
Interaction of copper(II) with cellulose pulp

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Cu(II) interaction with cellulose pulp was studied by means of polarography, AAS, and ultraviolet-visible spectrophotometry. The experiments were carried out at room temperature and at selected initial cellulose pulp pH values between 7.0–13.0.

The results show a trend of decreasing pH after hydrolysis of the pulp (2 % w/w) as well as after further addition of a Cu(II) salt (0.5 mmol/l; pCu = 3.3). The pCu in solutions with initial pH values from 7.0 to 11.0 remain in the range 3.4–3.9, implying an insignificant complexation of Cu(II). This is almost certainly caused by the relatively low solution pH (5.9–7.4) after pulp hydrolysis and Cu(II) salt addition. When the pH of these solutions was raised to 12.0, the complexing ability of the dissolved cellulose hydrolysis products rised, apparently due to the deprotonation of hydroxyl groups, and pCu reached 13.0–13.5.

When the Cu(II) salt was added directly into cellulose pulp slurry at the onset of the hydrolysis step, some of the Cu(II) ions were bound (due to adsorption and/or chemical bonds formation) to the cellulose fibres. The extent of this interaction depended on the initial pH. The bound fraction of the Cu(II) ions represented about 50–70% of the initial Cu(II) at pH 7.0 and about 90–95% at pH 13.0. The pCu in filtered solutions with initial pH values in the range 7.0–11.0 remained in the range 3.9–6.1. When the pH of any of the solutions with the initial pH values between 7.0 and 11.0 was increased to 12.0, the complexing ability rised dramatically, and pCu reached 12.9–15.1.

Key words: copper(II), cellulose pulp, cellulose alkaline cleavage, polarography, complexation

INTRODUCTION

Cellulose, perhaps the most prevalent natural polymer, is a relatively rigid-chain polymer. Its macromolecules are of a high degree of asymmetry due to the cyclic structure of constituent repeating units and the presence in each unit of strongly polar OH-groups in both primary and secondary positions [1].

Polysaccharides such as cellulose cleave during the alkali-catalysed hydrolytic reactions. In alkaline hydrolysis, the major loss of insoluble cellulose, in contrast to acidic degradation, is caused by endwise depolymerization reactions (peeling), leading to the formation of soluble carboxylic acid derivatives. The peeling reaction, which can take place even in mild alkali, is the most significant carbohydrate reaction in alkaline processes, especially in alkaline pulping [2]. The carboxylic and hydroxycarboxylic acids formed are strong ligands for the binding of heavy metal ions in alkaline media [3].

Generally, interactions between heavy metal ions, their salts or other compounds and cellulose or its derivatives can occur in mainly four ways: 1) intercalation into the cellulose matrix, 2) adsorption onto the cellulose fibres, 3) formation of chemical bonds with the reactive groups of cellulose, and 4) formation of complexes with dissolved cellulose hydrolysis products.

Cellulose derivatives such as carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) form polymer complexes with transition metal ions. In a systematic spectrophotometric study of the complexation of Cr(III) with CMC [4], it was shown that CMC (L) chelated to the metal ion according to the formula $\text{CrL}_2 \cdot 2\text{H}_2\text{O}$. The IR spectra revealed that the chelating sites of CMC were not only the carboxymethyl groups, via the ether- and carboxyl-oxygen atoms, but also the secondary hydroxyl groups [4]. The formation of CMC and HEC

complexes with Cr(III) and other transition metals (*e. g.*, Fe(III), Cu(II), Co(II) and Ni(II)) was confirmed and investigated by means of thermal and IR spectral analyses [5]. The spectra showed that the binding sites in Cr(III) and Ni(II) complexes were the ether oxygen between two ethoxyl groups and the oxygen of the hydroxyl group, while in the Co(II) and Cu(II) complexes the binding sites were the oxygen of ethoxyl groups and the primary alcoholic O atom of glucopyranose rings. These complexes would most likely exhibit an octahedral geometry with Cr(III), Ni(II), and Co(II), but a square planar configuration in the case of the Cu(II) complex [6].

The incorporation of metallic species into polymers is an active area of research. Intercalation of silver clusters [7], platinum and palladium aggregates [8] into cellulose has been studied by means of spectroscopic and microscopic methods. In addition, (Zr or Y)-oxalate-cellulose intercalation compounds were synthesized using a structurally modified cellulose with a high sorption capacity [9] and investigated using the X-ray structural analysis [10].

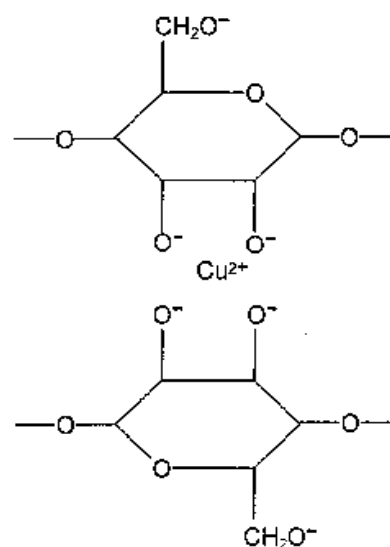
It was found that the formation of a zinc-cellulose complex during the pretreatment of cellulose improves the yield of glucose in both the enzymatic and acid hydrolysis of cellulose [11, 12]. The spectral characteristics of aqueous zinc chloride solutions (67% w/w) containing cellulose were also investigated [13]. The results suggest that zinc ion forms loose complexes with the C2 or C3 hydroxyl groups of glucopyranose. The absorption of light in the 200–220 nm range indicates the formation of these types of complexes. The presence of a calcium ion also enhances light absorption; however, the calcium ion alone cannot form a complex with cellulose [12].

