and what factors would allow to control them. That would involve:

1) A successive study of barely soluble compounds forming in the $CuSO_4 – K_4P_2O_7 – H_2O$ system depends on concentrations of reacting compounds, their ratio and pH of reaction mixture.

2) A study of chemical composition, structure and regularities of formation of a novel compound, which was found in pursuance of the 1) goal Its structure and regularities of formation.

3) To investigate the regularities of transition of single salt $Cu_2P_2O_7{\cdot}5H_2O$ into double salt $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$.

4) To compare the results obtained for the systems $CuSO_4 – K_4P_2O_7 – H_2O$ and $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$, and clarify the similarities and differences between them.

Statements to defence:

At least three poorly soluble compounds can be formed in the $CuSO_4 – K_4P_2O_7 – H_2O$ system: a single salt $Cu_2P_2O_7{\cdot}5H_2O$ and two dimorph's both having chemical formula $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$. A previously known form of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (we named it *Dimorph A*) transforms into a novel *Dimorph B*, which has a different structure. The similarities between the XRD patterns and vibrations spectra of copper–ammonium and copper–potassium *Dimorph's B* imply that they are isostructural. The values of the angle for copper–potassium and copper–ammonium salts and $Cu_2P_2O_7{\cdot}5H_2O$ are relatively low and vary within a narrow range ($123.1 – 127.1^{\circ}$).

The formation of the compounds significantly depends on the conditions of the experiment. A double salt in the $CuSO_4 – K_4P_2O_7 – H_2O$ system may be formed after some time in the reaction mixture as a result of the following 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 reaction has not been previously described for any polyphosphate system. Therefore, novel results of scientific investigation are presented.

The rate, duration and yield of heterogeneous reaction substantially depend on pH of the solution, $[Cu^{2+} + P_2O_7^{4-}]$ and n ($[P_2O_7^{4-}]$ / $[Cu^{2+}]$). At a relatively low pH the induction time is high, the reaction rate is low and duration is long. The maximal yields close to 100% can be achieved when $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M. At increased pH values, the induction time, the yield and duration of the reaction diminish. At increased $[Cu^{2+} + P_2O_7^{4-}]$ the induction time and duration of heterogeneous reaction also diminish. Reduction of n from 1 to 0.67 results in the substantial increase of both the induction time and duration of the reaction, while the yield notably diminishes.

Analogous heterogeneous reaction proceeds in the $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$ system. Formation of the precipitates in the $CuSO_4 – K_4P_2O_7 – H_2O$ and $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$ systems proceed in the same order: semiamorphous voluminous precipitates → $Cu_2P_2O_7{\cdot}5H_2O$ → $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ (Dimorph A) → $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ (Dimorph B), where Kat = K or NH_4.

Novelty of the work

While the properties and optimal synthesis methods of the diphosphates have been extensively studied due to their industrial importance, the mechanisms of their formation have not. However, the deeper fundamental understanding of the diphosphate formation mechanisms would lead to futher improvements of their synthesis, usage and handling.

Wide use and eventual disposal of the diphosphates rises concerns about their environmental impact. Under alkaline conditions diphosphates form highly soluble complexes with wide variety metal ions, including heavy metal ions. Because of that, their decontamination could become even more complicated. Research studies, performed at Department of Environmental Chemistry of the Institute of Chemistry have shown, that one other ways to decontaminate heavy metal-containing diphosphate solutions (e.g. spent galvanic solutions) is to mix them with some other spent galvanic solutions under controlled conditions. The knowledge of diphosphate formation mechanisms can become very useful trying to find the most cost efective and reliable ways of their decontamonation.

Publications

The results of investigations are published in 3 papers.

EXPERIMENTAL

Materials

All experiments were carried out with reagents at least of analytical grade of purity: $CuSO_4 \cdot 5H_2O$, $(NH_4)_4P_2O_7$, H_2SO_4, NaOH, KOH, K_2SO_4, $(NH_4)_2SO_4$. Extra pure potassium diphosphate ($K_4P_2O_7$) was purchased from Riedel – De Haën. All the solution were prepared in distilled water at 1 M concentration, and then diluted with distilled water down to 0.05 – 0.5 M concentrations as appropriate.

Sample preparation and investigations

1) Precipitation experiments.

All experiments were carried out at 18 ± 2°C. Stock 1M $CuSO_4$, 1M $K_4P_2O_7$ and 1M $(NH_4)_4P_2O_7$ solutions were diluted to the appropriate concentrations. The mixing of solutions was performed by pouring both solutions simultaneously into the beaker while continuously stirring with a magnetic stirrer. The required pH was immediately adjusted using concentrated and diluted (1M and 0.1M) H_2SO_4. As pH of the mixture increased slowly during the first 2-3 hours of mixing, it was corrected each 20 minutes. For the interaction time longer than 3 days, the reaction mixture was poured into a conical flack, corked with a polished glass plug and heat-sealed with paraffin to prevent evaporation. The suspensions were filtered using a Filtrak (Germany) filter „a slow filtering for finest deposits“ and a Buchner funnel with a vacuum-jet pump.

2) Colorimetric concentration determination of the diphosphates

Colorimetric determination of the diphosphate concentration was chosen for this study. Under acidic conditions, phosphate ions react with ammonium molybdate $(NH_4)_2MoO_4$ forming yellow heteropolyacid $H_7[P(Mo_2O_7)_6] \cdot 28H_2O$. The reduction reaction with $SnCl_2$ results in blue phosphorus - molybdenum complex. The intensity of the blue colour is directly proportional to initial phosphate ion concentration. As diphosphates do not form molybdenum-containing heteropolyacid, they had to be hydrolysed into phosphate using sulphuric acid before the colorimetric analysis. In order to achieve that, 2 ml of the solution sample was mixed with 2 ml H_2SO_4 and heated. After that, it was diluted with distilled water and analysed as described above. Light absorption was measured using photoelectric colorimeter ФЭК – 56 M and red light filter with $\lambda = 597 \pm 10$ nm. Method was validated using calibration curve, and phosphate concentration in the sample was determined using linear equation of the absorption dependence on phosphate concentration.

3) Colorimetric concentration determination of the ammonium

Under alkaline condition, ammonium ions react with Nesler‘s reagent K_2HgJ_4 forming yellow-brown mercury iodide. Light absorption was measured using photoelectric colorimeter ФЭК – 56 M and blue light filter with $\lambda = 400 \pm 5$ nm. Again, method was validated using calibration curve, and ammonium concentration in the sample was determined using linear equation of the absorption dependence on ammonium concentration.

4) pH measurements

Potenciometric measurements were performed with a pH meter- millivoltmeter ЭВ – 74 (Russia) with a scale resolution of 1 mV using a silver chloride electrode as a reference.

pH of the solutions was measured using universal ionmeter ЭВ – 74 (Belarus), equipped with glass electrode ЭСЛ – 43 – 07 (Belarus) for pH measurements, and Ag/AgCl electrode ЭСЛ – 43 – 07 (Belarus) filled with saturated KCl solution as a reference. For the pH meter calibration, standard buffer solutions appropriate for the pH interval of interest were used.

5) Fourier transformation infrared spectroscopy (FTIR).

FTIR spectra were recorded on a Hartman& Braun spectrometer at a spectral resolution of 4 cm^{-1} using KBr pellets to sustain the powdered sample in 4000 – 400 cm^{-1} and 2000 – 400 cm^{-1} intervals.

6) X-ray diffractometry (XRD).

XRD experiments were carried out on X-ray diffractometer DRON-2 using Cu K_α (U = 30 kV, I = 25 mA, λ = 1.5405 Å) radiation. The step scan mode with a step size of $\Delta\ 2\theta$ = 0.05° and a counting time of 5 – 8 s per step were used in the range 2θ = 5 – 45°.

7) Atomic Absorption Spectrometry (AAS).

Copper (II) and Potassium (I) were analysed by means of a “Perkin Elmer” 603 atomic absorption spectrophotometer with an oxidising acetylene-air flame using standard procedures.

Single element hollow cathode lamp “Intensitron” (USA) was used as a light source.

Standard solutions were prepared from monoelement stock solutions containing 1000 mg/l of Cu^{2+} and K^+, prepared using HNO_3 of „chemically pure“ grade. The measurements were carried out using Cu 324.9 nm and K 383.6 nm spectral lines. Linear concentration range was 0 – 5 mg/l for copper and 0 - 2 mg/l for potassium. For every experimental data point, the measurements were performed at least 15 times, and the mean value calculated.

8) P –O – P angle determination

The vibration spectra point was used to determine the bent P–O–P bridge angle for all of these compounds. The values of the angle for copper–potassium and copper–ammonium salts as well as for $Cu_2P_2O_7 \cdot 5H_2O$ were estimated using Lazarev's relationship and the plot given by Rulmont.

Lazarev's relationship:

$\Delta = (\nu_{as}\,P–O–P - \nu_s\,P–O–P) / (\nu_{as}\,P–O–P + \nu_s\,P–O–P) = f(\alpha)$

9) A yield and rate of the heterogeneous reaction

A yield of the heterogeneous reaction was calculated as a 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 by two ways:

1. Titrating the amount of H^+ ions released at the end of heterogeneous reaction;
2. Summating the titrations of amounts of H^+ ions released after testing the reaction rate.

