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Cu(II) complex formation with xylitol in alkaline solutions

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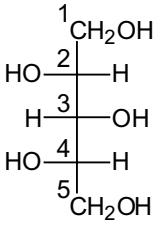
Abstract—The formation of four Cu(II)–xylitol complexes was observed in aqueous alkaline solutions ($11.0 \leqslant pH \leqslant 14.0$, $I = 1.0$, 20 °C) by means of direct current polarography and VIS spectrophotometry. Mononuclear hydroxy complexes, $CuXyl(OH)^-$ ($\log\beta = 17.7 \pm 0.5$), $CuXyl(OH)_2^{2-}$ ($\log\beta = 20.2 \pm 0.3$) and $CuXyl_2(OH)_2^{4-}$ ($\log\beta = 22.4 \pm 0.3$), are formed at high ligand-to-metal ratios (L:M $\geqslant$ 10), whereas dinuclear complex Cu_2Xyl ($\log\beta = 29.2 \pm 0.3$) is the predominant species at low ligand-to-metal ratio (L:M = 0.5). Diffusion coefficients and molar absorptivities of the complex species were determined. pH variable ^{13}C NMR suggested that pK_a values of xylitol are rather similar and equal to 13.8 ± 0.2, 13.9 ± 0.1 and 13.9 ± 0.2 for OH-groups adjacent to (C-1,C-5), (C-3) and (C-2,C-4) carbon atoms, respectively.

Keywords: Xylitol; Copper(II); Complex formation; Deprotonation

1. Introduction

Xylitol (Scheme 1) is a pentitol found in plants, fungus and algae.[1] Xylitol is also an important intermediate product in mammalian carbohydrate metabolism; for instance, human blood contains up to 8×10^{-5} M of xylitol.[2] Increased use of this polyol in food industry and medicine makes it even more common in human tissues. Xylitol is a potent metal ion chelator and is readily available (see a comprehensive review[1] on this topic) and environmentally friendly compound that can be used to bind and sequester adventitious metal ions. Stable metal–xylitol complexes are formed in alkaline solutions, where xylitol is expected to be in deprotonated form,[3] since only deprotonated alditols represent rather strong and efficient metal ion binding agents.[4–6] The previously reported pK_a value for xylitol ($pK_a = 13.73$)[7] was determined electrometrically, and deprotonation of the only one OH-group was suggested.[8] However, in a recent study,[9] deprotonation of all five OH-groups has been shown in the solid Co(III)–xylitol complex, suggesting that formation of multiply deprotonated xylitol species is also possible.



Scheme 1. Fischer formula of xylitol.

Complexes with metal-to-ligand ratio of 1:1 and 1:2 were suggested in solutions containing metal ions and xylitol. Hydrolyzed 1:1 Sb(III)–xylitol species were postulated based on a potentiometric study.[3] Complexes of 1:1 and 1:2 stoichiometry and of medium stability

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($\log\beta \approx 8$) were observed with trivalent lanthanides.[8,10] Only a weak 1:1 complex is formed with Pb(II) ($\log\beta = 1.1$–3.4).[8,11] Previous studies on Cu(II)–xylitol interaction in solution suggested the existence of positively charged Cu(II)-containing species,[12] and the formation of dinuclear $[Cu_2(OH)_2]^{2+}$ unit coordinated by xylitol ligand in tetradentate fashion.[13] The spectrophotometric determination of xylitol in the form of Cu(II) complex was also proposed.[14]

Our interest in species formed in alkaline Cu(II)–xylitol solutions was based on practical needs in Cu(II) removal from the paper pulp, since Cu(II) ions pose serious problems in pulp bleaching process catalysing hydrogen peroxide decomposition.[15] Cu(II) sequestering using a nontoxic and inexpensive ligand remains an important problem in the paper industry. Furthermore, recent studies[16] suggested that common alditols are effective Cu(II) chelators in solutions and can be used for the electroless copper deposition.

The purpose of this study was to determine stability and properties of Cu(II) and xylitol containing species in alkaline aqueous medium. Deprotonation of xylitol in alkaline solutions as a part of complex formation process was also examined by means of ^{13}C NMR and Raman spectroscopy.

