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SYNTHESIS OF COPPER COMPOSITES CONTAINING MALEIC ACID

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Abstract

The paper presents the results of a study of the possibility of the formation of maleate π-complexes of atomic copper in an aqueous solution. Taking into account the existing equilibria, the conditions for the synthesis of an organometallic dispersion by cementation with metallic zinc of a $CuSO_4$ solution containing maleic acid have been optimized. The composition of the powders was determined using energy dispersive spectroscopy, thermogravimetry, and complexometry. It was found that at a molar ratio of reagents Zn: $Cu^{2+} < 0.5$, only the monovalent copper complex $[Cu(C_4O_4H_3)(H_2O)]$ was formed, while at molar ratios Zn : Cu^{2+} between 0.5 and 1, obtained composite mixtures consisted of $[Cu(C_4O_4H_3)(H_2O)]$, H_2O (adsorbed), and Cu (metal). The formation of the π-complex of atomic copper $[Cu(C_4O_4H_4)]$ was not recorded. Due to the heterogeneity of the cementation process, the produced composites at Zn : $Cu^{2+} \geq 0.5$ are inhomogeneous. The copper content within samples produced at Zn : Cu^{2+} = 1 varies widely: from 47 wt. % up to 74 wt. %.

Keywords: microdispersion of copper; zinc cementation; maleic acid; energy dispersive spectroscopy; thermogravimetry.

СИНТЕЗ МІДНИХ КОМПОЗИТІВ, ЯКІ МІСТЯТЬ МАЛЕЇНОВУ КИСЛОТУ

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Анотація

В роботі представлені результати дослідження можливості утворення у водному середовищі малеїнатних π-комплексів атомарного купруму. З урахуванням існуючих рівноваг оптимізовано умови синтезу металоорганічної дисперсії цементацією металічним цинком розчину $CuSO_4$, що містить малеїнову кислоту. З використанням енергодисперсійної спектроскопії, термогравіметрії і комплексонометрії визначено склад порошків. Встановлено, що при мольному співвідношенні реагентів Zn : $Cu^{2+} < 0.5$ виділяється комплекс $[Cu(C_4O_4H_3)(H_2O)]$, а при Zn : $Cu^{2+} \geq 0.5$ – композитна суміш $[Cu(C_4O_4H_3)(H_2O)]$, H_2O (адсорбована), Cu (метал). Утворення π-комплексу атомарного купруму $[Cu(C_4O_4H_4)]$ не зафіксовано. У зв'язку з гетерогенністю процессу цементації виділяються неоднорідні композити, в яких вміст купруму в межах зразку коливається в широких межах: від 47 ваг. % до 74 ваг. %.

Ключові слова: мікродисперсія міді; цементація цинком; малеїнова кислота; енергодисперсійна спектроскопія; термогравіметрія

СИНТЕЗ МЕДНЫХ КОМПОЗИТОВ, СОДЕРЖАЩИХ МАЛЕИНОВУЮ КИСЛОТУ

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Аннотация

В работе представлены результаты исследования возможности образования в водной среде малеинатных π-комплексов атомарной меди. С учетом существующих равновесий оптимизированы условия синтеза металлорганической дисперсии цементацией металлическим цинком раствора $CuSO_4$, содержащего малеиновую кислоту. С использованием энергодисперсионной спектроскопии, термогравиметрии и комплексонометрии определен состав порошков. Установлено, что при мольном соотношении реагентов Zn : $Cu^{2+} < 0.5$ выделяется только комплекс одновалентной меди $[Cu(C_4O_4H_3)(H_2O)]$, а при Zn : $Cu^{2+} \geq 0.5$ – композитная смесь $[Cu(C_4O_4H_3)(H_2O)]$, H_2O (адсорбированная), Cu (металл). Образование π-комплекса атомарной меди $[Cu(C_4O_4H_4)]$ не зафиксировано. В связи с гетерогенностью процесса цементации выделяемые композиты неоднородны – содержание меди в пределах образца колеблется в широких пределах: от 47 мас. % до 74 мас. %.

Ключевые слова: микродисперсия меди; цементация цинком; малеиновая кислота; энергодисперсионная спектроскопия; термогравиметрия.