In the $CuSO_4$ – $(NH_4)_4P_2O_7$ – H_2O system yields were determined after the completion of heterogeneous reaction. Reaction mixture was filtered, and H^+ ion concentration was determined by the means of titration. Standardised NaOH solution (0.21N) was added to a known filtrate volume until it reached initial pH.

In the case of $CuSO_4$ – $K_4P_2O_7$ – H_2O system, solution was titrated using KOH solution every hour in order to return it to initial pH. At the end of the experiment titration values were added up in order to calculate the yield.

RESULTS AND DISCUSSION

1. A novel copper potassium diphosphate – dimorphic $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$

During the investigation of $CuSO_4$ – $K_4P_2O_7$ – H_2O system we perceived that a known double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ undergoes transformation into a novel compound which has not been described in any previous publication. The investigation of a mechanism of formation of barely soluble compounds in the system would be impossible without research of a composition and structure of the new compound. This investigation was performed.

Four of the precipitates, whose diffractograms contained the only the peeks corresponding to the novel compound were analysed (Table 1).

Table 1. Molar ratios of copper, potassium, diphosphate and water (calculated by subtraction) for precipitates determined by chemical analysis

pH	*n*	Duration of mixing, days	Cu : K : P_2O_7 : H_2O
4.0	1.0	30	1.00 : 0.68 : 0.67 : 1.03
5.0	1.0	15	1.00 : 0.68 : 0.66 : 1.00
5.5	1.0	10	1.00 : 0.67 : 0.68 : 1.02
5.0	1.5	10	1.00 : 0.66 : 0.67 : 0.99

In all four cases the formula of the compound corresponded to $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$. These results point to the fact that $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ has polymorphic properties. The previously described form is henceforth given the name *Dimorph A*, and the other form is described here under the name of *Dimorph B*.

Their XRD data are presented in Table 2. Analysis of the data shows that the new *Dimorph B* crystallizes in the same monoclinic system as *Dimorph A*.

Table 2 XRD patterns of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ and $Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ *Dimorph B*

$Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$				$Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$	
Dimorph A		*Dimorph B*		*Dimorph B*	
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
8.808	100	9.433	18	9.422	32
6.01	3	6.143	44	6.180	76
5.372	19	5.47	51	5.617	43
		5.278	27	5.305	36
		5.053	35	5.017	100
4.797	24	4.95	73		
4.517	3	4.541	14	4.628	30
4.338	6				
3.897	2	3.859	23	3.853	7
3.808	5	3.76	3	3.704	3
3.752	5				
3.621	1	3.595	2	3.633	7
3.426	48	3.451	17	3.444	19
		3.401	22	3.343	2
3.212	55	3.283	10	3.233	5
3.088	4	3.183	10		
3.031	46	3.025	61	3.071	47
		2.981	23	2.983	5

		2.955	22	2.923	8
2.901	18	2.932	23	2.891	51
		2.872	100	2.868	48
2.84	2	2.846	86	2.802	26
2.808	10				
2.783	15				
2.746	24	2.736	47	2.759	11
2.69	20	2.701	43	2.725	7
		2.644	23	2.653	11
2.614	3	2.617	21	2.637	11
2.582	4	2.566	5	2.534	5
2.539	25	2.529	4	2.503	2
2.455	8	2.475	1		
2.4	10	2.4	19	2.407	18
2.28	2			2.340	16
2.257	9	2.327	10	2.311	8
2.243	10	2.27	13	2.242	3
2.23	13	2.184	5	2.199	4
2.18	4	2.168	5	2.171	3

The time required for *Dimorph B* formation is highly dependant on pH and *n* as presented in Table 3.

Table 3 Dependence of *Dimorph B* Transition Time (τ)) on pH and *n* at [Cu^{2+}] = 0.05 M, pH 5.0

pH	*n*	τ, days
4.0	1.0	14-18, 17-24, 22-27
5.0	1.0	5, 6, 6-7, 7, 9-10, 11-
5.5	1.0	13
6.0	1.0	3, 4-5, 6-7
6.7	1.0	50-65, 80-110
5.0	1.25	>150, >150
5.0	1.5	4, 4, 5, 7
5.0	1.75	3, 4, 4, 5
		1, 1, 2, 2

Where τ is the interaction time required for both *Dimorph A* (or $Cu_2P_2O_7 \cdot 5H_2O$) and *Dimorph B* peeks to become visible in diffractograms.

The various duration of the transition *Dimorph A → Dimorph B that* process occurs under the exactly the same conditions can be explained by the stochastic nature of its initiation, and progression in an autocatalytic reaction manner. Indeed, if the reaction mixture is seeded with a small amount of *Dimorph B*, the transition occurs much faster.

The formation of *Dimorph B* was investigated. Every day a sample of the suspension was taken, filtered and carefully washed. After 30 days the samples were checked every 5 days. The shortest transition time (τ) was reached when pH was 5.5, and the rise of pH to 6.0 drastically increased τ (approximately ten-fold). The reduction of pH to 5.0 and 4.0 rose τ markedly (approximately two foldes and four foldes, respectively). Increase of *n* from 1.0 to 1.75 at constant $[Cu^{2+}]$ = 0.05 M and pH 5.0 substantially reduces τ. Apparently, the increase in unbound diphosphate ion concentration (at pH 5 the main form is $H_2P_2O_7^{2-}$) substantially accelerates the transition process. The moderate reproducibility shows that transition might be influenced by some uncontrolled and/or stochastic factors.

The analysis of IR spectra of *Dimorph A* and *Dimorph B* shows, that the absorption bands are significantly different (Table 4).

Table 4. Vibration frequencies of $Cu_3K_2(P_2O_7)_2\cdot 3H_2O$ and $Cu_3(NH_4)_2(P_2O_7)_2\cdot 3H_2O$ *Dimorph B* (cm^{-1})

$Cu_3K_2(P_2O_7)_2\cdot 3H_2O$		$Cu_3(NH_4)_2(P_2O_7)_2\cdot 3H_2O$	Assignment
Dimorph A	*Dimorph B*	*Dimorph B*	
1670 w	1680 w	1683 m	δH_2O
1630 w	1634 w		
		1440 s	δNH_4^+
		1411 m	
1190 s	1128 s	1127 s	νPO_3
1162 s	1089 s	1083 s	
1142 s	1037 m	1034 m	
1109 s			
1072 m			
1036 m			
1003 w			
918 m	954 s	960 s	ν_{as}P–O–P
889 s			
737 s	774 m	769 m	ν_sP–O–P
660 sh	656 w	664 w	γPOH?
624 w	624 w	607 sh	δPO_3
591 s	587 m	590 m	
563 s	536 m	541 m	

Sh: shoulder, s: strong, m: medium, w: weak

There are 7 distinct bands corresponding to P–O vibrations of terminal PO_3 moiety of the diphosphate group in the case of *Dimorph A*: 1190, 1162, 1142, 1109, 1072, 1036, 1003 cm^{-1}. In the case of *Dimorph B* there are only 3 bands at 1129, 1089 and 1036 cm^{-1} which suggests, that the P–O–P angle is closer to 180° in *Dimorph B* compared to *Dimorph A*.

Bands corresponding to ν_{as} P–O–P and ν_s P–O–P are shifted to shorter wavelengths in *Dimorph B* in comparison to *Dimorph A* (954 cm^{-1} instead of 918 and 889 cm^{-1}; and 774 cm^{-1} instead of 737 cm^{-1}, respectively).

The appearance of symmetric and antisymmetric bridge vibrations in the infrared spectra points to a bent P–O–P bridge configuration. The ν_s P–O–P vibrations are not observed in the infrared spectrum when the bridge is linear.

It's worth mentioning that, the band corresponding to ν_{as} P–O–P for the copper–potassium *Dimorph A*, which is analogous to the copper–ammonium *Dimorph A*, is split into two components. This confirms the lower symmetry of the crystal cell in comparison to both (copper–ammonium and copper–potassium) *Dimorph B,* where appropriate single bands exist.

The similarities between the XRD patterns and vibration spectra of the copper–ammonium and the copper–potassium *Dimorph B* imply that they are isostructural.

The values of the P–O–P angle were estimated using Lazarev's relationship for copper–ammonium and copper–potassium dimorph pairs and for $Cu_2P_2O_7{\cdot}5H_2O$ (Table 5).

Table 5 The values of the P–O–P angle for $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ (Kat = K, NH_4) and $Cu_2P_2O_7{\cdot}5H_2O$

Compound	100 Δ	P–O–P angle value
$Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*)	10.15	124.5
$Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*)	10.34	125.1
$Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*)	9.87	123.1
$Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*)	10.67	126.2
$Cu_2P_2O_7{\cdot}5H_2O$	10.88	127.1

All the angles are relatively low and vary within a narrow range (123.1 – 127.1°). As the result of transformation from *Dimorph A* to *Dimorph B* the P–O–P angle becomes slightly more obtuse. It should be noted however, that while the IR absorption bands undergo a significant wavelength shift, the difference between ν_{as} P–O–P and ν_s P–O–P remains virtually the same. That leads to conclusion, that all the P–O–P angles remain in a narrow range around 125° which lies at the lower end of the P–O–P angles observed in most diphosphates. As such a small change in P–O–P angle cannot explain the dramatic shift of IR absorption bands, it must be due to the some steric effects, obviously the different conformational orientation of $P_2O_7^{4-}$ ion.