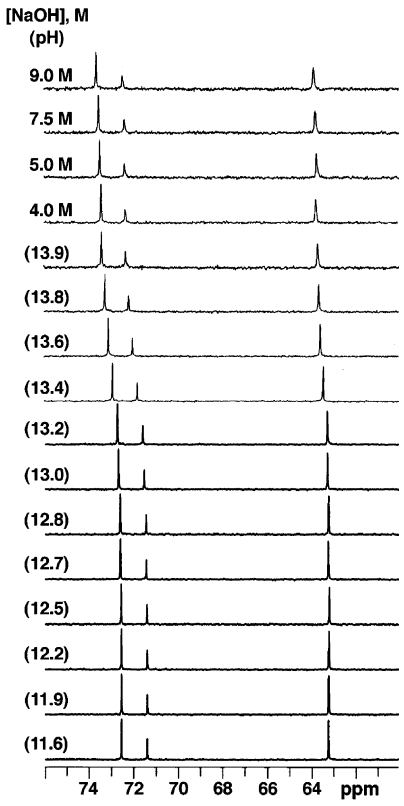

Figure 1. ^{13}C NMR spectra of xylitol (0.3 M) in aqueous NaOH solutions. The total NaOH concentration (M) is shown for each spectrum. The pH values presented were measured experimentally (22.5 °C).

2. Results and discussion

2.1. Deprotonation of xylitol in alkaline solutions

The ^{13}C NMR spectra obtained in 0.3 M xylitol aqueous solution exhibit three signals at 72.6, 71.4 and 63.3 ppm (Fig. 1, 0.005 M NaOH, solution pH 11.59), which were readily assigned to (C-2,C-4), (C-3) and (C-1,C-5) carbon atoms, respectively.[17] No changes in chemical shift were observed in the pH region 9.0–11.6 (data not shown), and we conclude that no deprotonation process takes place at lower pH. The shift of all resonance in successive pH region 11.6–13.0 was insignificant, whereas the further increase in solution pH resulted in a substantial downfield shift for all peaks, indicating deprotonation of all hydroxyl groups. The difference in chemical shift between the 0.005 M NaOH solution and the 9.2 M NaOH solution is the same for a (C-2,C-4) couple (1.1 ppm) and (C-3) atom (1.1 ppm), and significantly lower for a (C-1,C-5) couple (0.6 ppm). Based on this observation we conclude that in 9.2 M NaOH solution all hydroxyl groups are deprotonated to a great extent, since the recent study[18] has shown that the difference between the protonated and completely deprotonated forms of methanediol is 2–3 ppm.

The pK_a values were determined from δ (^{13}C) versus pH curves according to the standard procedure.[19,20] The pK_a values are equal to 13.8 ± 0.2, 13.9 ± 0.1 and 13.9 ± 0.2 for hydroxyl groups adjacent to (C-1,C-5), (C-3) and (C-2,C-4) carbons, respectively, which is in good agreement with the previously published pK_{a1} value[7]. Our study, however, shows that all OH-groups are involved in the deprotonation process.

The NIR (785 nm excitation) Raman spectra of 1 M xylitol in water and in 1 M sodium hydroxide were quite similar, although there were some clear differences in band intensities and widths (Fig. 2a). Also the UV (244 nm excitation) Raman spectrum of 1 M xylitol in water looked very similar except for the strong O–H stretching band at 3000–3700 cm^{-1} (Fig. 2b). In the UV Raman spectrum of 1 M xylitol in 1 M sodium hydroxide some bands (765, 1059, 1271, 1360–1390 cm^{-1}) in the fingerprint region were clearly resonance enhanced. This could originate from a bathochromic shift in the electronic absorption of the alcohol functionalities due to their ionization.[21] Although the assignment of these bands would require additional studies, UV resonance Raman spectroscopy looks a promising tool for the analysis of the ionized structures of polyhydroxy compounds.