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Introduction

Our quantum chemical analysis of the interaction of the reduction products of Cu^{2+} ions with unsaturated organic acids showed [1, 2] that both Cu^{+} ions or Cu^{0} atoms are capable of forming thermodynamically stable complexes, in which the central atom is bound to ligands not only with σ-bonds, but also with π-bonds. As is known, it is the dπ-pπ-binding action that allows the existence of complexes even with a formally zero-valent central atom. Classic examples of this type of substances are carbonyl complexes of nickel [3, 4] or other transition metals [5–7]. However for copper, there is information only about π-complexes of Cu^{+} ions, both in the dissolved forms [8] and in the form of crystalline compounds [9–13]. The existence of π-complexes of Cu^{0} atoms with organic unsaturated acids, predicted theoretically [2], has not yet been confirmed in practice. At the same time, these substances can be considered as promising stabilizers of copper nanodispersions, which have recently been increasingly used in various industries [14–18].

We attempted to synthesize compounds of the general form $[Cu^{0}(\pi\text{-}L)]$ by reduction of Cu^{2+} ions in the presence of maleic acid (H_2M) either electrochemically, or chemically with metallic zinc [19]. It was found that during electrochemical reduction, a fine-crystalline copper deposit is precipitated on the cathode, containing up to 98 wt. % metal and only about 2% of a non-metallic component. When acidic solutions of 0.1 M $CuSO_4$, and 0.1 M H_2M are treated with zinc powder at molar ratio $Zn : Cu^{2+} < 0.5$, organometallic dispersions are formed, in which the content of a non-metallic component was about 60 wt. %. Elemental analysis of these substances indicated that they all consist of hydrogenmaleate monoaquocopper(I) complex, $[Cu(C_4O_4H_3)(H_2O)]$. However, since the energy dispersive spectroscopy method used for the analysis does not measure hydrogen concentration, the analyte could be identified either with the monovalent copper complex $[Cu^{+}(C_4O_4H_3^{-})]$ or with the zero-valent copper complex $[Cu^{0}(C_4O_4H_4)]$. Moreover, the analyte might be a mixture of both Cu^{+} and Cu^{0} containing substances.

It was of interest to study the effect of preparative synthesis conditions on the composition of the organometallic dispersions, focusing primarily on component analysis.

Materials and methods

To optimize the synthesis conditions for the organometallic dispersions, the compositions of Cu^{2+} complexes in solutions with equimolar concentrations of 0.1 M $CuSO_4$, and 0.1 M H_2M were calculated as a function of the pH value. The range of pH 0–4 chosen by us did not require taking into account the equilibria with the participation of hydroxide ions.

In the calculations performed in Mathcad 15 [20, 21], the dissociation constants of maleic acid of ($pK_1 = 1.92$, $pK_2 = 6.23$) [22] and its complexes $[Cu(HM)]^{+}$ and $[Cu(M)]$ [23] of ($pK_1 = 2.88$) and ($pK_2 = 4.90$) were used, respectively. Fig. 1 shows the obtained molar ratios of copper maleate or hydrogen maleate complexes at pH between 0 and 4.5.