2. Formation of barely soluble compounds in the system $CuSO_4$ – $K_4P_2O_7$ – H_2O

2.1. Role of pH and $[Cu^{2+} + P_2O_7^{4-}]$ on precipitate formation

At 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 have been investigated.

Our investigation showed that three poorly soluble compounds can be formed in the system $CuSO_4$ – $K_4P_2O_7$ – H_2O: single salt $Ca_2P_2O_7{\cdot}5H_2O$ and two polymorphs of double salt $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ named *Dimorph A* and *Dimorph B*. 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.

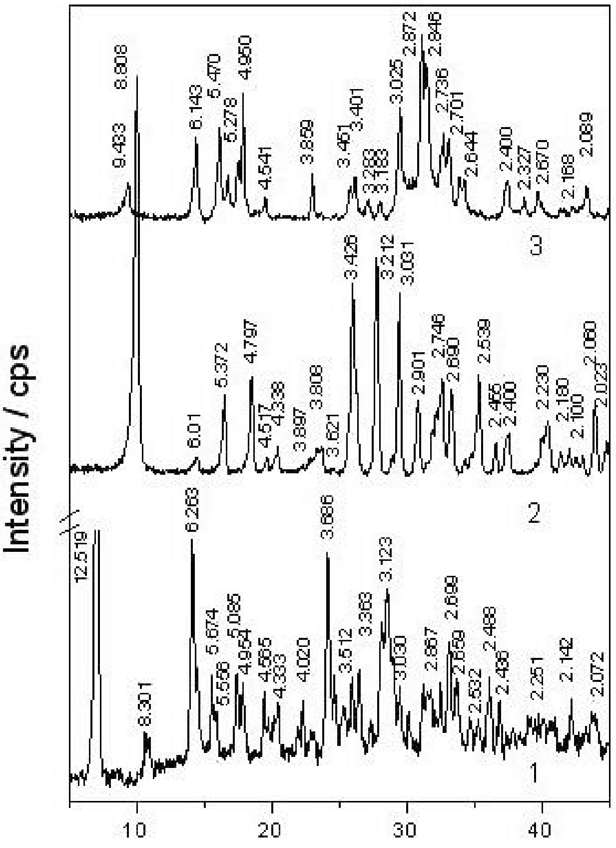

Fig. 1. X–ray diffractograms of: 1 – $Cu_2P_2O_7{\cdot}5H_2O$, 2 – $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*), 3 – $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*).

As soon as $CuSO_4$ and $K_4P_2O_7$ solutions were mixed and pH was adjusted, a colloidal solution started to form immediately, which then transformed into a voluminous gelatinous precipitate after a few minutes. 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 constant pH, during the first 2–3 hours it had to be adjusted (we used H_2SO_4). This indicates that transformation of instable initial compounds with either release of OH^- ions or connection of H^+ ions occurs. X–ray diffractograms of precipitate samples taken after 1−4 hours show, that fine crystalline defective $Cu_2P_2O_7{\cdot}5H_2O$ is formed if pH of the reaction mixture is ≤ 5.5.

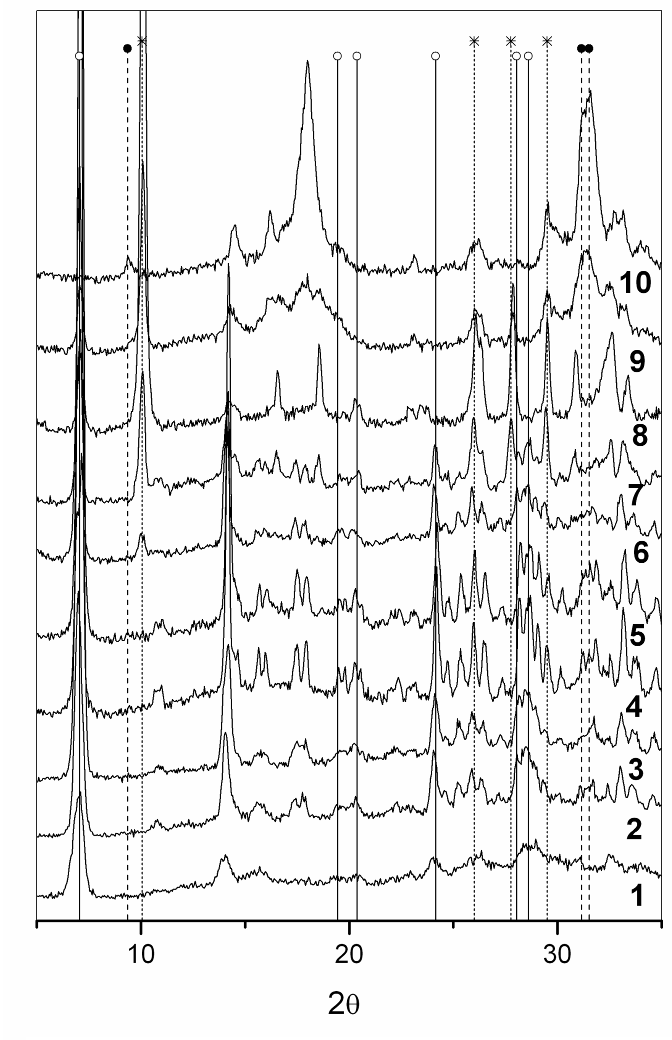

Fig. 2. X–ray diffractograms of precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$, initial adjusted pH 5.0. Duration of mixing and pH: 1 – 15 min, 5.0; 2 – 1 h, 5.0; 3 – 2 h, 5.0; 4 – 18 h, 5.00; 5 – 30 h, 3.75; 6 – 40 h, 3.65; 7 – 48 h, 3.50; 8 – 4 days, 2.70;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

At first the formation of poorly soluble compounds at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M and $n = 1$ was investigated. In order to ascertain the reproducibility of the results, six experiments were performed under exactly the same conditions at pH 5.0. X−ray diffractograms of precipitates obtained after 1h of mixing show formation of fine crystalline defective single salt $Cu_2P_2O_7{\cdot}5H_2O$. Its crystallinity improves under continuous mixing without any change in the pH of the reaction mixtures. After some time this pH began to decrease without visible changes in diffractograms. Afterwards, a gradual formation of fine crystalline double salt $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) became visible in diffractograms. Over time the intensity of the peaks of double salt increases with the decrease in the intensity of the peaks of the single salt. Later the decrease in pH stopped and after some time the transformation of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) into the corresponding *Dimorph B* occurred. Substantial diffractograms of one such experiment are shown in Fig. 2.

The time after which the decrease in pH of reaction mixtures was detected (induction time), was in the range of 15−24 hours and the duration of this process was in the range of 90−130 hours. The transformation of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) into $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*) began after 5−11 days and continued for 1−3 days. The reproducibility of the results was moderate.

Dynamics of the ratio $[K^+]$ / $[Cu^{2+}]$ in the precipitates of one experiment *versus* the duration of interaction was investigated. Initially this ratio was low and it diminished as soon as the pH began to decrease. Likely, the reason of moderate decrease in the $[K^+]$ / $[Cu^{2+}]$ ratio was the improvement and grows of $Cu_2P_2O_7 \cdot 5H_2O$ crystals as a result of this the amount of mother solution enclosed between the crystals diminishes. As soon as pH began to decrease, the ratio began to increase and reached values close to 0.67 which is equal to the molar ratio of $[K^+]$ / $[Cu^{2+}]$ in double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (Table 6).

Table 6. Dependence of pH of reaction mixture and $[K^+]$ / $[Cu^{2+}]$ ratio in precipitates on duration of mixing of reaction mixture at various initial pH, $[CuSO_4] = [K_4P_2O_7] = 0.05$ M.

Initial pH	Duration of interaction	pH	$\vert K^+\vert / \vert Cu^{2+}\vert$
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 results show that after induction time, when visibly only the improvement in crystallinity of $Cu_2P_2O_7{\cdot}5H_2O$ occurs, the following heterogeneous reaction begins:

$$3Cu_2P_2O_7{\cdot}5H_2O\downarrow + H_2P_2O_7^{2-} + 4K^+ \Rightarrow 2Cu_3K_2(P_2O_7)_2{\cdot}3H_2O\downarrow + 2H^+ + 9H_2O$$

A $H_2P_2O_7^{2-}$ is the main form of diphosphate ion that exists under the pH range 2–6. It is clear that this reaction may proceed only through rather instable intermediate products. The rate of the reaction therefore may be easily controlled by periodically keeping pH to a previous value using a standardized solution of strong alkali. In order not to complicate the system additionally a KOH solution (0.35 N) was used. As the rate of the reaction was rather moderate, the addition of alkali solution was chosen to be performed at hourly intervals and the addition of KOH to achieve the required pH took less than one minute to perform.

In order to ascertain the reproducibility of the results six experiments were performed under the same conditions (Table 7).

Table 7. Results of 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
20 ± 4	23 ± 2	95 ± 2

Uneven jumpy progress is characteristic to this reaction (three curves are given in Fig. 3). The reproducibility of the results is moderate.

The induction time was in the range of 16−26 h, the duration of this process was in the range of 24–32 h. The maximal rates where in the range of 1.3−1.7 mM/h Cu^{2+}.