2.2. Cu(II) complex formation with xylitol under conditions of metal ion excess

In solutions with a molar ratio Cu(II)–xylitol equal to 2:1 the formation of a $Cu(OH)_2$ precipitate was observed at pH below 11.5, indicating that xylitol did

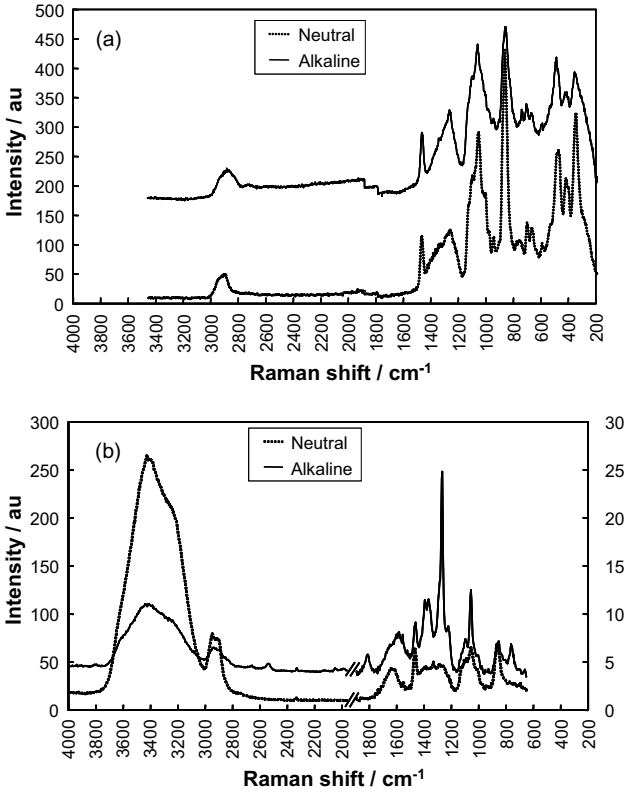

Figure 2. NIR (a) and UV (b) Raman spectra of xylitol (1.0 M) in neutral (dashed lines) and 1.0 M NaOH (solid lines) aqueous solutions.

not interact with Cu(II) under these conditions. At higher pH no precipitate was formed and the solution became blue in colour, which is indicative of Cu(II) complex formation. When the ratio Cu(II)–xylitol was increased, $Cu(OH)_2$ precipitate was immediately observed, indicating that one xylitol molecule is able to chelate at most two Cu(II) ions. In the pH range from 11.5 to 13.3 absorption spectra of all solutions with the Cu(II)–xylitol ratio 2:1 remained unchanged indicating that only one complex species exists in this entire pH range. Curve 1 in Figure 3 shows the spectrum of dinuclear Cu_2Xyl complex at pH = 12.6 with an absorption maximum (λ_{max}) at 650 nm and a molar extinction coefficient (ε) 77 $M^{-1}\,cm^{-1}$.

Stability of dinuclear complex was determined using competitive complexation[22] in the presence of NTA (nitrilotriacetic acid, H_3X). NTA was chosen, since in the pH region 12.0–12.7 it forms only one species $CuX(OH)^{2-}$ ($\log\beta_{CuX(OH)^{2-}} = 16.3$),[23] whose absorbance spectrum is significantly different from that of Cu(II)–xylitol. Curve 9 in Figure 3 shows the typical $CuX(OH)^{2-}$ spectrum with a maximum at 764 nm and the molar extinction coefficient 60 $M^{-1}\,cm^{-1}$. Upon NTA addition to the Cu(II)–xylitol solution the absorbance decreases below 672 nm and increases above 672 nm (Fig. 3). Furthermore, the absorption maximum shifts to longer wavelengths with increasing NTA concentration. The absorbance spectra in Figure 3 clearly show the conversion of the Cu(II)–xylitol complex into the $CuX(OH)^{2-}$ complex, and one isosbestic point at 672 nm confirms that only two principal species exist in solution. Under experimental conditions (pH = 12.6) NTA ligand is completely deprotonated ($pK_{a4} \sim 9.7$),[24] whereas xylitol is still significantly protonated ($pK_a = 13.9$ based on our pH variable ^{13}C NMR study). Nevertheless, a strong binding ability to the Cu(II) ion allows xylitol to compete with a four-dentate chelator NTA^{3-}. Self-consistent results were obtained from experiments under various NTA concentrations assuming that a predominant dinuclear species is Cu_2Xyl with $\log\beta_{Cu_2Xyl} = 29.2 \pm 0.3$ (Table 1).