The high solubility of cellulose in amine-containing Cu(II) solutions is well known, but the exact role of Cu(II) in the cellulose-dissolution process and the nature of the Cu(II) coordination are ill-defined [14]. Analytical studies have suggested that the ratio of Cu(II) to cellulose glucopyranose units in the soluble complex is 1 : 2 [15].

Several workers have studied interactions among Cu(II)-amine complexes and cellulose by adsorption of amine complexes onto fibrous cellulose. These systems have been studied with ESR spectroscopy, and well-resolved spectra have been observed after treatment of the adsorbed complexes with sodium hydroxide. The spectra have been interpreted in terms of axially symmetric Cu(II) centers bonded directly to the cellulose, with their major symmetry axes perpendicular to the cellulose fibres [16–18].

Electron spin resonance has been also used to study and characterise Cu(II)-cellulose complexes

formed in solution. These have been compared with Cu(II) centers formed on adsorption by fibrous cellulose [19]. The free hydrated Cu(II) ion in aqueous solution exhibits characteristic ESR parameters associated with the hexahydrated ion. On adsorption of this species onto cellulose the parameters remain essentially unchanged, except that the room-temperature spectrum is anisotropic, suggesting that the adsorbed Cu(II) species, while bonded in some way to the cellulose, retain most or all of their coordinated water molecules. Further treatment of this species with NaOH produces a new narrow-line ESR spectrum. Analysis of this spectrum indicates that each Cu(II) centre is coordinated to two glucose units, and the ESR parameters of the centre are characteristic of a Cu(II) ion in a square-planar or a tetragonally distorted octahedral configuration. According to the data in [16], the major symmetry axis of this centre is perpendicular to the cellulose molecule, and the equatorial ligands are most likely OH groups on two neighbouring cellulose molecules. On the basis of additional experimental data the authors of [19] suggested that these OH groups are deprotonated and that each glucose unit of cellulose acts as a bidentate ligand to the Cu(II) ion. There is only one suitable site on the glucose units for such bidentate coordination, and that is through deprotonated OH groups on C-2 and C-3 (Scheme 1). These OH groups, both of which are equatorial relative to the pyranoside ring, are well-situated to form five-membered chelates which are generally characterized by high stability [20]. The proposed structure leads to an extensive three-dimensional lattice of Cu(II) bridging cellulose molecules in the gel [19].



Scheme 1. Proposed equatorial coordination of Cu(II) in homogeneous Cu(II)-cellulose gels [19]

Copper(II) ions interfere with the catalytic decomposition of hydrogen peroxide during the bleaching of cellulose pulp. Our preliminary investigations showed different behaviour of Cu(II) ions depending on solution pH in cellulose pulp [21]. Therefore the aim of the work reported herein was to determine the level of complexation of copper(II) ions (by means of polarography) in hydrolysed cellulose pulp at different pH values.

MATERIALS AND METHODS

Materials. Analytical grade chemicals were used, and dried cellulose pulp was obtained from a Finnish kraft pulp mill. Sufficiently concentrated solution of NaOH was used for adjusting the solution pH. Sufficiently concentrated NaNO₃ solution was added to keep the ionic strength (*I*) of the polarographic experimental solutions constant and equal 0.1 mol/l.

D. C. polarography. Polarographic curves were recorded by a PU-1 polarograph (Belarus) using a dropping mercury electrode in a thermostated three-electrode cell at 20 ± 0.1 °C. The potential scanning rate was 100 mV/min. The characteristics of the dropping mercury capillary were as follows: *m* = 2.95 mg/s, *t* = 3.73 s. The reference electrode was an Ag/AgCl electrode filled with a saturated KCl solution. The solutions were de-aerated by bubbling Ar through the solution.

The values of the actual half-wave potential $E_{1/2}$ were determined within ± 1 mV from a plot of $\log(\bar{i}/\bar{i}_{\text{lim}} - \bar{i})$ against *E*. The values of the transition coefficient α and the reversible half-wave potential $E'_{1/2}$ were calculated using the following method [22]:

$$\alpha = 2.303 \frac{RT}{nF} \left\{ \frac{\Delta \log(\bar{i}/\bar{i}_{\text{lim}} - \bar{i})}{\Delta(-E)} \right\}_{E \rightarrow -\infty}, \quad (1)$$

$$E'_{1/2} = E_{1/11} - 2.303 \frac{RT}{nF} \left\{ \log \left[10 - \exp \frac{\alpha nF}{RT} (E_{1/11} - E'_{1/2}) \right] \right\}, \quad (2)$$

where $E'_{1/2}$ is the half-wave potential determined by extrapolation of the linear part of the graph $\log(\bar{i}/\bar{i}_{\text{lim}} - \bar{i})$ against *E* at sufficiently negative potentials, and $E_{1/11}$ is the potential where the current exceeds the value equal to 1/11 of the limiting current value.

The values of the diffusion coefficient (*D*) were calculated using the Ilkovic equation [23]:

$$D^{1/2} = \frac{\bar{i}_{\text{dif}}}{607 n c m^{2/3} t^{1/6}}, \quad (3)$$

where \bar{i}_{dif} is the limiting diffusion current (μA), *n* is the number of electrons involved in electrochemical reaction, *c* is the total concentration of Cu(II) ions (mmol/l), *m* is the flow rate of Hg (mg/s), *t* is the time of the drop formation (s).