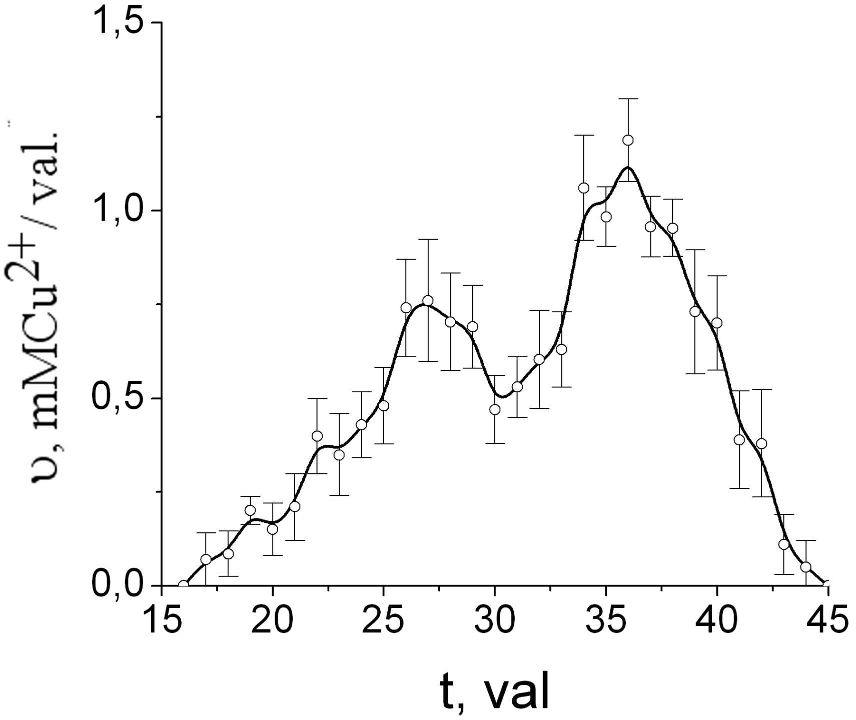

Fig. 3. Dependence of heterogeneous reaction rate on duration of interaction at [Cu^{2+} + $P_2O_7^{4-}$] = 0.1 M, n = 1, pH = 5.0

The calculated yield of the reaction was in the range of 92−98 %. Similar results of the yield (94−100 %) were obtained in the previous experiment after titration of the reaction mixture after the reaction was completed.

In cases where initial 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 XRD analysis the precipitates obtained after 15 min were highly defective $Cu_2P_2O_7 \cdot 5H_2O$. Their structure remarkably improved after as little as 1 hour of mixing. The improvement slowly continued 10–16 days without any change in the pH of the reaction mixture. A decrease in reaction mixture pH (heterogeneous reaction) began after a substantially longer time period in comparison to the previously performed experiment with the initial pH value set to 5.0. However, no marked changes were seen in initial diffractograms. When pH was further even diminished, a substantial disorder in the structure of the precipitate was observed. Afterwards the peaks of fine crystalline $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*) emerged and later began to dominate in diffractograms. Under the lowest pH only the peaks of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*) were seen, as the phase of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) was invisible in diffractograms. Apparently, at a low pH $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) transits to $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph*

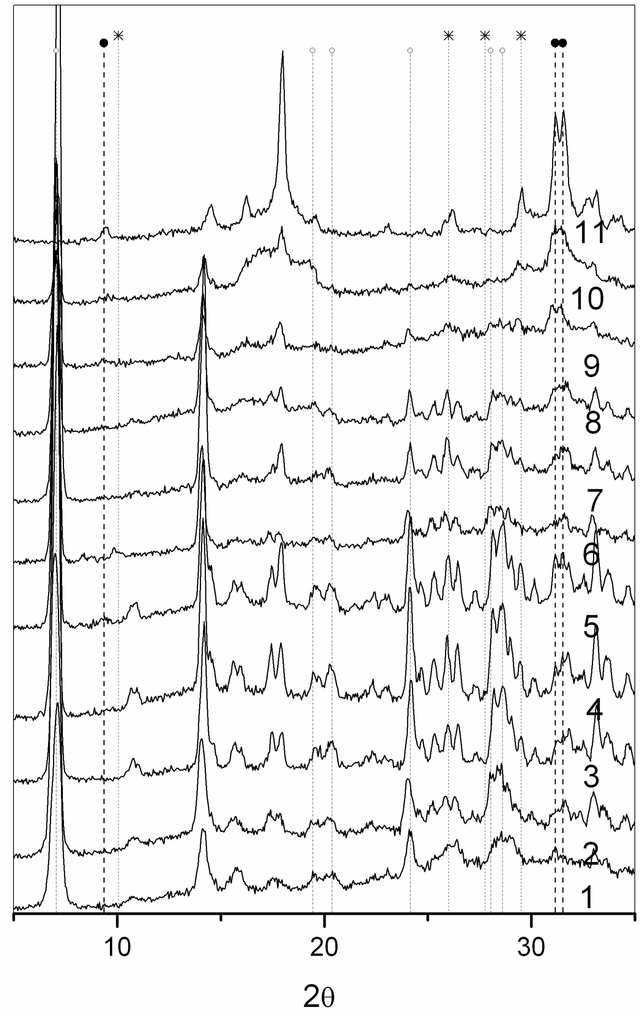

Fig. 4. X−ray diffractograms of precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, *n* = 1, initial adjusted pH 4.00. Duration of mixing and pH: 1 – 15 min, 4.0; 2 – 1 h, 4.0; 3 – 10 days, 4.00; 4 – 12 days, 3.82; 5 – 15 days, 3.35; 6 – 16 days, 3.22; 7 – 18 days, 3.07; 8 – 20 days, 2.86; 9 – 24 days, 2.55; 10 – 26 days, 2.39; 11 – 30 days, 2.26. Substantial peaks are noted ○ – for $Cu_2P_2O_7 \cdot 5H_2O$, * – for $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*), ● – for $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*).

B) at a very high rate which made the detection of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) hardly possible. The calculated values of yield of heterogeneous reaction were 97, 99 and 102 %, which is slightly higher than those at pH 5.0.

At pH 5.5 the experiment was performed in triplicate. The transformation from semiamorphous precipitate into fine crystalline $Cu_2P_2O_7{\cdot}5H_2O$ lasted 6–10 hours, which is 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 continued for 80–120 hours. Already after 3–6 days the transformation of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) into $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*) began, the process continued for no longer than two days. Representative diffractograms of one of the experiments are shown in Fig. 5.

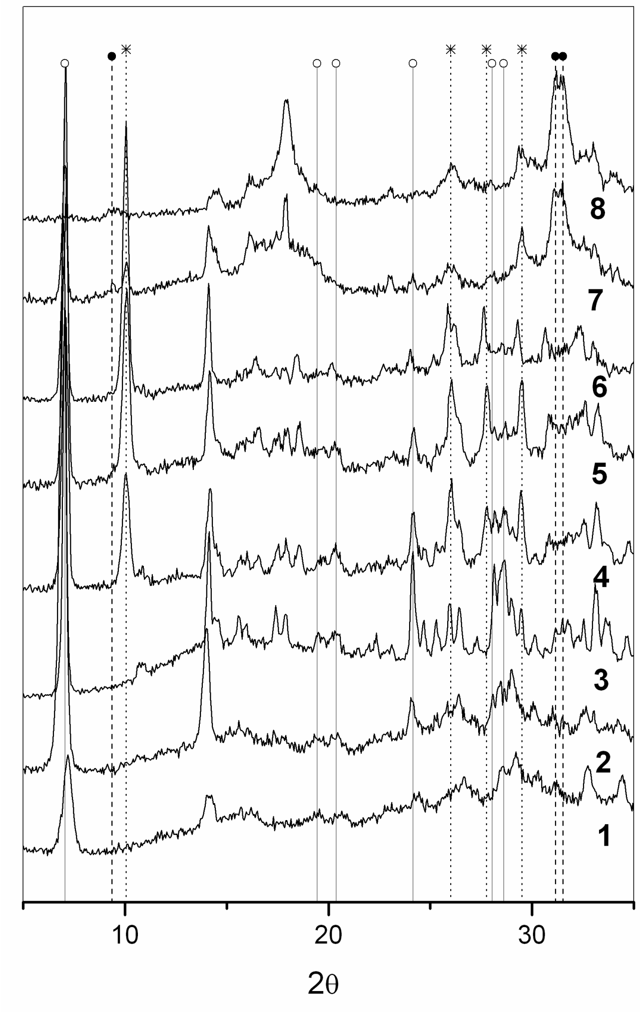

Fig. 5. X–ray diffractograms of precipitates obtained from reaction mixture at $[Cu^{2+} + P_2O_7^{4-}]$ = 0.1 M, n = 1, initial adjusted pH 5.5. Duration of mixing and pH: 1 – 15 min, 5.5; 2 – 2 h, 5.5; 3 – 12 h, 5.50; 4 – 18 h, 5.38; 5 – 24 h, 4.73; 6 – 2 days, 4.50; 7 – 3 days, 3.45; 8 – 7 days, 3.06. Substantial peaks are noted ○ – for $Cu_2P_2O_7{\cdot}5H_2O$, * – for $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*), ● – for $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*).