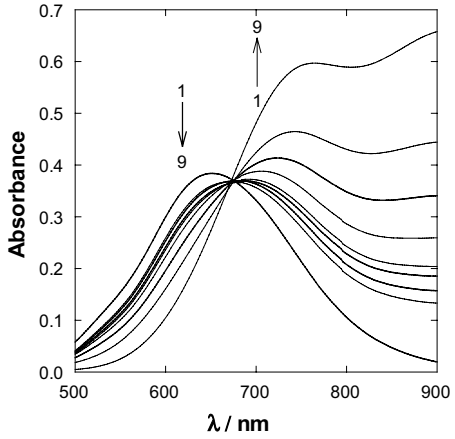

Figure 3. Cu(II) light absorption spectra in alkaline solutions of xylitol (1), NTA (9) and their mixture (2–8). Solution composition (M): $[Cu(II)]_0 = 0.010$; $[xylitol]_0$: (1–8) 0.005, (9) 0; $[NTA]_0$: (1) 0, (2) 0.006, (3) 0.007, (4) 0.008, (5) 0.010, (6) 0.015, (7) 0.020, (8) 0.050, (9) 0.020. Solution pH = 12.6; I = 1.0; 20 °C.

2.3. Cu(II) complex formation with xylitol under conditions of xylitol excess

No Cu(II)–xylitol complex formation was observed at pH < 10, even if there was a considerable excess of xylitol in the solution. Formation of the $Cu(OH)_2$ precipitate was visually observed in the solution at pH 8–10, and there was actually no polarographic wave of Cu(II) reduction.

Typical quasi-reversible reduction polarographic waves appear when solution pH is raised above 11. A limiting reduction current was found to be a linear function of the square root of the mercury column height, and its increase with temperature was small (1.23% per 1 °C). Therefore, we conclude that the limiting current is under diffusion control, and that reversible half-wave potentials $E^r_{1/2}$ for Cu(II) complex reduction can be obtained according to Matsuda–Ayabe's method.[25] Polarographic waves shift towards more negative potentials with solution pH (Fig. 4), suggesting that Cu(II)–xylitol interaction increases with increasing

Table 1. Data on equilibria in the system Cu(II)–xylitol(Xyl)–NTA(H_3X) calculated from the spectrophotometric data of Figure 3

$[NTA\ (H_3X)]_0$ (mM)	$[CuX(OH)^{2-}]$[a] (mM)	$[Cu_2Xyl]$[a] (mM)	$[X^{3-}]$ (mM)	$[Xyl]_0 - [Cu_2Xyl]$ (mM)	$[Xyl^{4-}]$ (mM)	−log[Cu(II)] (M)	$\log \beta_{Cu_2Xyl}$
6.0	1.8	4.1	4.2	0.9	0.043	15.25	29.0
7.0	2.2	3.9	4.8	1.1	0.053	15.27	28.9
8.0	2.6	3.7	5.4	1.3	0.062	15.29	28.9
10.0	2.8	3.6	7.2	1.4	0.067	15.34	29.0
15.0	3.8	3.1	11.2	1.9	0.091	15.40	29.2
20.0	5.0	2.5	15.0	2.5	0.119	15.41	29.2
50.0	6.6	1.7	43.4	3.3	0.158	15.75	29.9
							Mean 29.2 ± 0.3

$[Cu(II)]_0 = 0.010$ M, $[Xyl]_0 = 0.005$ M; pH = 12.6; $I = 1.0$; 20 °C.
[a]Averages of the values calculated at 725, 750, 775, 800, 825, 850 and 900 nm wavelengths.

xylitol deprotonation. In the absence of chelating ligands the predominant Cu(II)-containing species in solution is tetrahydroxycuprate(II) $Cu(OH)_4^{2-}$.[23] In Figure 4 (white marks) we show Cu(II) reduction half-wave potential as a function of solution pH with no ligand added. In solutions with xylitol the values of half-wave potentials were always more negative than those in solution without it, suggesting Cu(II) complexation with xylitol.