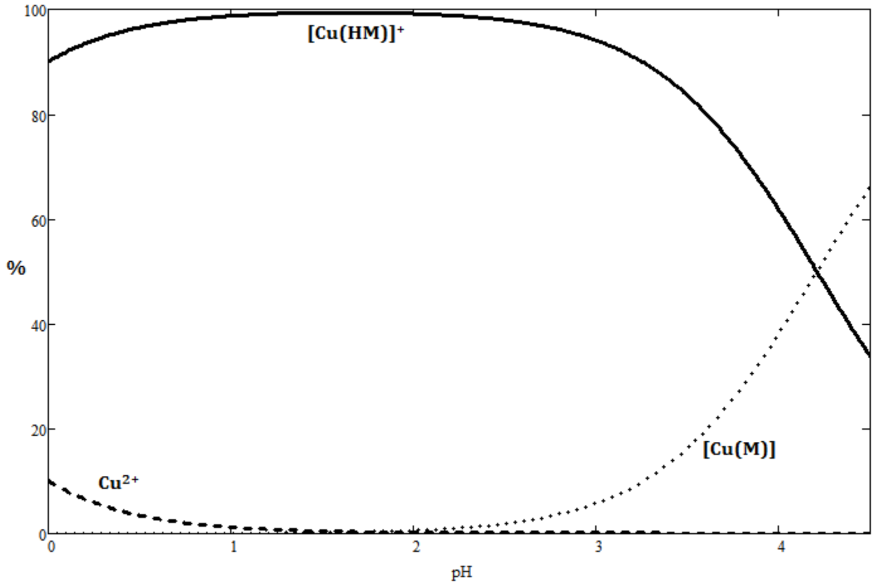


Fig. 1. Speciation curves of Cu(II) complexes with maleic acid

As can be seen from this figure, the best conditions for the synthesis of Cu^+ or Cu^0 complexes with hydrogen maleate ion are in solutions at pH = 1.5 – 2, where almost 100 % Cu^{2+} ions are bound into the $[Cu(HM)]^+$ complex. The $[Cu(HM)]^+$ complex in a noticeable amount can exist both at pH < 1.5 or > 2. Thus, at pH = 4, about 60 % of Cu^{2+} ions are bound into the $[Cu(HM)]^+$ complex, and at pH = 0.5 about 96 %. Therefore, the $[Cu(HM)]^+$ complex will dominantly react with zinc in solutions with pH = 2 ± 1.

Further, it was necessary to take into account the effect of the molar ratio of the Cu^{2+} (added as $CuSO_4$ and H_2M in aqueous solution) and Zn reagents on the composition of the reduction product. In reaction of one-electron reduction of Cu^{2+} ions by metallic Zn:

$$2[Cu(HM)]^+ + Zn = 2[Cu(HM)] + Zn^{2+} \qquad (1)$$

the Zn : Cu^{2+} molar ratio is 0.5. Since, in addition to Cu^{2+} ions, H_3O^+ ions are also oxidizing agents for zinc, we chose the initial molar ratio Zn : Cu^{2+} = 0.2, which guarantees the completion of the metallic Zn quantitative oxidation (1).

To assess the contribution of further reduction of [Cu(HM)] complexes with zinc to zero-valent copper by the reaction

$$2[Cu(HM)] + Zn = 2[Cu(HM)]^- + Zn^{2+} \qquad (2)$$

we gradually changed the Zn : Cu^{2+} molar ratio to 1.

Note that the above reactions (1) and (2) are schematic. They lack water, which is in the internal coordination sphere of the complexes.

The reactions of synthesis of organometallic powders were carried out in open glass beakers using magnetic stirrers. After mixing separately prepared 25 ml of 0.1 M $CuSO_4$ with 25 ml of 0.1 M H_2M in a beaker, the acidity of the solution was adjusted with aqueous NaOH (1 M) while being monitored with an EV-74 ion meter (Gomel, Belarus). A predetermined amount of zinc powder, 99.0 % pure, particle sizes of 3.0–4.5 μm (grade ПЦ1, Germany) was gradually added to the prepared solution in the duration of 5 minutes with active stirring. The formed precipitates were filtered off, washed consecutively with aqueous solution of maleic acid (pH = 1) until there were no Zn^{2+} ions in the filtrate and then with distilled water, after which they were dried at 25 °C to constant weight.

The total copper content in the obtained products was determined using the complexometric method [24]. For this, their weighed portions (200 mg) were dissolved in 5 mL of 30 wt. % nitric acid, the liquid quantitatively transferred into 50 ml volumetric flasks and then further diluted with distilled water. Aliquots (10 ml) of these solutions were each combined in three separate beakers with 50 ml of distilled water, 5 ml of ammonia solution (25 wt. %) and the indicator murexide, after which titration was carried out with a solution of Trilon B (0.1 N). The average titration volume was calculated titrant volumes in these three parallel experiments. The determination error did not exceed 0.5 %.

Thermal analysis of the obtained micropowders was carried out on a Simultaneous Thermal Analyzer (STA) 6000 (PerkinElmer, USA), with recording of TG and DTA dependences. The standard was Al_2O_3. The temperature sweep rate was 10 °C/min in the range from 20 °C to 850 °C.

The elemental composition of individual powder fractions was determined by energy dispersive spectroscopy using a HITACHI SU5000 (Japan) electron microscope (thanks to Prof. Dr. Ibrahim Yilmaz and Dr. FarukÖzel, KaramanogluMehmetbey University, Karaman, Turkey, for their help in spectral and microscopic studies).

The reagent solutions were prepared in distilled water from reagent grade $CuSO_4 \cdot 5H_2O$, NaOH, or analytical grade maleic acid.