Until the beginning of heterogeneous reaction, the ratio $[K^+]$ / $[Cu^{2+}]$ was significantly higher in comparison to those in our previous experiments (Table 6). When pH began to decrease, the ratio begins to increase and reached values close to 0.67.

The yield of heterogeneous reaction only reached 47, 55 and 59%. The yield was determined when the reaction was finished. The obtained results can be explained as follows: a part of Cu^{2+} ions precipitate as an amorphous double salt at this pH just in first minutes of interaction (according to the data of chemical and XRD analysis). As a significant fraction of Cu^{2+} ions is already precipitated and do not participate in subsequent reactions, the yield of heterogeneous reaction is rather low (around 50%).

At the two highest pH values investigated (6.0 and 6.5) the reduction of pH was undetectable. When the pH was adjusted to 6.0, the precipitate obtained after 15 min and 4 hours were semiamorphous (Fig. 6). The peaks in diffractogram of the precipitate, obtained after 4 hours of mixing, were slightly sharper and more clearly defined, but it was impossible to obtain information about its composition. The diffractogram of the precipitate obtained after 8 hours of mixing was complicated, however peaks characteristic to both $Cu_2P_2O_7{\cdot}5H_2O$ and $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) are visible. After 18 hours of interaction the peaks of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) became dominating, and after 24 hours they became sole peaks seen in diffractograms. After a long time (45 and 75 days) only some improvement of the $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) structure and insignificant decrease in pH (~0.2) occurred. After that a transition of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) to $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*) began and continued 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 6).

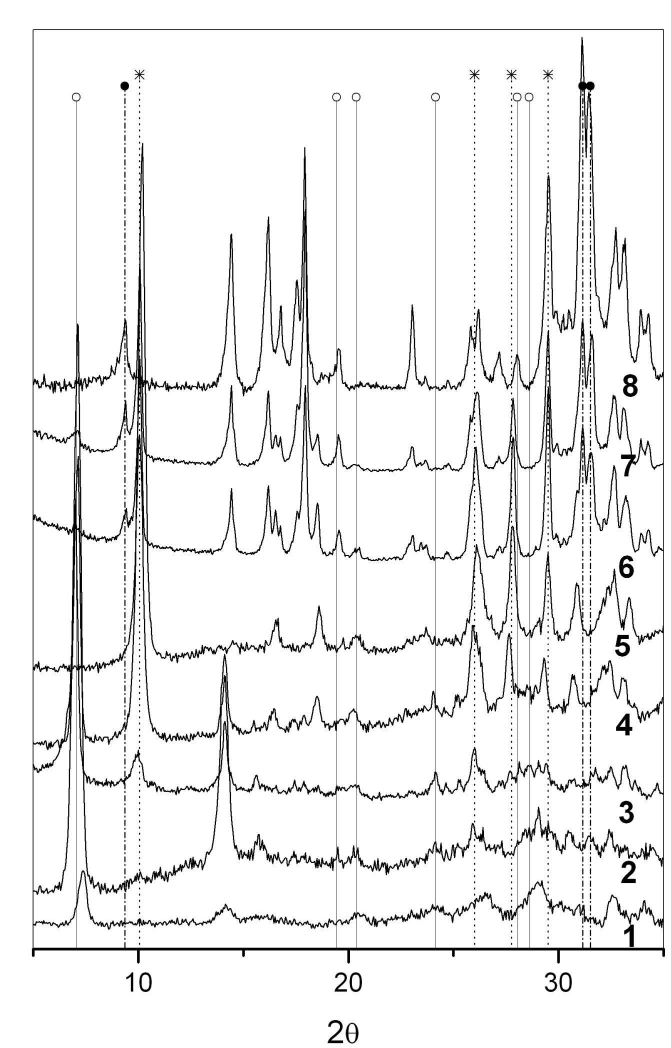

Fig. 6. X−ray diffractograms of precipitates obtained from reaction mixture at [Cu^{2+} + $P_2O_7^{4-}$] = 0.1 M, *n* = 1, initial adjusted pH 6.0. Duration of mixing and pH: 1 – 15 min, 6.0; 2 – 4 h, 6.00; 3 – 8 h, 6.00; 4 – 18 h, 6.00; 5 – 24 h, 5.98; 6 – 50 days, 5.96; 7 – 55 days, 5.95; 8 – 70 days, 5.95. Substantial peaks are noted ○ – for $Cu_2P_2O_7{\cdot}5H_2O$, * – for $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*), ● – for $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph B*).

Analysis of FTIR spectra of the

precipitates coincide with results of chemical and XRD analysis. The mixture of $Cu_2P_2O_7 \cdot 5H_2O$ and $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) may be seen in FTIR spectra of precipitate obtained after minimal duration of interaction (15 min). The FTIR spectra shows that at prolonged interaction time the interaction of the fraction of $Cu_2P_2O_7 \cdot 5H_2O$ in the precipitate substantially diminishes, and $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) begins to dominate.

However, the reason why the heterogeneous reaction was not observed is not entirely clear.

When the concentrations of $CuSO_4$ and $K_4P_2O_7$ at $n = 1$ in the reaction mixture were halved, the formation of a double salt was substantially slowed down. When pH was adjusted to 5.0, $Cu_2P_2O_7 \cdot 5H_2O$ formed and only after 12 and 17 days the heterogeneous reaction began and continued for 16 and 20 days. The calculated yield of 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 after as little as 2–3 hours and continued no longer than two days in the investigated initial pH range of 4.0–5.5.

The rates of 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 medium reproducibility of the results obtained when $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M, $n = 1$. The duration of heterogeneous reaction substantially decreases with increases in the initial pH (Fig. 7).

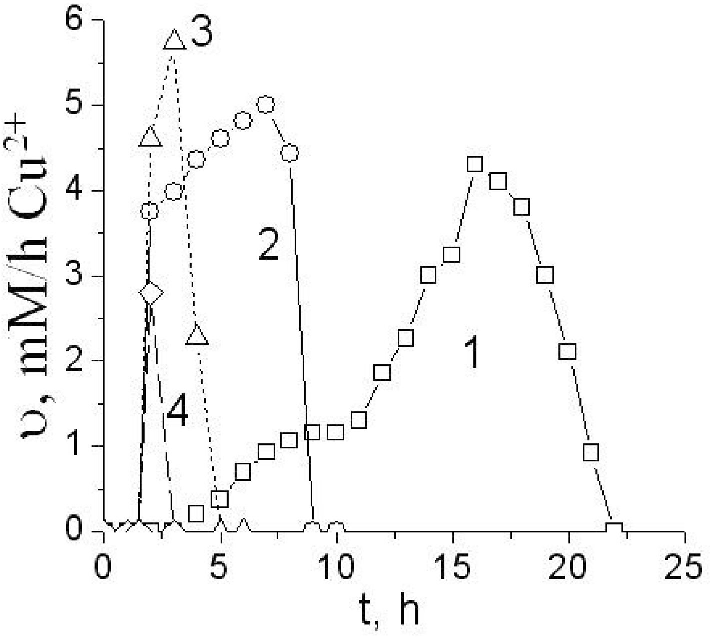

Fig. 7. Dependence of heterogeneous reaction rate on duration of interaction at $[Cu^{2+} + P_2O_7^{4-}] = 0.25$ M, $n = 1$. Initial adjusted pH: 1 – 4.0, 2 – 4.5, 3 – 5.0, 4 – 5.2.

The maximal rate was obtained at pH 5.0 at rates of 5.5, 5.6 and 6.0 mM/h Cu^{2+}. At pH 5.5 the heterogeneous reaction was not observed, however the reaction was not observed at higher pH in the previous experiment series either, when [Cu^{2+} + $P_2O_7^{4-}$] was 0.1 M. The calculated yield of 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 heterogeneous reaction increased 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 heterogeneous reaction distinctly diminishes and reaches maximum of 1.8–2.1 mM/h Cu^{2+} at the initial pH 5.5, when 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 as little as ~55 %.

When |Cu^{2+} + $P_2O_7^{4-}$| was increased to 0.5 M (n = 1), the heterogeneous reaction began after as little as half an hour of mixing and continued for no longer than one day. The product of the reaction was in all cases $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*), that transited after some time into $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*). A dependence of the rate of heterogeneous reaction on initial adjusted pH in the pH range 3.5–5.5 was investigated (Fig. 8).