The stoichiometry of Cu(II)–xylitol species was determined from the half-wave potential shift $\Delta E^r_{1/2}$ dependence on xylitol concentration and solution pH (Fig. 4). Varying solution pH and keeping xylitol concentration constant the slope $d\Delta E^r_{1/2}/dpH$ was obtained. The 65–120 mV per pH unit value indicates that in case of one-step two electron reduction, one Cu(II) ion is surrounded by two to four groups including both xylitol and possibly OH^-. Varying the total xylitol concentration (C_{Xyl}) and keeping solution pH constant the slope $d(\Delta E^r_{1/2})/d\log C_{Xyl}$ was found. The 27–60 mV value per one logarithm unit of concentration suggests that either one or two xylitol molecules are coordinated to one Cu(II) centre. As a result, the species with general formula $CuXyl_n(OH)_m^{2-2n-m}$ (here $n = 1$ or 2 and $m = 1$ or 2) are plausible. The speciation analysis indicates that only three species are present at detectable levels in the pH range from 11 to 14. These species are $CuXyl(OH)^-$, $CuXyl(OH)_2^{2-}$ and $CuXyl_2(OH)_2^{4-}$ with the stability constant logarithms 17.7 ± 0.5, 20.2 ± 0.3 and 22.4 ± 0.3, respectively. The amount of dinuclear Cu(II)–xylitol complex in solutions with a 10-fold ligand excess is negligible (less than 1%) and does not have any influence on the mononuclear species stability constants.

With increasing solution pH the concentration of free Cu(II) ions decreases; for instance, at pH 14.0 it is 10^6–10^8 times lower than that at pH 11.5 (Fig. 5). In all cases the concentration of free Cu(II) ions in solutions with xylitol (Fig. 5, curves 1–3) is below the $Cu(OH)_2$ solubility limit (Fig. 5, curve 4). The experimentally measured concentrations of free Cu(II) (Fig. 5, black marks) are in good agreement with those obtained using stability constants.

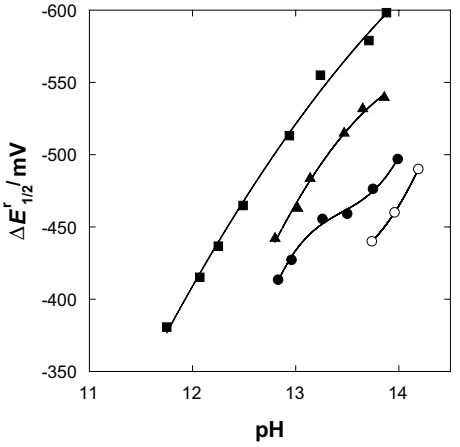

Figure 4. Dependence of $\Delta E^r_{1/2}$ of Cu(II) reduction on solution pH. Solution composition (M): $[Cu(II)]_0 = 0.0005$; $[xylitol]_0$: ● 0.005, ▲ 0.05, ■ 0.5 ($I = 1.0$), ○ 0 ($I = 3.0$); 20 °C.

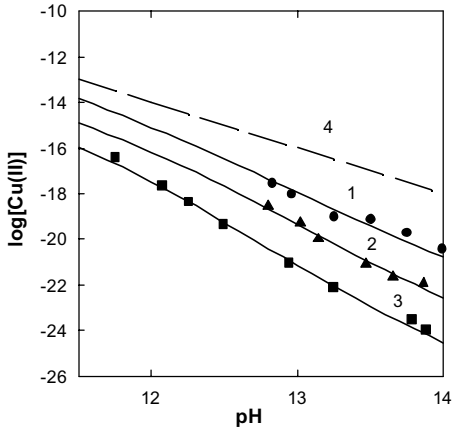

Figure 5. Dependence of concentration of free Cu(II) ions in xylitol containing solutions on pH. Solution composition (M): $[Cu(II)]_0 = 0.0005$; [xylitol]$_0$: (1) 0.005, (2) 0.05, (3) 0.5 ($I = 1.0$); 20 °C. Dashed line (4) represents concentration of free Cu(II) ions calculated from solubility product of $Cu(OH)_2$ [$SP \sim 10^{-18}$ (Ref. 24)]. Solid lines represent values calculated from the following stability constants: $\log\beta_{Cu_2Xyl} = 29.2$, $\log\beta_{CuXyl(OH)^-} = 17.7$, $\log\beta_{CuXyl(OH)_2^{2-}} = 20.2$, $\log\beta_{CuXyl_2(OH)_2^{4-}} = 22.4$, $\log\beta_{Cu(OH)_4^{2-}} = 15.5$. Black marks: experimentally determined values of the concentration of free Cu(II) ions.