Results and discussions

Fig. 2 shows the effect of the molar ratio of reagents (Zn : Cu^{2+}) on the total copper content in the resulting products.

This dependence can be separated into two regions. In the first, in the Zn : Cu^{2+} molar ratio < 0.5, the copper content is stable: 32.5 ± 0.5 wt. % (within the error of the analytical method, which corresponds to 32.31 wt. % copper in $[Cu(C_4O_4H_3)(H_2O)]$. In the second region corresponding to Zn : Cu^{2+} molar ratios from 0.5 to 1.0, the copper content gradually increases from 33.9 to 56.6 wt. %. The increase of copper content in the precipitated reaction products in that range was accompanied by changes in their color: light yellow-green of precipitates formed at Zn : Cu^{2+} molar ratios < 0.5 has acquired a brown tint at the Zn : Cu^{2+} molar ratios ≥ 0.5; the tint gradually increased with the increase of the Zn : Cu^{2+} molar ratio.

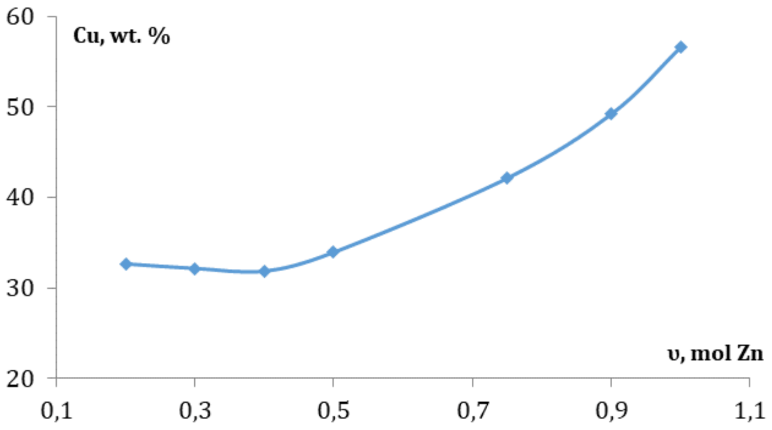
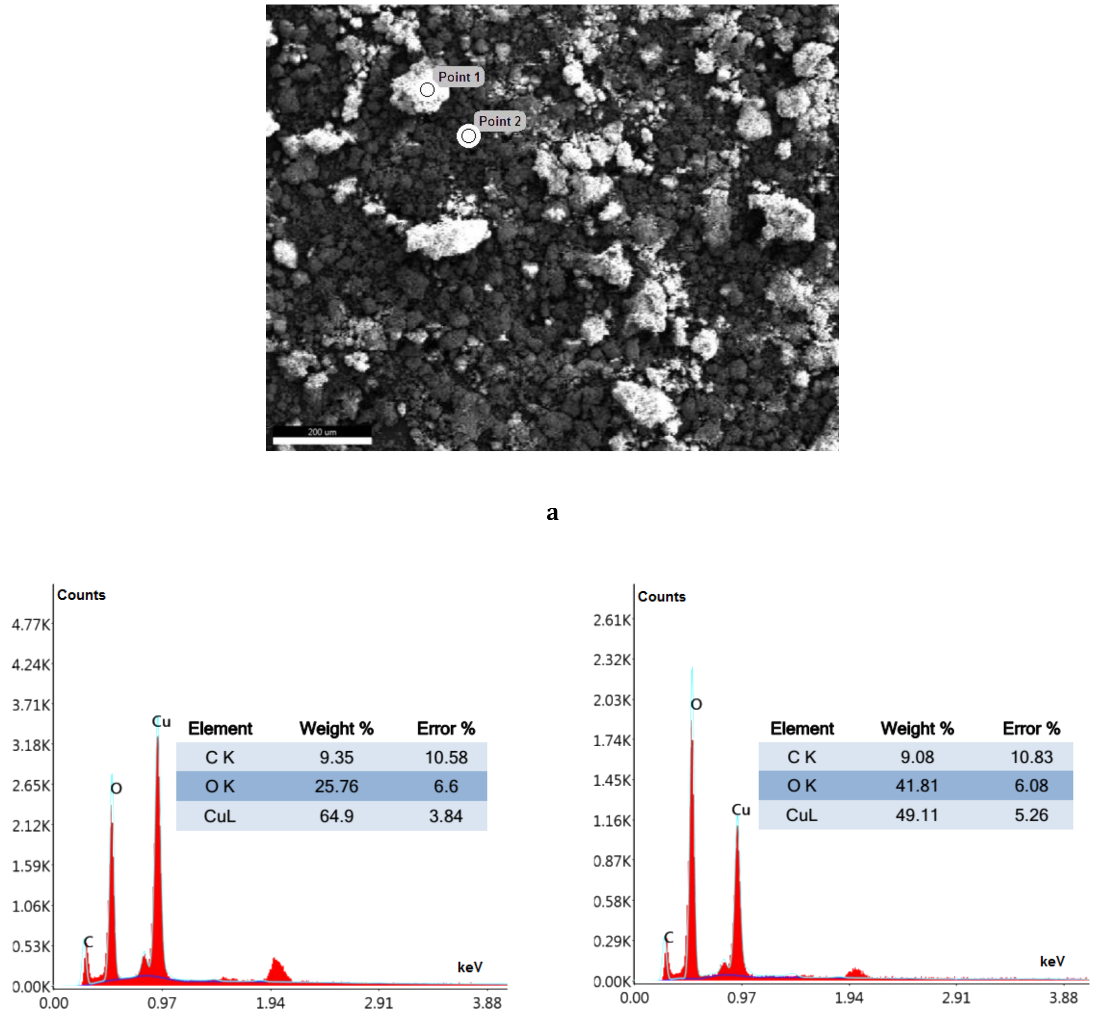