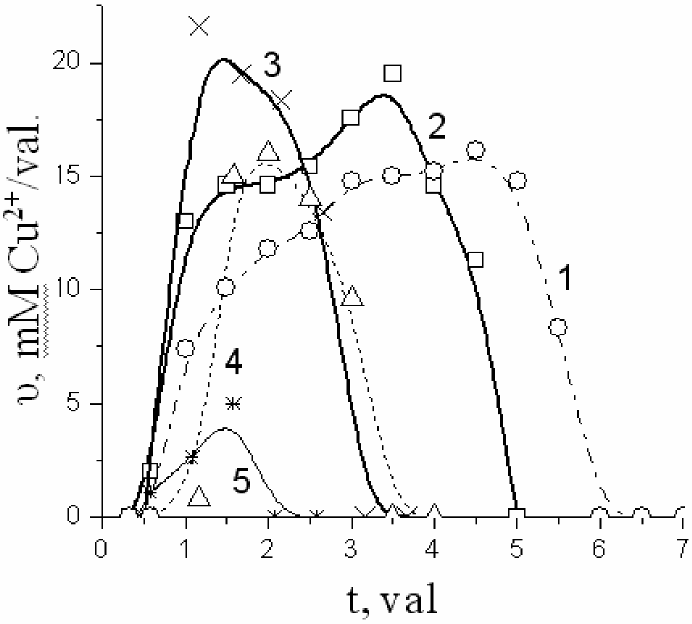

Fig. 8. Dependence of heterogeneous reaction rate on duration of interaction at |Cu^{2+} + $P_2O_7^{4-}$| = 0.5 M, n = 1, under pH initially adjusted to: 1 – 3.5; 2 – 3.7; 3 – 4.0; 4 – 4.2; 5 – 4.5

Experiments were run in triplicate, and the reproducibility of the results was rather good. The duration of heterogeneous reaction was longest (~ 5.5 h) at the pH 3.5 and gradually diminished with the increase of pH. The maximal rate of heterogeneous reaction was observed at pH 4.0: 20.1, 20.4 and 21.8 (20.8 ± 0.9) mM Cu^{2+}/h. At pH 5.0 and 5.5, however, the heterogeneous reaction was not observed. The increase of $|Cu^{2+} + P_2O_7^{4-}|$ prevents heterogeneous reaction progressively lower pH values.

A yield of heterogeneous reaction was determined by adding up the volumes of standardized KOH solution, used for the determination of the heterogeneous reaction rate (8 table).

8 table. Dependence of heterogeneous reaction yield on the pH of reaction mixture, $|Cu^{2+} + P_2O_7^{4-}| = 0.5$ M, $n = 1$.

pH	Yield, %
3.5	72; 74; 76 (74 ± 2)
3.7	74; 75; 78 (76 ± 2)
4.0	48; 50; 50 (49 ± 1)
4.2	33; 34; 36 (34 ± 2)
4.5	5.3; 5.6; 5.7 (5.5 ± 0.1)
5.0	0; 0
5.5	0; 0

The obtained results show, that with increase of $|Cu^{2+} + P_2O_7^{4-}|$:

1. The yield of heterogeneous reaction decreases. On the other hand, the amount of semiamorphous double salt, which forms in first few minutes of interaction, increases.
2. The induction time and duration of heterogeneous reaction diminishes, and its maximal rate increases.
3. The maximal yield of heterogeneous reaction is achieved and prevention of heterogeneous reaction is observed under progressively lower pH values

2.2. Role of excess of diphosphate ions on precipitate formation

The series of experiments were performed at constant $|Cu^{2+}|$ = 0.05 M, and the ratio *n* was investigated at the values of 1.25, 1.5 and 1.75. The results obtained were compared with the previously obtained results where *n* = 1.

At first, reaction was performed under conditions where *n* was set to 1.5, and initial pH was 5.0. The experiment was repeated four times, and representative diffractograms are show in Fig. 9.

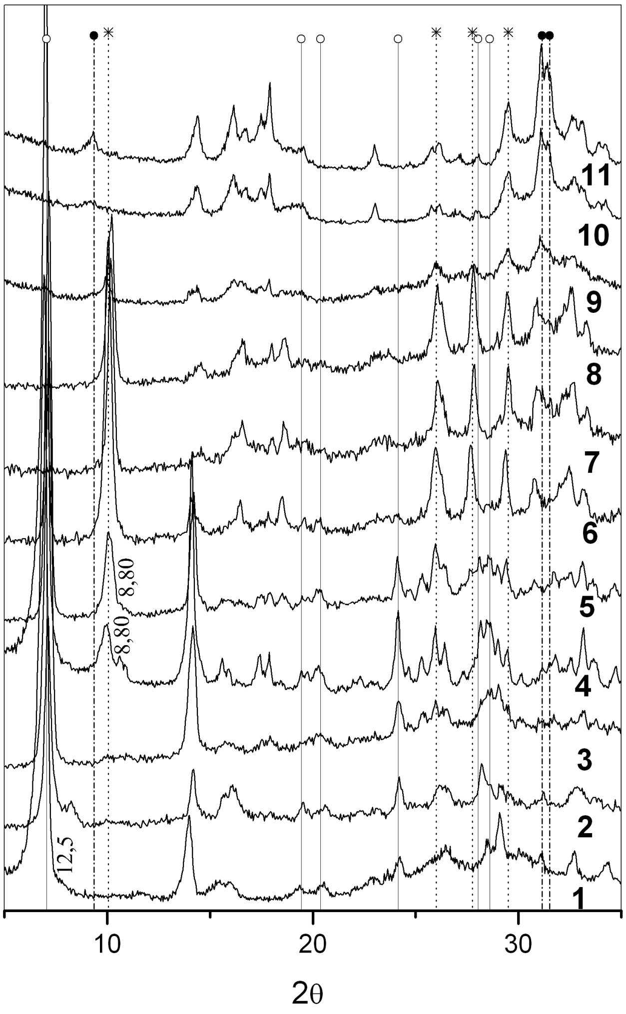

Fig. 9. X–ray diffractograms of precipitates obtained from reaction mixture at $|Cu^{2+} + P_2O_7^{4-}|$ = 0.1 M, *n* = 1.5, initial adjusted pH 5.0. Duration of mixing and pH: 1 – 15 min, 5.0; 2 – 1 h, 5.0; 3 – 2 h, 5.0; 4 – 4 h, 5.0; 5 – 6 h, 4.92; 6 – 20 h, 4.01; 7 – 28 h, 3.60; 8 – 48 h, 3.58; 9 – 3 days, 3.56; 10 – 4 days, 3.56; 11 – 6 days, 3.55. Substantial peaks are noted ○ – for $Cu_2P_2O_7 \cdot 5H_2O$, * – for $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*), ● – for $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*)

The diffractograms indicate, that precipitates obtained after 15 min and 1 h of mixing were semiamorphous, as the peaks cannot be assigned to any known crystalline copper phosphate or their mixture, except a very prominent peak corresponding to interplanar distance *d* = 12.5 Å, characteristic for the single salt $Cu_2P_2O_7 \cdot 5H_2O$. The AAS analysis of the precipitate formed after 1 hour of interaction has shown, that it contains large amount of K^+ with molar ratio $|K^+| / |Cu^{2+}|$ of 0.19 ± 0.02. After 2 h of mixing, however, the fine crystalline single salt $Cu_2P_2O_7 \cdot 5H_2O$ forms. After 4 – 6 h of interaction, diffraction peak with *d* = 8.81 Å, corresponding to most intensive peak of the largest interplanar distance of double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ *(Dimorph A)*, appears, while the pH of reaction mixture remains unchanged. A further continuous mixing of the reaction mixture results in the slow decrease of pH and the increased intensity of the peak (*d* = 8.81 Å). It indicates, that semiamorphous double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$, formed in first minutes of interaction, begins to crystallize. Even further mixing of the reaction mixture results in gradual fading of the single salt $Cu_2P_2O_7 \cdot 5H_2O$ peaks, and the rise of the peaks corresponding to the double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ *Dimorph A* in diffractograms (9 fig.), as the heterogeneous reaction proceeds. Heterogeneous reaction does not start until 4 - 6 h of mixing, and continues for about 48 h. Polymorphous transformation *Dymorph A → Dimorph B* takes 3 to 5 days. The yield of heterogeneous reaction was 36, 40 ir 42 (39 ± 3) %, which confirms the assumption that substantial part of copper ions precipitate in form of amorphous double salt during the first few minutes of interaction. The obtained results were compared with results of analogous experiment, where *n* = 1. This comparison shows that the increase of *n* results in:

1. diminished induction time and heterogeneous reaction duration, and increased maximal heterogeneous reaction rate;
2. substantially decreased maximum yield of heterogeneous reaction, and the increased amount of semiamorphous double salt, forming in first minutes of interaction;
3. decreased transition time of polymorphous transformation (Dimorph A → Dimorph B).

When initial pH was reduced to 4.0 (*n* = 1.5), in comparison with previous experiment at pH 5.0, heterogeneous reaction began later (after 8 -10 h) and continued longer (about 3 days) as was expected. The yield of heterogeneous reaction was larger: 79, 82 and 83 (81 ± 2) %.

At the values of *n* = 1.25 and initial pH of 5.0, heterogeneous reaction began after much shorter time (10 – 13 h) in comparison with previous experiment at *n* = 1, and continued for 50 to 80 hours. The yield of heterogeneous reaction was lower (78 ± 2) %, and the amount of K^+ in precipitate was significantly higher. The molar ratio $|K^+| / |Cu^{2+}| = 0.043 \pm 0.003$ was found in precipitates obtained after 1 h of mixing.

The initial pH of 5.0 and *n* of 1.75 resulted in increased longevity of semiamorphous structure of precipitates. It remained detectable for 3 – 4 h after initiation of the interaction, which is much longer than it was in precipitates obtained at lesser *n*. After 3 – 4 h the heterogeneous reaction began and has completed in as little as 2 – 3 h. The pH decreased only to values of 4.4 – 4.5, which is a much smaller change than it was in experiments at $n = 1.5$. The yield of heterogeneous reaction is lower: 29 ± 2 % and the K^+ ion content in the precipitate is higher. In the precipitates obtained after 1 h of mixing, the molar ratio $|K^+| / |Cu^{2+}| = 0.24 \pm 0.02$. The polymorphous transformation occurred more quickly (1 – 2 days).