According to the calculations of distribution of Cu(II) among the complexes with xylitol (Fig. 6), we found that $CuXyl(OH)^-$ is the predominant species at pH 11–11.5 when xylitol is in high excess (100 times or more). At pH above 12 two species $CuXyl(OH)_2^{2-}$ and $CuXyl_2(OH)_2^{4-}$ are present, and $CuXyl(OH)_2^{2-}$ dominates at pH 12.8 when Cu(II)–xylitol ratio is 1:10, whereas $CuXyl_2(OH)_2^{4-}$ dominates at higher Cu(II)–xylitol ratios (1:100 and above) and pH > 13. The diffusion coefficients for individual Cu(II) species were determined polarographically under conditions where each complex species was predominant. Results are shown in Table 2. The diffusion coefficient value decreases with increase in number and/or size of particles involved in complex composition. The values obtained are similar to those of Cu(II) and saccharose complexes.[26]

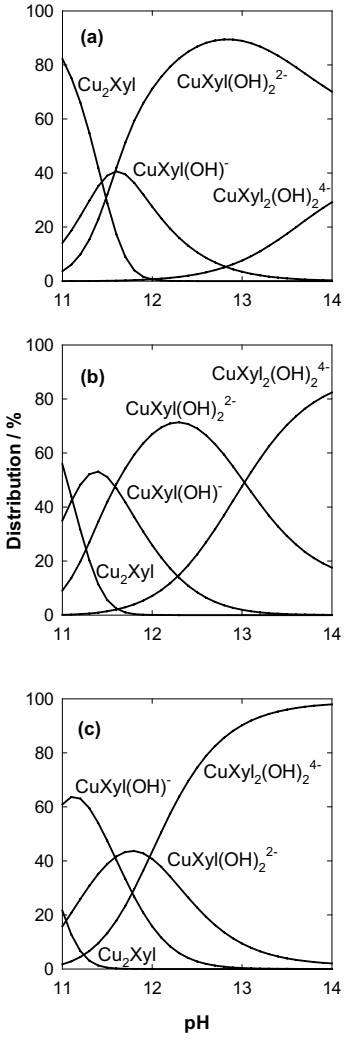

Figure 6. Distribution of Cu(II) among the complexes in solutions containing (M): $[Cu(II)]_0 = 0.0005$; $[xylitol]_0$: (a) 0.005, (b) 0.05, (c) 0.5; $I = 1.0$; 20 °C ($\log \beta_{Cu_2Xyl} = 29.2$, $\log \beta_{CuXyl(OH)^-} = 17.7$, $\log \beta_{CuXyl(OH)_2^{2-}} = 20.2$, $\log \beta_{CuXyl_2(OH)_2^{4-}} = 22.4$, $\log \beta_{Cu(OH)_4^{2-}} = 15.5$).

The absorbance of individual species $CuXyl(OH)_2^{2-}$ and $CuXyl_2(OH)_2^{4-}$ was determined under predominance conditions for each species (it was not possible to obtain conditions where $CuXyl(OH)^-$ species was predominant in spectrophotometrical measurements). The typical spectra with predominating Cu(II)–xylitol complexes are shown in Figure 7, and its characteristics are summarized in Table 3.

Cu(II) speciation studies with similar polyhydroxylic compounds such as saccharose,[27] glycerol[27] and β-cyclodextrin[28,29] show that ligand deprotonation to some extent is required in order to form a stable complex. Only when pH is above some lower limit the experimental detection of Cu(II) complexes is possible. This lower pH limit (pH_{low}) depends on the ligand pK_a however, the difference ($pK_a - pH_{low}$) presumably is constant for polyhydroxylic ligands and is equal to 2.5 ± 0.5. Further investigations of alditol deprotonation in alkaline solutions will be helpful to understand metal ion interaction with polyhydroxylic ligands.

Comparing the stability of xylitol complexes with Cu(II) and known complexes with other metals, we conclude that Cu(II)–xylitol complexes are much more stable than those of Pb(II)[8,11] and trivalent lanthanides complexes,[8,10] and slightly more stable than Mo(VI)–xylitol ($\log \beta = 16.25$)[5] and W(VI)–xylitol ($\log \beta = 18.50$)[5] complexes.