Fig. 2. Dependence of the copper content in the organometallic dispersion on the amount of moles of zinc (ν) (added as powder) and $CuSO_4$ in solution

It is logical to come to the conclusion that at the Zn : Cu^{2+} molar ratios < 0.5, only reaction (1) has occurred and the [Cu(HM)] complex formed, while at the Zn : Cu^{2+} molar ratios ≥ 0.5, reaction (2) also started to take place, generating zero-valent copper.



Element	Weight %	Error %
C K	9.35	10.58
O K	25.76	6.6
CuL	64.9	3.84

Element	Weight %	Error %
C K	9.08	10.83
O K	41.81	6.08
CuL	49.11	5.26

b

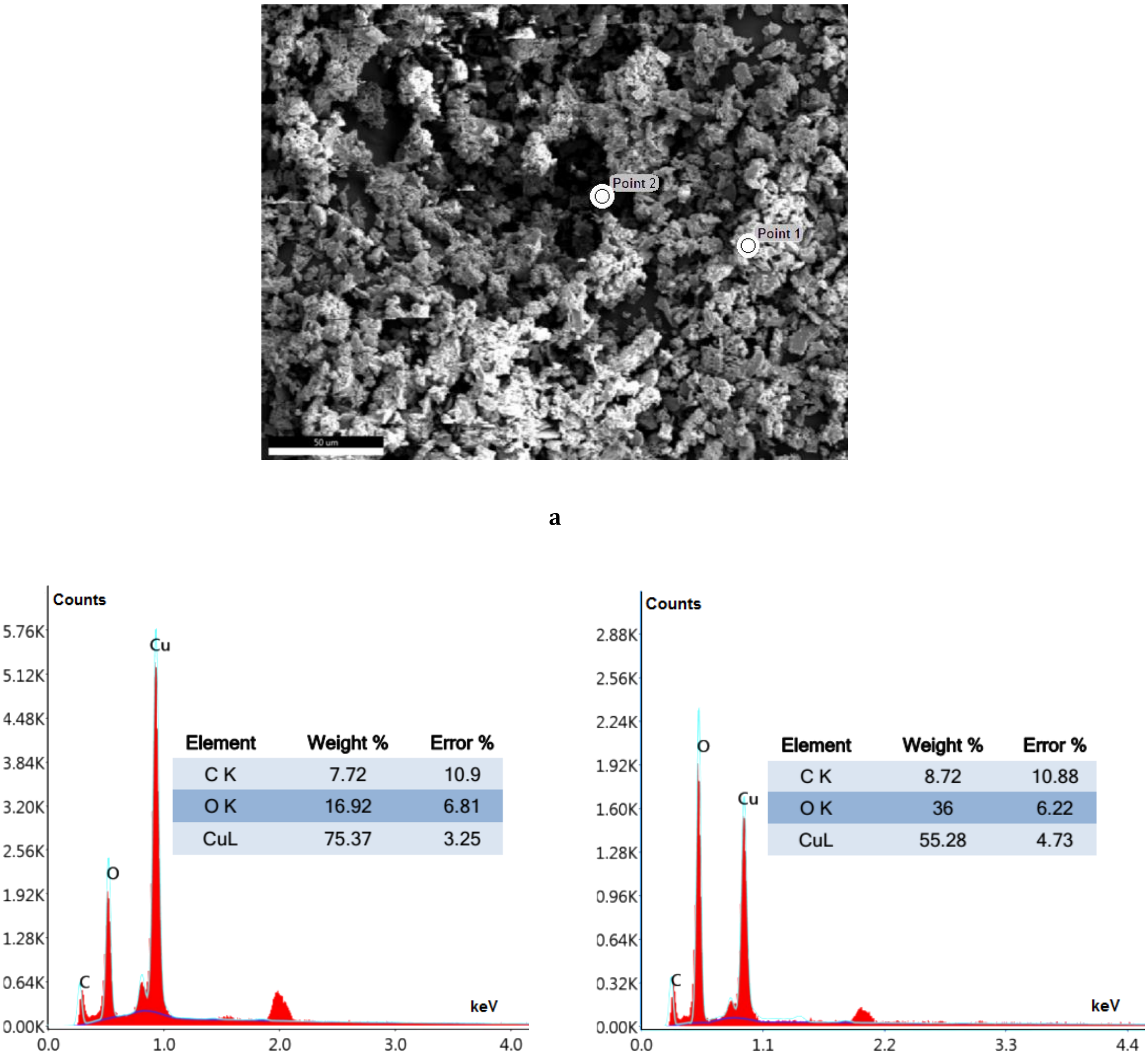
c

Fig. 3. a – Electron microscopy image of Sample No. 1; b – Analysis results at the Point 1; c – Analysis results at the Point 2

At the same time, if copper atoms were bound into the π-complex [Cu(π-H_2M)], the molecular weight of which differs from that of the [Cu(π-HM)] complex by only one atomic mass unit, the copper content in the precipitate would not be practically affected. In fact, we observe a gradual increase in copper content with the increase of the Zn : Cu^{2+} molar ratio from 0.5 to 1. Therefore, the results obtained unambiguously indicate that zero-valent copper in the precipitate is not in the form of a π-complex, but in the state of metallic Cu. This means that reaction (2) ends with the decomposition of the hypothetical intermediate structure:

$$[Cu(HM)]^- \rightarrow Cu^0 + HM^-. \qquad (3)$$

To further investigate the component composition of the synthesized powders, we used the energy dispersive spectroscopy of samples synthesized in the same experiment at a molar ratio of the Zn : Cu^{2+} = 1. Sample No. 1 was separated from the slurry in 1 hr., sample No. 2 in 24 hr.



a

Element	Weight %	Error %
C K	7.72	10.9
O K	16.92	6.81
CuL	75.37	3.25

b

Element	Weight %	Error %
C K	8.72	10.88
O K	36	6.22
CuL	55.28	4.73

c

Fig. 4. a – Electron microscopy image of Sample No. 2; b – Analysis results at the Point 1; c – Analysis results at the Point 2

The results of the elemental microanalysis of brown powders of Samples No. 1 and No. 2 shown in Fig. 3 and Fig. 4 indicate the almost identical level of the carbon component in the tested areas (7.72 ÷ 9.35 wt. % (with 10 % determination error), and a wide variation in levels of oxygen (16.92 ÷ 41.81 wt. %) and copper (49.11 ÷ 75.37 wt. %).

It was assumed therefore that in the resulting dark powders (Samples No. 1 and 2), in addition to the $Cu(C_4O_4H_3)$ complex, which has a fixed ratio of elements, there are substances whose amounts not only vary widely within the same sample but also depend on the synthesis duration. It is logical to primarily consider water and metallic copper as those substances.