Corrections for the decrease in \bar{i}_{lim} were made in the calculation of $\Delta E'_{1/2}$ for the case of complex formation [23]:

$$\Delta E'_{1/2} = (E'_{1/2})_{\text{compl}} - (E'_{1/2})_{\text{free}} \frac{RT}{nF} \log \sqrt{\frac{\bar{i}_{\text{lim free}}}{\bar{i}_{\text{lim compl}}}}, \quad (4)$$

Concentrations of free (uncomplexed) Cu²⁺ ions were calculated from $\Delta E'_{1/2}$:

$$\text{pCu} = nF/2.303RT(-\Delta E'_{1/2}) - \log[\text{Cu(II)}]_0, \quad (5)$$

where $[\text{Cu(II)}]_0$ is the total Cu(II) concentration.

In the case of partial Cu(II) loss in the solution due to binding to cellulose fibres, the total Cu(II) concentration ($[\text{Cu(II)}]_0$) was found using AAS analyses of the filtered solutions (see below), and the value of $\bar{i}_{\text{lim free}}$ was determined from the calibration graph.

Spectrophotometry. The UV-visible spectra were recorded with a Perkin Elmer Lambda 35 UV/VIS spectrometer at 20 °C in 1.0 cm path length quartz cells. The optical blank solution was pure water.

AAS analysis. Total copper(II) in the filtered solutions was determined with the aid of a Perkin Elmer 603 atomic absorption spectrophotometer (AAS) using standard procedures.

pH measurements. Measurements of the solutions pH were carried out on a Mettler Toledo MP 220 pH-meter using a Mettler Toledo InLab 410 glass electrode.

Procedure. The pulp (as received) was torn into small pieces and soaked overnight at room temperature in triply distilled water prior to mixing and use for further experiments. The pH in the obtained solutions did not exceed 7.0, the mean value being 6.6–6.8.

The investigations were performed at room temperature in two different ways:

1. Separate samples of the pulp slurry (concentration 2% w/w) were hydrolysed at selected initial pH values between 7.0 and 13.0 for 1, 24 and 72 h, then filtered (vacuum filtration through Buchner funnels). A Cu(II) salt (copper(II) nitrate) was then added to the filtrates to make the concentration 0.5 mmol/l (pCu = 3.3). This is Series I.

2. The slurry samples (concentration 2% w/w) was hydrolysed at the initial pH values selected between 7.0 and 13.0 in the presence of 0.5 mmol/l Cu(II) for 1, 24 and 72 h and then filtered (vacuum filtration through Buchner funnels). This is Series II.

Further analyses were carried out by means of the d.c. polarography and AAS.

RESULTS AND DISCUSSION

Series I

The results obtained in the first series (Tables 1 and 2) show a trend of decreasing pH as a consequence of pulp hydrolysis for initial pH values between 8.0 and 13.0. This can be attributed to the hydrolytic depolymerization of cellulose as well as the interaction of cellulose fibres with alkali. A mixture of carboxylic and hydroxycarboxylic acids is formed in the course of the depolymerization [2], *e. g.*, one of those substances might be 1,4-anhydro-3-de-

logarithms of the stability constants are quite low and equal to 2–5 [3, 25–27].

The values of the Cu(II) reduction limiting current in the filtered solutions of cellulose pulp hydrolysed at different initial pH values are quite similar in the pH range 5.70–6.57 (Tables 1 and 2), the mean value being 2.9 μA . The calculated mean value of the diffusion coefficient of Cu(II) complexes in these solutions is $3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, less than that of uncomplexed Cu(II) obtained in 0.1 mol/l NaNO_3 ($6.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The mean of the diffusion coefficients of Cu(II) complexes determined in the solutions under investigation is comparable to the values of diffusion coefficients of Cu(II) complexes with ligands of relatively low molecular mass, *e. g.*, glycerol, tartaric acid, saccharose [28].

A comparison of UV-visible absorption spectra of uncomplexed Cu(II) with that of Cu(II) obtained in the filtered solutions of cellulose pulp hydrolysed at different initial pH values shows either a decrease in absorbance or changes in both peak shape

Table 1. Characteristics of solutions formed by 2% cellulose pulp hydrolysis (1 h) and interaction with 0.5 mmol/l Cu(II) after pulp filtration

Initial pulp pH	pH after filtration	pH after Cu(II) addition	i_{lim} , μA	$\Delta E^r_{1/2}$, mV	pCu
7.00	7.20	5.76	2.4	-16	3.9
8.00	7.80	5.70	2.7	-12	3.7
9.00	7.93	5.86	2.9	-14	3.8
10.00	9.18	5.92	3.4	-13	3.8
11.00	10.85	6.30	2.7	-16	3.9
12.00	12.03	12.03	precipitate	precipitate	precipitate
13.00	12.90	12.95	precipitate	precipitate	precipitate

oxyptitol-2-carboxylic acid [24]. It can be noted that the duration of cellulose hydrolysis did not have a notable influence on the observed pH decrease in the solutions investigated (*cf.* Tables 1 and 2). Addition of Cu(II) to the filtrate obtained after removal of cellulose fibers yields a further decrease in solution pH (Tables 1 and 2). This latter decrease can be ascribed to Cu(II) complex formation with the products of cellulose hydrolysis. If the complexation occurs with compounds containing carboxylic groups, displacement of the acid hydrogen ions by Cu(II) ions will lower the solution pH. This presumption is supported by a rather insignificant decrease in the concentration of free Cu(II) ions (from pCu = 3.3 to pCu = 3.4–3.9), when the initial pulp pH was 7 and 10 and the pH after Cu(II) addition did not exceed 7 (Tables 1 and 2). These results are in agreement with data on the stability of Cu(II) complexes with carboxylic acids, which show that the

and absorbance. This confirms a complex formation in the system under investigation (Fig. 1). Some differences in the spectra are observed as a function of the initial pulp pH and/or solution pH after Cu(II) addition. There are small increases in light absorption maxima and shifts to shorter wavelengths, indicating minor differences in Cu(II) complexation as a function of pH (Fig. 1).