3. Experimental

3.1. Materials and preparation of solutions

Xylitol was obtained from Fluka Bio Chemika (Switzerland). Unless otherwise specified, analytical grade reagents were used without further purification. $NaNO_3$ and NaOH solutions were used to keep ionic strength (I) of the solutions constant and equal to 1 M in polarographic and spectrophotometric experiments. The solutions were prepared in triply distilled water. pH was

Table 2. Diffusion coefficient (D) values of Cu(II) species with xylitol (Xyl) calculated from polarographic data ($I = 1.0$; 20 °C)

Solution composition (M)	Predominating complex compound	$D \times 10^6$ ($cm^2\,s^{-1}$)
$[Cu(II)]_0 = 0.0005$, $[Xyl]_0 = 0.5$; pH = 11.2	$CuXyl(OH)^-$	1.7
$[Cu(II)]_0 = 0.0005$, $[Xyl]_0 = 0.005$; pH = 12.8	$CuXyl(OH)_2^{2-}$	1.5
$[Cu(II)]_0 = 0.0005$, $[Xyl]_0 = 0.5$; pH = 13.9	$CuXyl_2(OH)_2^{4-}$	1.0

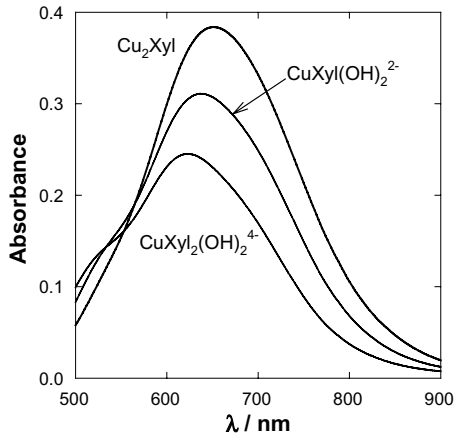

Figure 7. Light absorption spectra of Cu(II)–xylitol solutions with the dominating complexes: **Cu_2Xyl** (0.005 M xylitol; pH = 12.60), **$CuXyl(OH)_2^{2-}$** (0.05 M xylitol; pH = 12.5), **$CuXyl_2(OH)_2^{4-}$** (0.1 M xylitol; pH = 13.9). $[Cu(II)]_0 = 0.01$ M; $I = 1.0$, 20 °C.

Table 3. Optical characteristics of Cu(II) complexes with xylitol (Xyl) ($I = 1.0$; 20 °C)

Solution composition (M)	Predominating complex compound	λ (nm)	ε ($M^{-1}\,cm^{-1}$)
$[Cu(II)]_0 = 0.01$, $[Xyl]_0 = 0.005$; pH = 12.6	Cu_2Xyl	650	77
$[Cu(II)]_0 = 0.01$, $[Xyl]_0 = 0.05$; pH = 12.5	$CuXyl(OH)_2^{2-}$	638	32
$[Cu(II)]_0 = 0.01$, $[Xyl]_0 = 0.1$; pH = 13.9	$CuXyl_2(OH)_2^{4-}$	624	25

measured with a Toledo Mettler *MP 220* pH-meter. When pH exceeded 13.9, pH was calculated from Eq. 1 using published[30] pK_w and OH^- activity values.

$$pH = pK_w - pOH. \quad (1)$$

3.2. NMR spectroscopy

$^{13}C\{^1H\}$ high-resolution NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 100.6 MHz. Chemical shifts were referred to internal ethanol ($\delta = 17.47$ and 58.05 ppm from Me_4Si)[31] and then converted to the tetramethylsilane (TMS, $\delta = 0$ ppm) scale (estimated precision ±0.01 ppm). NMR samples contained 0.3 M of xylitol, NaOH (total concentration from 0.01 to 9.2 M), and 10 vol% of D_2O (lock). Solution pH was measured before and after spectra were recorded. The difference between obtained values was less than 0.02 pH unit. The spectra were acquired within 30 min after solution preparation at ambient temperature (22.5 °C).

3.3. Raman spectroscopy

The NIR Raman spectra were recorded with a Kaiser Optical Systems Hololab microscope using 785 nm excitation wavelength and 10× objective. The laser power at the sample level was 50 mW. The backscattered Raman photons were detected with a multichannel charge-coupled device (CCD) array detector at spectral range 100–3500 cm^{-1} with 4 cm^{-1} spectral resolution. The data acquisition time was 15 s. UV resonance Raman spectra were collected with a Renishaw 1000 UV Raman spectrometer equipped with a Leica DMLM microscope (15× objective) and an Innova 90C FreD frequency-doubled Ar^+ ion laser (Coherent Inc.). The excitation wavelength was 244 nm. The power at the sample was 1.3 mW. The acquisition time was 20 s, the spectral range was 500–2000 cm^{-1} and resolution about 7 cm^{-1}.