When initial pH was reduced to 4.0, the induction time increased until 5 – 8 h, substantially increased the duration of heterogeneous reaction (1 – 2 days) and the yield of the reaction increased to 84 ± 2 %. Maximal reaction rate was in the range 1.6 – 1.8 mM Cu^{2+}/h.

The data presented above indicates, that the duration, yield, induction time of heterogeneous reaction and transition time of polymorphous transformation diminishes with increase of n at a constant Cu^{2+} ion concentration.

2.3. Influence of potassium ions on precipitate formation.

The investigation was performed at $|Cu^{2+} + P_2O_7^{4-}| = 0.1$ M, $n = 1$ and the initial pH of the reaction mixture set to 5.0. The role of potassium ions was investigated by pouring 0.6 M K_2SO_4 solution into reaction mixture in order to increase K^+ concentration from 0.2 M to 0.6 M.

Experiments were performed in triplicate. As determined by XRD, the precipitates obtained after 15 min and 1 h of mixing were semiamorphous. After 2 hours pH of the mixture slightly decreased to 4.80 – 4.85. The diffractograms of precipitates showed a mixture of fine crystalline defective single salt $Cu_2P_2O_7 \cdot 5H_2O$ and double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ *(Dimorph A)*. After 4 h of mixing pH decreased to 3.8 – 3.9, and well-defined peaks of double salt *(Dimorph A)* were seen in diffractograms together with a single $d = 12.4$ Å peak, which corresponds to the most prominent peak of single salt. After 4 hours, the prolonged mixing times did not yield any significant change in the pH of reaction mixture or the diffractograms of the precipitates. The polymorphous transformation began after 17 ± 4 days and continued 5 – 7 days.

Calculated value of the heterogeneous reaction yield was 44 ± 2 %.

The molar ratio $|K^+| / |Cu^{2+}| = 0.22 \pm 0.01$ was found in precipitates obtained after 1 h of mixing. Therefore, a three-fold increase of the K^+ concentration in the reaction mixture caused the amount of potassium in the precipitate to increase by approximately one order of magnitude. (6 table). However, the induction time of heterogeneous reaction decreased from 15 - 24 h until ~ 2 h, and the duration of the reaction – from 90 - 130 h to ~ 4 h.

Remarkably diminished yield of heterogeneous reaction and substantially increased quantity of K^+ ions in the precipitates suggest, that the formation of substantial amount of amorphous double salt occurs in first few minutes of interaction. The beginning of salt crystallization was observed after 2 h of mixing.

3. A role of seed crystals on precipitate formation

At first a suspension of double salt $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ *(Dimorph A)* was tested as seed crystals. Homogenized suspension was added to reaction mixture ($|Cu^{2+} + P_2O_7^{4-}| = 0.1$ M, *n* = 1, initial pH = 5.0), obtained after 4 days of mixing of an identical system at the ratio 1 : 4. Heterogeneous reaction began much earlier in comparison to unseeded reaction (30 min vs. 15 – 24 h). The decrease of pH of the reaction mixture proceeded at rates, similar to rates obtained in the system without a seed crystals, however the heterogeneous reaction finished at markedly higher pH (3.0 ± 0.1 instead of 2.5 ± 0.1). The yield of heterogeneous reaction substantially decreased from approx. 95 % (without seed crystals) to 43 ± 4 %. The drastic decrease of induction time of heterogeneous reaction with addition of seed crystals implies that the heterogeneous reaction is autocatalytic.

Similarly it was established, that other double copper diphosphates $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ *Dimorph B*, $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ *Dimorph A* and $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ *Dimorph B* proceed analogous as seed crystals.

4. Investigation of precipitate formation in the system $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$

The formation of barely soluble compounds from reaction mixtures $|Cu^{2+} + P_2O_7^{4-}| = 0.1$ M, *n* = 1 and the initial pH between 3.0 and 6.0 was investigated.

The results of investigation show, that heterogeneous reaction in this system proceeds in a manner similar to the system $CuSO_4 – K_4P_2O_7 – H_2O$ (9 table).

9 table. Dependence of induction time, duration and the yield of heterogeneous reaction on initial pH of reaction mixture, $|Cu^{2+} + P_2O_7^{4-}| = 0.1$ M, $n = 1$

Initially adjusted pH	Heterogeneous reaction		
	Induction time	Duration of reaction	Yield, %
3.0	6.6 days; 8.2 days (7.4 ± 1.1)	12 days; 16 days (14 ± 2.8)	97; 100 (98 ± 2)
3.2	5.0 days; 5.7 days (5.3 ± 0.5)	7 days; 10 days (8.5 ± 2.1)	94; 99 (96 ± 3)
3.5	2.5 days; 3.0 days (2.7 ± 0.3)	5 days; 8 days (6.5 ± 2.1)	95; 98 (96 ± 2)
3.7	17 h; 24 h (20 ± 5)	4 days; 4 days	94; 95 (94 ± 1)
4.0	16 h; 18 h; 23 h; 24 h (20 ± 4)	1.1 days; 1.2 days; 1.5 days; 1.6 days (1.3 ± 0.2)	48; 48; 50; 55 (50 ± 3)
5.0	3 h; 3 h	19 h; 22 h (20.5 ± 2.1)	37; 41 (39 ± 3)
5.5	3 h; 3 h		21; 23 (22 ± 1)
6.0			0; 0

More detailed investigation was performed in the pH range 3.7 – 6.0. When the initial pH was adjusted to 3.7, the precipitates obtained after 15 min and 2 h mixing, were semiamorphous. After 4 h of mixing clear peaks of the single salt $Cu_2P_2O_7 \cdot 5H_2O$ emerge in diffractograms of precipitates, and remain virtually unchanged for 16-22 hours of mixing. After that, heterogeneous reaction began. As soon as pH decreased by as little as 0.1, a small clear peak at d = 9.42 Å emerged, which corresponds to $Cu_3(NH_4)_2(P_2O_7)_2{\cdot}3H_2O$ *Dimorph B*. After that, the intensity of single salt peaks decreased, and the less prominent next peaks of double salt *Dimorph B* emerged. The longer the mixing times were, the greater was their intensity. After 4 days, the heterogeneous reaction was complete with only peaks characteristic to *Dimorph B* visible in diffractograms, sharp and clear. Therefore, in this respect $CuSO_4$ – $(NH_4)_2P_2O_7$ – H_2O system behaves in a same way the system $CuSO_4$ – $K_4P_2O_7$ – H_2O does. Namely, if reaction proceeds at a relatively low initial pH values, the peaks of double salt *Dimorph A* are invisible in diffractograms. Apparently *Dimorph A* transits to *Dimorph B* at a rate so high, it makes the detection of *Dimorph A* impossible.

The results of chemical analysis of precipitates (table) show that at first (after 15min and 2 h of interaction) precipitates contain high amounts of NH_4^+, which under longer mixing times rapidly diminishes, and the ratio $|NH_4^+| / |Cu^{2+}|$ drops below 0.04. However, as soon as pH begins to decrease, the $|NH_4^+| / |Cu^{2+}|$ ratio begins to increase and reaches a value close to 0.67. If the initial pH was set to 4.0, the precipitates remained semiamorphous for approx. 1 day, which is substantially longer than in the case of initial pH of 3.7. The heterogeneous reaction began approximately after one day of mixing and the peaks of double salt *Dimorph B* emerged, its intensity progressively increased. The yield of heterogeneous reaction, however, substantially decreased to approx. 50 %. The amount of NH_4^+ in recipitate obtained at initial pH set to 4.0 was substantially higher than in precipitates obtained at initial pH set to 3.7.

10 table. Dependence of pH and $|NH_4^+| / |Cu^{2+}|$ in precipitates on the duration of mixing. $|Cu^{2+} + P_2O_7^{4-}| = 0.1$ M and $n = 1$.

Initial pH	Duration of mixing	pH of reaction mixture	$\|NH_4^+\| / \|Cu^{2+}\|$
3.7	15 min	3.7	0.20; 0.21
	2 h	3.7	0.08; 0.10
	4 h	3.69	< 0.04; < 0.04
	16 h	3.72	< 0.04; < 0.04
	18 h	3.60	< 0.04
	24 h	3.18	0.20
	30 h	3.00	0.29
	36 h	2.82	0.34
	48 h	2.33	0.52
	72 h	2.18	0.64
4.0	15 min	4.0	0.28
	2 h	4.0	0.18
	18 h	4.01	0.22
	20 h	3.95	0.26
	30 h	3.18	0.54
	120 h	2.55	0.65

5.0	15 min	5.0	0.46
	2 h	5.0	0.24
	4 h	4.60	0.32
	8 h	4.54	0.40
	12 h	4.13	0.63
	48 h	4.08	0.62
6.0	15 min	6.0	0.46
	2 h	6.0	0.61
	6 h	6.0	0.64
	24 h	6.01	0.63
	120 h	5.97	0.64

The initial pH of 5.0 results in the heterogeneous reaction beginning substantially earlier and continuing for the shorter period of time than in the previous experiment. The peaks corresponding to single salt were invisible in diffractograms. Only traces of the fine crystalline double salt *Dimorph A* were detected. The yield of heterogeneous reaction was ~40 %, which is lower than the yields obtained in the previous experiments at lower pH values. The amounts of NH_4^+ ions in precipitates were substantially higher.