Note that, when comparing results of the experiments in the first series obtained at different pulp pH values and hydrolysis times (Fig. 2), the levels of Cu(II) complexation in the pH range 7.0–10.0 (initial pulp pH) do not differ significantly (Fig. 2a). The concentrations of free copper(II) ions in these solutions are not dramatically lower than the initial concentration of the uncomplexed Cu(II) added, showing that cellulose depolymerization products with weak complexing abilities are formed under the study conditions. At the longest hydrolysis time (72 h)

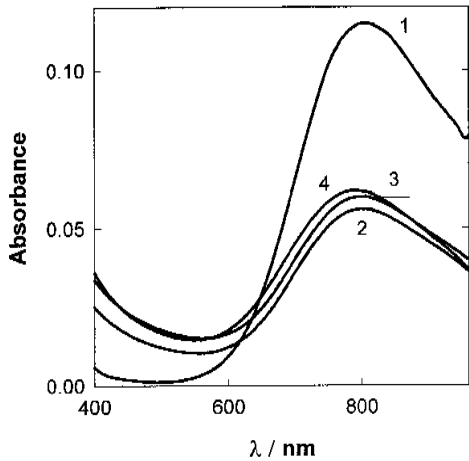


Fig. 1. Cu(II) spectra in filtered solutions obtained after hydrolysis of 2% cellulose pulp for 24 h. $[Cu(II)]_0 = 5$ mmol/l. Initial pulp pH/pH after hydrolysis and filtration/pH after Cu(II) addition: 2 – 8.00/7.30/5.01, 3 – 9.00/7.48/5.07, 4 – 10.00/9.20/5.29. Curve 1 represents the spectrum of uncomplexed Cu(II)

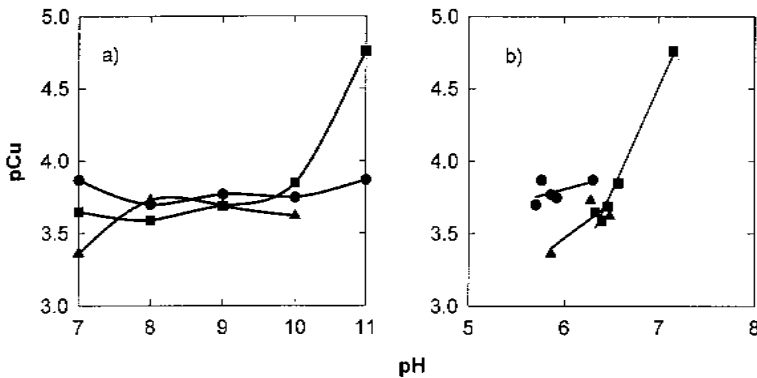


Fig. 2. Dependence of pCu on pH after interaction with 0.5 mmol/l Cu(II) after pulp filtration. Hydrolysis time (hours): ● – 1, ▲ – 24, ■ – 72. a – initial pH of cellulose pulp, b – pH after pulp filtration and Cu(II) addition

and the highest initial pH (11.0) for which no $Cu(OH)_2$ precipitate formed (Table 2), the concentration of free copper(II) ions decreased by about one order of magnitude compared to those at lower pH values (Fig. 2a). Apparently, different cellulose destruction compounds with higher complexing abilities are formed in the solution after hydrolysis at higher initial pulp pH values. This presumption is supported by UV-visible spectrophotometry which shows quite different spectra obtained when the initial pulp pH was 10.0 and 11.0 in comparison with that when the initial pulp pH was 8.0–9.0 and 12.0–13.0 (Fig. 3).

It is worth noting that the shapes of plots showing the dependence of Cu(II) complexation on the final pH (after pulp hydrolysis, filtration and Cu(II) addition) (Fig. 2b) differ from those plotted versus the initial pulp pH (Fig. 2a). The slopes of these plots depend on pH and cellulose pulp hydrolysis time and are somewhat steeper for longer hydrolysis times (Fig. 2b). This effect is most likely related to deprotonation of carboxylic acids formed in the bulk solution and to subsequent changes in Cu(II) complexation (*cf.* Fig. 1).