Based on this reasoning, we calculated the composition of brown powders based on three substances: $Cu(C_4O_4H_3)$, H_2O, and Cu. The calculation algorithm included two steps. First, the amounts of oxygen, hydrogen and copper in the $Cu(C_4O_4H_3)$ compound were calculated based on the carbon content. The resulting quantities of chemically bound copper or oxygen were subtracted from those obtained by analysis. Second, the remaining quantities of oxygen and copper were assigned to water and metallic copper, respectively. We did not take into account the possibility of partial oxidation or hydrolysis of copper moieties to corresponding oxides or hydroxides. The results obtained are summarized in the Table 1.

As can be seen from the table, the heterogeneity of reactions (1) and (2) affects the extent of the reduction of copper ions with zinc metal in separate areas (points) within the same sample; thus, in Sample No. 1 (one hr. synthesis), the copper content in two analyzed points 1 and 2 was 47.0 wt. % or 63.1 wt. %, respectively. We assume also that in the zone remote from the zinc particles, less metallic copper is formed, and more in the proximity zone. Lighter particles (points No. 1, Fig. 4) are characterized by a lower copper content, and darker ones (points No. 2, Fig. 4) – by higher.

As for water, it is obviously necessary to distinguish two forms in which it could be present in the reaction products: chemically bound in an aqua complex or adsorbed by hydrophilic powder particles.

To determine the amount of adsorbed water, we subtracted the amount of water bound into the complex $[Cu(C_4O_4H_3)(H_2O)]$ from its total in samples. As can be seen from the table, in the areas enriched in metallic copper, the amount of adsorbed water drops sharply: in the first sample, from 29.3 wt. % to 11.6 wt. %, in the second – from 23.1 wt. % up to 5.1 wt. %, which is obviously due to the non-hygroscopicity of the metal. In general, the effect of metallic copper on the hygroscopicity of the composite is well described by a second degree polynomial (Fig. 5). Calculations of the yield of the reaction products can serve as an additional confirmation of the version about the formation of metallic copper rather than the $[Cu\ (\pi\text{-}C_4O_4H_4)]$ complex. Using the data on the composition of sample No. 2 from the Table 1, we determined the amount of zinc consumed for the synthesis of the mixture to be 64.4 wt. % Cu(metal), 30.5 wt. % $[Cu(C_4O_4H_3)(H_2O)]$, and 5.1 wt. % H_2O. This value was 97 % of the weight of the introduced zinc, so 3 % zinc apparently interacted with hydrogen ions.

On the derivatogram (Fig. 6, curve 1), obtained after the sample produced at the Zn : Cu^{2+} molar ratio = 0.2 was preheated at 120 °C, three sections can be distinguished, corresponding to the processes that occur with the substance of the powder when heated. The temperature range of the section *A* (150–250 °C) is comparable to the temperature of dehydration of copper aqua complexes [25]. In sections *B* and *C*, thermal decomposition of the dehydrated complex $[Cu(C_4O_4H_3)]$ occurs.

If we assume that the final decomposition product of the $[Cu(C_4O_4H_3)(H_2O)]$ complex is CuO, then the weight loss of the initial sample should be −62.9 wt. %. According to the Curve 1 in Fig. 6, the total weight loss at the 100 % conversion is −59.1 wt. %. It turned out that this value is in good agreement with another possible cracking product, copper carbide CuC_2, for which the theoretical value of Δm is −59.2 wt. %.

Fig. 6 shows also the TG dependence for the powder obtained at a molar ratio of Zn : Cu^{2+} = 1 (Curve 2). Comparison of the Curve 2 in Fig. 6 with the Curve 1 for the complex $[Cu(C_4O_4H_3)(H_2O)]$ confirms our assumption regarding the product being a mixture: the maximum decrease in the sample mass is not −59.1 wt. % but −35.8 wt. % and is proportional to the estimated content of $[Cu(C_4O_4H_3)(H_2O)]$ in the mixture.