The yield of heterogeneous reaction substantially decreased to 22 %, when initial pH 5.5 was adjusted. Under the initial pH 6.0 the pH remained constant (with detection limits) which means, that the heterogeneous reaction does not proceed.

Role of ammonium ions on precipitate formation.

The investigation was performed at $|Cu^{2+} + P_2O_7^{4-}| = 0.1$ M, $n = 1$ and initial pH set to 3.7. 4.0 M $(NH_4)_2SO_4$ solution was poured into reaction mixture in order to increase NH_4^+ ion concentration from 0.2 M to 5.0 M. A high concentration of NH_4^+ ions in solution substantially impact on processes proceeding in the system. In the absence of $(NH_4)_2SO_4$, fine crystalline single salt forms after 4 h of interaction, and heterogeneous reaction begins after one day and continues for 4 days. The only product of the reaction is *Dimorph B*, as the peaks corresponding to *Dimorph A* were absent in the diffractograms. In the presence of the $(NH_4)_2SO_4$ however, heterogeneous reaction began much earlier (after ~15 min) and continued for much shorter period of time (after ~1 h). The yield of the reaction decreased from near100 % to 53 ± 3 %.

5. A comparison of precipitate formation in the systems $CuSO_4 – K_4P_2O_7 – H_2O$ and $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$

The precipitate formation in the systems $CuSO_4 – K_4P_2O_7 – H_2O$ (henceforth K-system) and $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$ (henceforth NH_4-system) occurs in a rather similar manner: semiamorphous voluminous precipitates → $Cu_2P_2O_7{\cdot}5H_2O$ → $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ *(Dimorph A)* → $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ *(Dimorph B)*, where Kat = K or NH_4.

The similarities between the XRD patterns and vibrations spectra of copper–ammonium and copper–potassium *Dimorph B's* imply that they are isostructural. Likewise, the FTIR spectra of both compounds are very similar. These data indicate, that energy states of diphosphate ions in those two compounds are very similar.

Dimorph A in NH_4-system transits to *Dimorph B* after substantially shorter time than it does in K-system. This transformation does not happen continuously, however. For a while, only the peaks corresponding to *Dimorph A are* visible in diffractograms, and after some time a rather rapid polymorphous transformation occurs. Apparently, polymorphous transformation is an autocatalytic reaction, as after the addition of a small amount of *Dimorph B* into reaction mixture the transformation occurs substantially faster.

In the NH_4-system heterogeneous reaction begins and finishes at substantially shorter times than it does in the K-system. The yield of the reaction begins to decrease in NH_4-system at smaller pH than in K-system.

CONCLUSIONS

1. At least three poorly soluble compounds can be formed in the system $CuSO_4$ – $K_4P_2O_7$ – H_2O: a single salt $Cu_2P_2O_7{\cdot}5H_2O$ and two dimorph's $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$. A known form of $Cu_3K_2(P_2O_7)_2{\cdot}3H_2O$ (*Dimorph A*) transforms into a novel *Dimorph B*, which has a different structure. The formation of the compounds substantially depends on the conditions of experiment. The similarities between the XRD patterns and vibrations spectra of copper–ammonium and copper–potassium *Dimorph's B* imply that they are isostructural, with both of them being monoclinic.

2. The vibration spectra indicate a bent P–O–P bridge angle for all of these compounds. The values of this angle for copper–potassium and copper–ammonium salts as well as for $Cu_2P_2O_7{\cdot}5H_2O$ are relatively low and vary within a narrow range (123.1 – 127.1°). As the result of transformation of *Dimorph A* to *Dimorph B* the P–O–P angle becomes slightly more obtuse.

3. Apparently, during the transformation, the spatial orientation between the PO_4 tetrahedrons changes significantly, which explains the major differences in their spectra.

4. Under permitting conditions a double salt forms 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 publication.

The rate, duration and yield of heterogeneous reaction substantially depend on the pH of the reaction mixture, $[Cu^{2+} + P_2O_7^{4-}]$ and n $([P_2O_7^{4-}] / [Cu^{2+}])$. At a relatively low pH the induction time is high, the rate of this reaction is low, duration is long, the yield of this reaction is maximal (nearby 100 %, when $[Cu^{2+} + P_2O_7^{4-}] = 0.1$ M). At increased pH values, the induction time, the yield and duration of heterogeneous reaction diminish. At pH ≥ 6 heterogeneous reaction does not proceed, although the product of interaction is a double salt.

5. Heterogeneous reaction progress in the $CuSO_4$ – $(NH_4)_4P_2O_7$ – H_2O system in a similar manner: semiamorphous voluminous precipitates → $Cu_2P_2O_7{\cdot}5H_2O$ → $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ (Dimorph A) → $Cu_3Kat_2(P_2O_7)_2{\cdot}3H_2O$ (Dimorph B), where Kat = K or NH_4. Under the analogous reaction conditions, there are marked differences between behavior of NH_4^+ and K^+ ions in the $CuSO_4$ – $Kat_4P_2O_7$ – H_2O system. In the case of NH_4^+, heterogeneous reaction and the transition from *Dimorph A* to *Dimorph B*

happens much faster than it does in the case of K^+. The yields of heterogeneous reaction in the case of K^+ are much higher at low pH values than they are in case of NH_4^+.

List of publikation

1. A. Pigaga, O. Timofejeva, Quantitative Representation of Tananaev‘s Effect, Rus. J. Appl. Sci., 2004, 77 (7).
2. A. Pigaga, O. Timofejeva, V. Pakštas, R. Butkienė, J. Vaičiūnienė, Formation of barely soluble compounds in the system CuSO4 – K4P2O7 – H2O, Chemija, 1 (2009) 19 – 26.
3. A. Pigaga, O. Timofejeva, V. Pakštas, R. Butkienė, J. Vaičiūnienė, A novel copper potassium diphosphate – dimorphic $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$, Chemija, 1 (2009) 27 – 32.

REZIUMĖ

Naudojant *IR*-spektrometrijos, rentgenofazinės analizės, atominės absorbcinės spektroskopijos, kolorimetrijos analizės metodus buvo ištirta sistemose $CuSO_4$ – $K_4P_2O_7$ – H_2O ir $CuSO_4$ – $(NH_4)_4P_2O_7$ – H_2O susidarančių mažai tirpių junginių sudėtis, jų susidarymo dėsningumai ir vykstančios reakcijos, įvairių veiksnių įtaką nuosėdų sudėčiai ir struktūrai. Nustatyta, kad sistemoje $CuSO_4$ – $K_4P_2O_7$ – H_2O, be jau žinomų mažai tirpių junginių (paprastosios druskos $Cu_2P_2O_7 \cdot 5H_2O$ ir dvigubosios druskos $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$), susidaro ir naujas mokslinėje literatūroje neaprašytas junginys (*Dimorfas B*), dvigubajai druskai patiriant polimorfinį perėjimą. Polimorfinio perėjimo trukmė labai priklauso nuo pH ir reaguojančių jonų koncentracijų. FTIR duomenų analizė parodė, kad difosfato jonų energetinė būsena Cu – K ir Cu – NH_4 *Dimorfuose B* panaši. Jų rentgenogramos yra panašios, tikėtina, kad šie junginiai – izostruktūriniai, jų kristalinės gardelės tipas – monoklininis. Naudojant Lazarevo lygtį, bei Rulmonto priklausomybę buvo apskaičiuoti Cu – K ir Cu – NH_4 *Dimorfų A* ir *B* bei paprastosios druskos P – O – P kampai, gauta, kad jie mažai keičiasi siaurame 123,1 – 127,1 ° intervale.

Nustatyta, kad dviguboji druska susidaro iš paprastosios, vykstant heterogeninei reakcijai:

$$3Cu_2P_2O_7 \cdot 5H_2O\downarrow + H_2P_2O_7^{2-} + 4K^+ \rightarrow 2Cu_3K_2(P_2O_7)_2 \cdot 3H_2O\downarrow + 2H^+ + 9H_2O.$$

Mokslinėje literatūroje tokia reakcija neaprašyta jokiai difosfatų sistemai, jos tyrimo duomenys yra nauji. Taip pat nustatyta, kad heterogeninės reakcijos indukcijos laikas, greitis, trukmė ir išeiga labai priklauso nuo reakcijos mišinių pH, $|Cu^{2+} + P_2O_7^{4-}|$ ir n ($|P_2O_7^{4-}| / |Cu^{2+}|$).

Tyrimai parodė, kad heterogeninė reakcija vyksta ir sistemoje $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$. Nuosėdų formavimasis $CuSO_4 – K_4P_2O_7 – H_2O$ ir $CuSO_4 – (NH_4)_4P_2O_7 – H_2O$ sistemose vyksta panašiai, susidarant: dalinai amorfinėms didelio tūrio nuosėdoms → paprastajai druskai $Cu_2P_2O_7 \cdot 5H_2O$ → dvigubajai druskai $Cu_3(Kat)_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorfas A*) → dvigubajai druskai $Cu_3(Kat)_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorfas B*), kur Kat = K arba NH_4.

CURRICULUM VITAE

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