In aqueous solution, carbohydrate complexes are formed by the displacement of water molecules from the first coordination sphere of cations by the alcoholic hydroxy groups. Since the water molecules solvate cations much better than monohydric alcohols or diols, the latter cannot form stable complexes with cations in neutral aqueous solutions [29]. However, deprotonated carbohydrates and polyols represent rather strong and efficient metal binding agents [30–

Table 2. Characteristics of solutions formed by 2% cellulose pulp alkaline hydrolysis and interaction with 0.5 mmol/l Cu(II) after pulp filtration

Hydrolysis time, h	Initial pulp pH	pH after filtration	pH after Cu(II) addition	i_{lim} , μA	$\Delta E'_{1/2}$, mV	pCu	i_{lim} , μA	$\Delta E'_{1/2}$, mV	pCu
after adjusting to pH = 12.00									
24	7.00	7.46	5.86	3.0	–2	3.4	0.7	–295	13.5
	8.00	7.36	6.28	3.2	–12	3.7	0.5	–285	13.1
	9.00	7.56	6.45	3.3	–11	3.7	0.6	–286	13.2
	10.00	8.35	6.48	2.9	–9	3.6	0.7	–287	13.2
	11.00	10.20	7.43	precipitate	precipitate	precipitate	precipitate	precipitate	precipitate
	12.00	11.64	11.63	precipitate	precipitate	precipitate	precipitate	precipitate	precipitate
	13.00	12.74	12.72	0.5	–369	16.0	–	–	–
72	7.00	7.28	6.33	3.3	–10	3.7	0.8	–283	13.0
	8.00	7.50	6.40	2.8	–8	3.6	0.6	–283	13.0
	9.00	7.58	6.46	2.7	–11	3.7	0.6	–279	12.9
	10.00	8.39	6.57	2.6	–16	3.8	0.5	–286	13.2
	11.00	9.76	7.15	0.6	–42	4.8	0.3	–289	13.3
	12.00	11.53	11.20	precipitate	precipitate	precipitate	precipitate	precipitate	precipitate
	13.00	12.83	12.80	precipitate	precipitate	precipitate	–	–	–

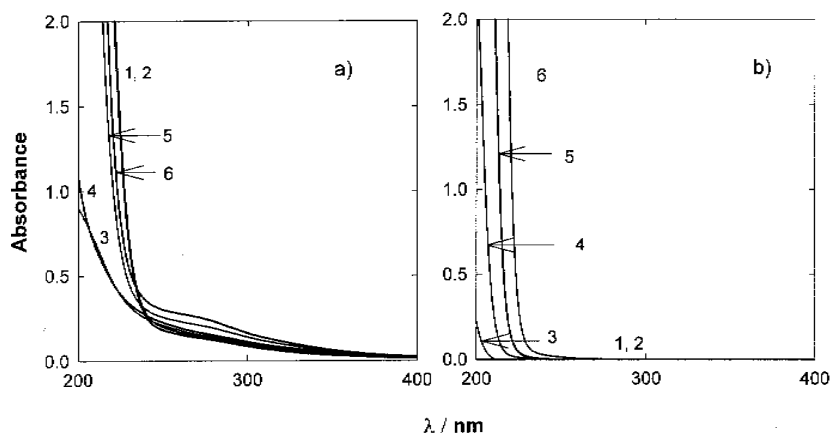


Fig. 3. UV-spectra of: a) – filtered alkaline solutions obtained after 2% cellulose pulp hydrolysis for 24 h. Initial pulp pH/pH after hydrolysis and filtration: 1 – 8.00/7.30, 2 – 9.00/7.48, 3 – 10.00/9.20, 4 – 11.00/10.04, 5 – 12.00/11.96, 6 – 13.00/12.65; b) – sodium hydroxide solutions with pH: 1 – 8.00, 2 – 9.00, 3 – 10.00, 4 – 11.00, 5 – 12.00, 6 – 13.00

33]. The same tendency is observed for hydroxycarboxylic acids with deprotonated OH-group, *e. g.*, it was found that in alkaline medium *L*- and *DL*-tartaric acids formed rather strong complexes with Cu(II), with log stability constants in the range of 18–22 [34].

In other words, alcoholic OH groups can exhibit a strong complexing ability, but only in high pH solutions. Since compounds containing such groups can be formed during the hydrolysis of cellulose pulp, we conducted further investigations of the complexing abilities of cellulose pulp hydrolysis products at higher pH. After the cellulose was hydrolyzed at a range of pH values, we adjusted each of the corresponding filtrates to pH 12.0 and then re-evaluated the Cu(II) complexation.

When the duration of the pulp hydrolysis was 1 hour and the filtrate pH was adjusted to 12.0 and Cu(II) was added, a Cu(OH)₂ precipitate formed in all cases, indicating a low complexing ability in the solutions obtained. For longer hydrolysis times, however, no precipitate was formed after Cu(II) addition regardless of the initial pH of the pulp slurries. In fact, the filtrate solutions become blue in color, which is indicative of the presence of Cu(II) complexes (different from those formed at lower pH values, for which light absorbance is much lower). The half-wave potential for Cu(II) reduction shifts over 250 mV and reaches –280 – –295 mV. Thus, the complexing ability of the dissolved cellulose hydrolysis products rises drastically due to deprotonation at higher pH (Table 2). The UV-spectra for the non-pH adjusted filtrates also show changes when the filtrates are adjusted to 12 (Fig. 4). These differences can be attributed to the deprotonation of OH[–] groups at higher pH values.

Also note that the results obtained after adjusting the pH to 12.0 (Table 2) show Cu(II) complexation levels that are essentially independent of the initial pulp pH. The calculated pCu values in these solutions range from 13.0 to 13.5.