3.4. Spectrophotometry

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

The molar extinction coefficient for individual complex at wavelength λ_i was calculated according to

$$\varepsilon_{\lambda_i} = A_{\lambda_i}/cl \quad (M^{-1}\,cm^{-1}), \quad (2)$$

where c is concentration (M) of the complexes, A_{λ_i} is the light absorbance at wavelength λ_i, l is the path length (cm).

In case of competitive complexation[22,28] in solution containing Cu(II), xylitol and nitrilotriacetate the concentrations of dinuclear Cu_2Xyl and mononuclear $CuX(OH)^{2-}$ (here X^{3-} is nitrilotriacetate anion) species were found by solving system of equations:

$$\begin{cases} 2c_{Cu_2Xyl} + c_{CuX(OH)^{2-}} = [Cu(II)]_0, \\ c_{Cu_2Xyl}\varepsilon_{\lambda_{iCu_2Xyl}} + c_{CuX(OH)^{2-}}\varepsilon_{\lambda_{iCuX(OH)^{2-}}} = A_{\lambda_i}/l, \end{cases} \quad (3)$$

where c is concentration (M) of complex species, $[Cu(II)]_0$ is the total Cu(II) concentration (M) in solution, A_{λ_i} is the total absorbance at wavelength λ_i, l is the path length (cm). For any specific wavelength λ_i the individual molar extinction coefficient of Cu_2Xyl ($\varepsilon_{\lambda_{iCu_2Xyl}}$) and $CuX(OH)^{2-}$ ($\varepsilon_{\lambda_{iCuX(OH)^{2-}}}$) was obtained using Eq. 2 from individual absorbance spectra.

The stability constant of dinuclear complex Cu_2Xyl was obtained from Eq. 4, and the concentration of free Cu(II) was calculated using Eq. 5.

$$\beta = [Cu_2Xyl]/[Cu(II)]^2[Xyl^{4-}], \quad (4)$$

$$[Cu(II)] = [CuX(OH)^{2-}]/\beta_{CuX(OH)^{2-}} \cdot [X^{3-}] \cdot a_{OH^-}. \quad (5)$$

Activity of OH^- ions (a_{OH^-}) was obtained from Eq. 1.

3.5. Polarography

The direct current polarographic curves were recorded by a *PU-1* polarograph using a dropping mercury electrode in a thermostated three-electrode cell at 20 ± 0.1 °C. The solutions were deaerated by bubbling Ar through the solution. The values of the diffusion coefficient D were calculated from the limiting current $\bar{i}_{\lim}$ using the Ilkovič equation.[32]

The values of the actual half-wave potential $E_{1/2}$ were determined from a plot of $\log(\bar{i}/\bar{i}_{\lim} - \bar{i})$ against E. The values of the reversible half-wave potential $E^{r}_{1/2}$ were calculated using the method described earlier[25]. The corrections for a decrease in $\bar{i}_{\lim}$ were made in calculation of the reversible half-wave potential shift $\Delta E^{r}_{1/2}$ for the case of complex formation.[32] Additional corrections were made for liquid-junction potential.[33] The values of $\Delta E^{r}_{1/2}$ were used for calculations of parameters of Cu(II) complexes according to[32]

$$\sum_{x_i,y=0}^{N} \beta_{x_i y_i} [L^{n-}]^{x_i} a_{OH^-}^{y_i} = \exp[(nF/RT)(-\Delta E^{r}_{1/2})] - 1, \quad (6)$$

where $[L^{n-}]$ is an equilibrium concentration of the deprotonated form of xylitol, and a stands for activity of OH^- ions.

The composition and stability constants of Cu(II) complexes were obtained during iterative approximation by minimizing the least-squares functional obtained from Eq. 6. To estimate the accuracy of the stability constants, we made an assumption that the determination of the reversible half-wave potential was within ±2 mV. If the accuracy of any stability constant caused the divergence to infinity in the next iteration, then this species was removed from the list of possible species since its stability did not have any influence on the least squares sum.

Concentration of free (uncomplexed) Cu(II) ions was calculated from $\Delta E^{r}_{1/2}$:

$$\log[\mathrm{Cu(II)}] = \log[\mathrm{Cu(II)}]_0 - nF/2.303RT(-\Delta E^{r}_{1/2}), \quad (7)$$

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

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