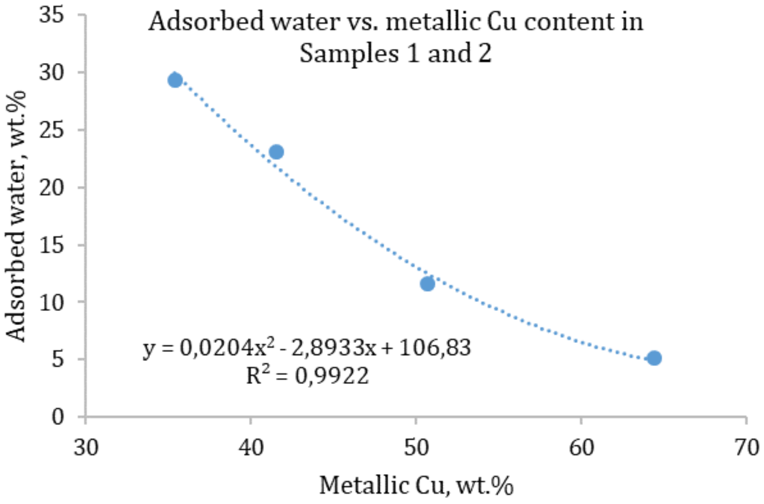


Fig. 5. Dependence of calculated values of adsorbed water vs. metallic Cu in Samples 1 and 2

Table 1

The results of calculating the composition of powder samples by components based on elemental microanalysis (Fig. 3, 4)

No.	Analysis points	Content of components, wt. %					
		$Cu(C_4O_4H_3)$	Cu		H_2O		
			total	metal	total	chem. bound	ads.
1	1	32.5	47.0	35.4	32.1	2.8	29.3
	2	34.8	63.1	50.7	14.5	2.9	11.6
2	1	32.6	53.1	41.5	25.9	2.8	23.1
	2	28.1	74.4	64.4	7.5	2.4	5.1

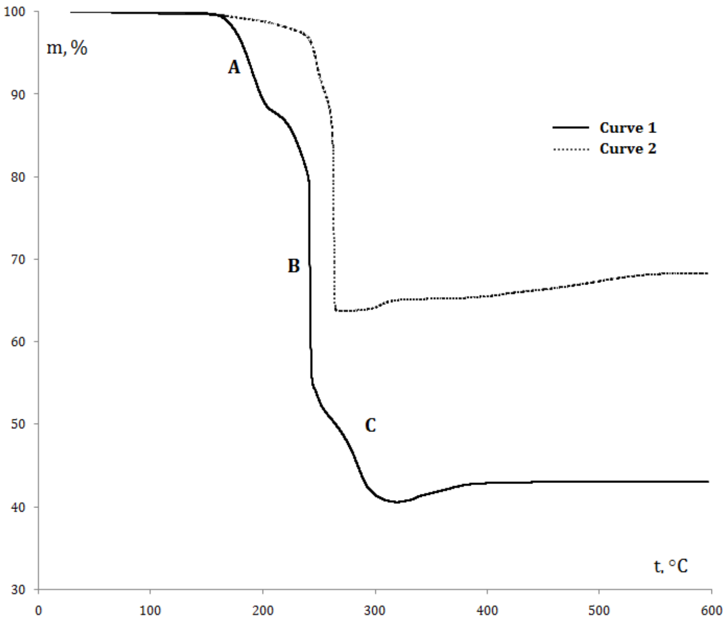


Fig. 6. TG-dependences of powders obtained at a molar ratio Zn : Cu^{2+} = 0.2 (1) and 1.0 (2)

As can be seen from columns Cu(metal) and H_2O(ads.) of the Table 1 and graphic representation of this dependence on Fig. 5, the higher the content of metallic copper in the tested areas, the lower the amount of adsorbed water. This gradually decrease of adsorbed water contentcan therefore be attributed to the non-hygroscopicity of the metal.

The change in the character of the TG curve of the composite powder (Fig. 6, Curve 2) in comparison with the corresponding curve (1) for the $[Cu(C_4O_4H_3)(H_2O)]$ complex indicates that the synthesized composite is not a mechanical mixture of the complex and metallic copper.

Conclusions

It was found that when metallic zinc acts on Cu^{2+} ions in weakly acidic solutions containing maleic acid, precipitates are formed, whose composition depends on the molar ratio of the reactants. At $Zn : Cu^{2+} < 0.5$, only the $[Cu(C_4O_4H_3)(H_2O)]$ complex is released, and at $Zn : Cu^{2+} \geq 0.5$ – the composite mixture of $[Cu(C_4O_4H_3)(H_2O)]$, H_2O(adsorbed), and Cu(metal). The formation of the π-complex of atomic copper $[Cu(C_4O_4H_4)]$ was not detected. Due to the heterogeneity of the reaction, the copper content within the sample obtained at $Zn : Cu^{2+}$ molar ratio = 1.0 varies within wide limits – from 47 wt. % up to 74 wt. %.

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