In addition, the mean value of Cu(II) reduction limiting current, equal to 0.6 μA (Table 2), is about a factor of 5 lower than that obtained prior to pH adjustment to 12.0. The calculated mean value of the diffusion coefficient of Cu(II) complexes in the solutions after pH adjustment to 12.00 is $1.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, *i. e.* more than 20 times lower than before pH adjustment. Such low Cu(II) diffusion

coefficient values are characteristic of Cu(II) complexes with large size, *e. g.*, macromolecular, ligands [35]. Estimation of the approximate diameter of Cu(II) complex species according to the data of graph given in [28] yields about 10–20 nm. Apparently, the ligands that cause a relatively high Cu(II) complexation level at pH ≥ 12.0 are cellulose hydrolysis products of high molecular mass containing OH-groups.

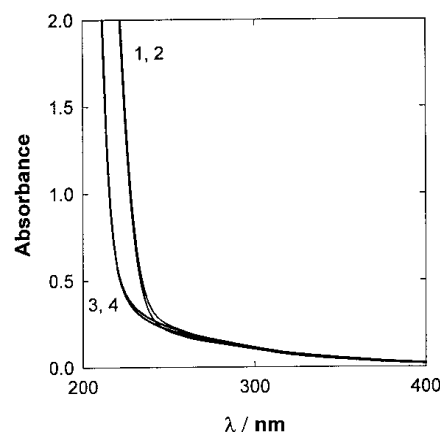


Fig. 4. UV-spectra filtered alkaline solutions obtained after 2% cellulose pulp hydrolysis for 24 h at initial pulp pH: 1 – 8.00, 2 – 9.00, 3 – 10.00, 4 – 11.00, and adjusted up to pH 12.00

Series II

When the Cu(II) salt was added directly into the cellulose slurry, part of Cu(II) (presumably, initially partially in the form of Cu(OH)₂, especially at higher pH values) was bound by adsorption, intercalation and/or chemical bond formation to cellulose fibers.

Table 3. Characteristics of solutions formed by 2% cellulose pulp alkaline hydrolysis in the presence of 0.5 mmol/l Cu(II)

Hydrolysis time, h	Initial pulp pH	pH after filtration	Cu(II), mmol/l after filtration	i_{lim} , μ A	$\Delta E'_{1/2}$, mV	pCu	i_{lim} , μ A	$\Delta E'_{1/2}$, mV	pCu
after adjusting to pH = 12.00									
1	7.00	5.25	0.25	2.2	-12	4.0	0.2	-273	13.0
	8.00	5.53	0.25	2.0	-12	4.0	0.3	-270	12.9
	9.00	5.65	0.20	1.6	-4	3.9	0.3	-279	13.4
	10.00	5.35	0.21	1.9	-10	4.0	0.3	-279	13.3
	11.00	6.25	0.16	0.8	-14	4.3	0.4	-275	13.3
	12.00	11.70	0.12	0.2	-244	12.3	0.3	-261	12.9
	13.00	13.02	0.06	0.2	-361	16.7	-	-	-
24	7.00	5.30	0.05	0.7	-1	4.4	0.2	-302	14.8
	8.00	5.10	0.10	1.4	-9	4.3	0.4	-287	13.9
	9.00	5.48	0.10	1.1	-8	4.3	0.4	-285	13.8
	10.00	5.94	0.02	0.4	-13	5.2	0.2	-301	15.1
	11.00	10.38	0.10	0.1	-137	8.8	0.2	-289	14.0
	12.00	11.80	0.03	0.1	-243	12.9	-	-	-
	13.00	12.73	0.02	0.1	-359	17.2	-	-	-
72	7.00	5.71	0.16	1.2	-6	4.0	0.2	-297	14.0
	8.00	5.95	0.06	0.6	-15	4.7	0.2	-293	14.4
	9.00	5.89	0.07	0.5	-15	4.7	0.3	-289	14.2
	10.00	6.35	0.05	0.3	-22	5.1	0.2	-292	14.4
	11.00	7.60	0.04	0.2	-51	6.1	0.1	-287	14.3
	12.00	11.39	0.04	0.1	-240	12.6	0.1	-285	14.2
	13.00	12.57	0.03	0.1	-343	16.4	-	-	-

The extent and nature of these associations depended on initial pH.

This binding of Cu(II) reaches *ca.* 50–70% of the initial Cu(II) amount at pH 7.0 and *ca.* 90–95% at pH 13.0 (Table 3 and Fig. 5a). Two general trends are observed – the residual amount of Cu(II) in the bulk solution decreases with increasing pH and with increasing the duration of hydrolysis (Fig. 5). The dependence on the initial pulp pH is particularly clear for the experiment with a 1-hour hydrolysis time (Fig. 5). The influence of the duration of cellulose pulp hydrolysis on Cu(II) binding to cellulose

fibers is largest at lower pH values (pH 7.0–10.0), presumably due to a longer time needed to establish the equilibrium. The effect of hydrolysis time on Cu(II) binding to cellulose fibers diminishes markedly at the highest pH investigated (pH 13.0) (Fig. 5). In this case we have a rather concentrated solution of alkali, and it is known that alkali can intercalate into a cellulose matrix and change its structure. Seemingly, alkali intercalation is fast enough and the altered cellulose matrix is favorable for binding Cu(II). This process might include the formation of Cu(II) hydroxy-complexes, since these

complexes are known to form with polyhydroxylic compounds such as dextran [35], saccharose [36, 37], and glycerol [36, 38].

The calculated values of pCu in the solutions with initial pH values between 7.0 and 11.0 remain in the range 3.9–4.3, showing lower concentrations of free Cu(II) ions compared to those in Series I (*cf.* Figs. 2 and 6). This is probably due in part to the binding of part of the initial Cu(II) into cellulose fibers. A sharp increase in pCu to 12.3–12.9 and to 16.4–17.2 was observed at pH 12.0 and 13.0, respectively.

When the pH of the solutions with initial pH values between 7.0 and 11.0 is adjusted to 12.0, the complexing ability of

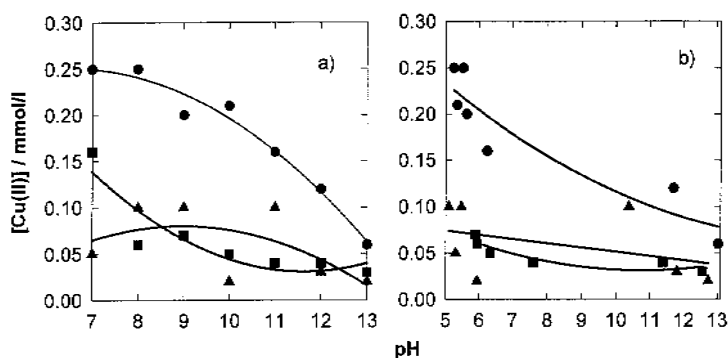


Fig. 5. Dependence of residual amount of Cu(II) on pH. Hydrolysis time (hours): ● – 1, ▲ – 24, ■ – 72. a – initial pH of cellulose pulp, b – pH after pulp filtration

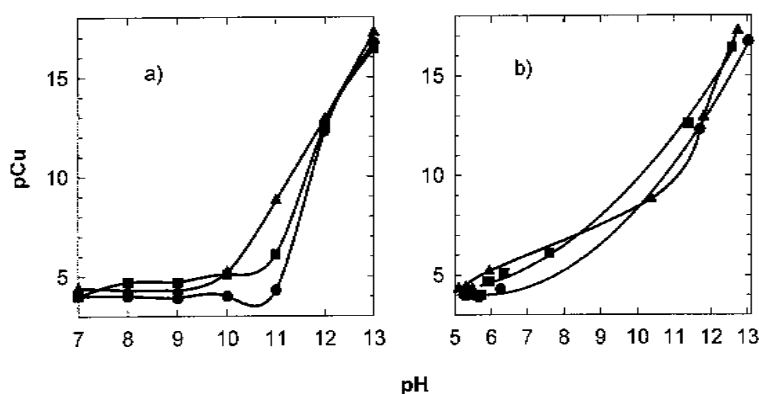


Fig. 6. Dependence of pCu on pH in filtered solutions obtained after 2% cellulose pulp hydrolysis in the presence of 5 mmol/l of Cu(II). Hydrolysis time (hours): ● – 1, ▲ – 24, ■ – 72. *a* – initial pH of cellulose pulp, *b* – pH after pulp filtration

hydrolyzed cellulose pulp rises and pCu reaches 12.9–15.1. A comparison of these data with those from Series I (pCu 13.0–13.5) shows that pCu is larger when the cellulose pulp is hydrolyzed in the presence of Cu(II) (*cf.* Tables 2 and 3). On the one hand, this decrease could be attributed to the binding of most of the Cu(II) into cellulose fibers (up to 96%). On the other hand, calculations show that this increase in pCu does not result only from a decrease in the total concentration of Cu(II) in the solution, but also from different complexing properties of the solution containing cellulose depolymerization (hydrolysis) products when cellulose pulp has been hydrolyzed in the presence of Cu(II). For example, when 0.5 mmol/l of Cu(II) interacts with the filtered solution obtained after cellulose pulp hydrolysis at the initial pH 10.0 for 24 h and the resulting solution is adjusted to pH 12.0, the pCu value determined is equal to 13.2 (Table 2). Under similar conditions, when the cellulose pulp has been hydrolyzed in the presence of Cu(II), the total concentration of Cu(II) in the bulk solution diminishes to 0.02 mmol/l, and the pCu value increases up to 15.1 (Table 3). The decrease in total Cu(II) concentration from 0.5 to 0.02 mmol/l without additional complex formation should yield an increase in pCu value by 1.4 units. Actually, the observed increase is higher (1.9 pCu units), showing differences in the complexing ability of the solutions obtained, seemingly due to different cellulose hydrolysis products formed.

The UV-visible spectra of the solutions obtained after cellulose pulp hydrolysis in the presence of Cu(II) show formation of Cu(II) complexes that depend on the pH (Fig. 7). The spectra labeled 2 and 3, recorded at lower pH (Fig. 7) are similar to those from the first series (Fig. 1, spectra 2–4) showing, presumably, coordination of Cu(II) to compounds

containing carboxylic groups. Comparison of the spectra obtained in the Series II with that of Series I shows minor decrease in Cu(II) complex light absorbance (*ca.* 10%) when cellulose pulp was hydrolysed in presence of Cu(II). This decrease could be attributed to loss of copper(II) due to it bound to cellulose fibers. At higher pH values, however, the spectra change. For example, in the solutions with pH values between 11.33 and 12.35, the absorption maxima decrease (partly it can be connected with the above-mentioned Cu(II) loss due to interaction with cellulose fibers) and shift to shorter wavelengths (Fig. 7, spectra 4–6). Again, the chan-

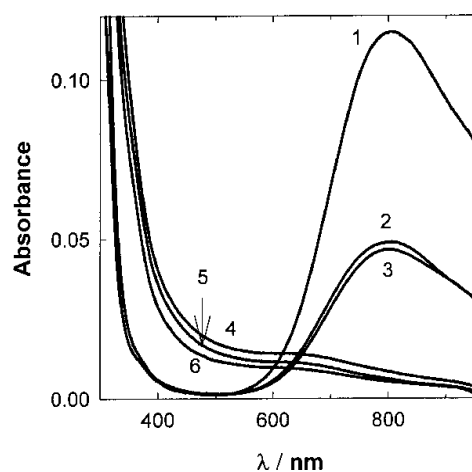


Fig. 7. Cu(II) spectra in filtered solutions obtained after 2% cellulose pulp hydrolysis in the presence of 5 mmol/l of Cu(II) for 24 h. Initial pulp pH/pH after hydrolysis and filtration: 2 – 8.00/4.23, 3 – 10.00/4.81, 4 – 12.00/11.33, 5 – the same as 4, but pH adjusted up to 12.00, 6 – 13.00/12.35. Curve 1 represents spectrum of uncomplexed 5 mmol/l of Cu(II)

ges observed, especially the shift to shorter wavelengths, might be attributable to Cu(II) complex formation with deprotonated OH-groups of hydroxycarboxylic acids or other compounds containing OH-groups.

On the one hand, this preliminary study has shown that polarography, alone or jointly with atomic absorption spectrometry, is a powerful tool for investigations of the complexation of heavy metal ions in cellulose pulps or solutions of other macromolecular compounds. On the other hand, the polarographic method provides a very sensitive general tool for determination of the concentration of uncomplexed (“free”) heavy metal ions. This will

allow, for example, investigations involving determination of the levels of free Cu(II) ions that interfere with the catalytic decomposition of hydrogen peroxide during the bleaching of cellulose pulp in the presence of a variety of ligands.

CONCLUSIONS

1. Copper(II) forms weak complexes with the dissolved products of cellulose pulp alkaline hydrolysis. The complex formation is accompanied by a decrease in solution pH, presumably due to the replacement of the acid hydrogen ions by Cu(II) ions in compounds containing carboxylic acid groups. The insignificant complexation of Cu(II) ions at pH 7–11 (pCu rises from 3.3 to 3.4–3.9) is related to the relatively low solution pH after pulp hydrolysis and addition of Cu(II) (pH 5.9–7.4).

2. When the pH of the above-mentioned solutions was adjusted upward to 12.0, the complexing ability rose, apparently due to the deprotonization of hydroxylic groups of the dissolved cellulose hydrolysis products. The free Cu(II) levels fell drastically and pCu reached 13.0–13.5.

3. After addition of Cu(II) salt directly into cellulose pulp, part of Cu(II) is bound (due to adsorption and/or chemical bond formation) to cellulose fibers. The binding of Cu(II) depends on the pH of the cellulose pulp and reaches 50–70% of the initial Cu(II) amount at pH 7.0 and 90–95% at pH 13.0.

ACKNOWLEDGEMENTS

E. N. thanks Helsinki University of Technology for a short-term visiting grant, which initiated this work. J. V. is grateful to Lithuanian State Science and Studies Foundation for awarding a fellowship.

Received February 25 2002

Accepted 2 April 2002

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VARIO(II) JONŲ SAŪVEIKA SU CELIULIOZĖS PULPA

S a n t r a u k a

Cu(II) jonų sąveika su celiuliozės pulpa buvo tirta nuolatinės srovės, atominės absorbcinės spektrometrijos ir spektrofotometrijos metodais kambario temperatūroje, kai pradinis celiuliozės pulpos pH buvo 7,0–13,0.

Nustatyta, kad vykstant 2 sv. % celiuliozės pulpos šarminei hidrolizei, tirpalo pH mažėja. pH sumažėjimas, ste-

bimas pridėjus Cu(II) druską (0,5 mmol/l) į po hidrolizės nufiltruotos pulpos tirpalą, aiškinamas Cu(II) kompleksų susidarymu su ištirpusiais hidrolizės produktais, atskylant protonams nuo karboksilinių grupių. Tirpaluose, kurių pradinis pH buvo 7,0–11,0, apskaičiuotosios pCu vertės yra 3,4–3,9 ir nedaug skiriasi nuo pradinės pCu vertės, kuri yra 3,3. Nedidelis Cu(II) jonų kompleksinimas aiškinamas mažomis tirpalų pH vertėmis (5,9–7,4). Padidinus tų pačių tirpalų pH vertes iki 12,0, ištirpusių celiuliozės hidrolizės produktų kompleksinanti geba išauga, matyt, dėl OH grupių deprotonizacijos, ir pCu siekia 13,0–13,5.

Vykdamas celiuliozės pulpos šarminę hidrolizę, esant Cu(II) druskai, dalį Cu(II) jonų suriša celiuliozės skaidulos, vykstant adsorbicijai ir/arba susidarant cheminiams ryšiams. Cu(II) jonų surišimas priklauso nuo tirpalo pH ir siekia ~50–70% nuo pradinio Cu(II) kiekio, kai pradinis celiuliozės pulpos pH buvo 7,0, bei ~90–95%, kai pH buvo 13,0. Tirpaluose, kurių pradinis pH buvo 7,0–11,0, apskaičiuotosios pCu vertės yra 3,9–6,1. Padidinus tų pačių tirpalų pH vertes iki 12,0, tirpalų kompleksinanti geba išauga, ir pCu būna 12,9–15,1. Staigus pCu padidėjimas (iki 17,2) stebimas, kai pradinis celiuliozės pulpos pH buvo 12,0 ir 13,0.