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Carbohydrate Polymers 50 (2002) 159–164

Carbohydrate Polymers

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Interaction of Cu(II) with dextran in alkaline solutions

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Received 26 July 2001; revised 2 January 2002; accepted 7 January 2002

Abstract

Polarographic and spectrophotometric investigations of Cu(II) complex formation with dextran at 20 °C and $J = 0.1$ mol l^{-1} showed that the complexation of Cu(II) ions begins at pH over 7. The formation of Cu(II) hydroxycomplexes with deprotonized dextran monomer units was observed at pH 8–12. With further increase in solution pH, the Cu(II)-dextran complex decomposes and converts to $Cu(OH)_4^{2-}$.

The concentration of uncomplexed Cu(II) ions was determined in the solutions containing 5 mmol l^{-1} Cu(II) and 10–30 g l^{-1} dextran. Concentration of free Cu(II) ions diminishes by 14 orders of magnitude at pH 12.75 comparing with pH 7.

Keywords: Dextran; Copper(II); Dextran–copper(II) complexes; Polarography; Spectrophotometry

1. Introduction

Dextran $(C_6H_{10}O_5)_n$ (Scheme 1) is a natural carbohydrate polymer used in many areas of chemistry, technology and medicine (Webber, Munk, & Tuzar, 1995). Dextran complexes with metal ions are known and used.

The iron dextran complex used as hematinic has been studied using Mössbauer spectroscopy, both as a frozen aqueous solution and in the solid state. The iron in the complex was found to be all high-spin Fe^{3+} (Coe, Bowen, Bereman, & Monte, 1994). The same results were confirmed in further work (Coe et al., 1995b). It was shown that the iron dextran complex is a colloidal solution that contains iron(III) hydroxide (Reyes et al., 2000). A study of the iron dextran complex particle size in the solution was carried out by means of quasi-elastic laser light scattering. The results show that the range of particle sizes (i.e. the diameter of the particle including the iron core and the dextran coat) was approximately 10–40 nm (Coe, Bereman, & Monte, 1995a). It must be noted that complexes of dextran and magnetic metals (Fe, Ni) or magnetic metallic compounds are used as thermotherapeutic agents for treatment of cancer (Tanzawa & Nagae, 1990).

The investigations showed that dextran forms water-soluble complexes with several other metal ions. Interaction of Tb(III), Al(III) and Ca(II) with dextran at pH 3.0–6.6 is described in (Soares, Rodrigues, & Alario, 1993). Authors found that the dextran binding ratio decreases with pH and participation of OH^- groups from water increases with pH in the metal ion coordination sphere. Interactions of Cu(II), Ni(II) and Fe(III) with dextran were used for separation of metal ions by ultrafiltration (Solpan & Sahan, 1995). The chelating ability of dextran for Cd(II) and Pb(II) has been studied by potentiometry method. It was found that optimal pH range suitable for complexation is from 6 to 8 (Maslowska, Kurkowska-Mielczarek, & Ahamdi, 1996). The conditions of the maximum metal ion binding in dextran solutions were determined for Mn(II) at pH 10.9, for Zn(II) at pH 11.6 and for Cu(II) at pH 10.6 (Tolmachev & Lugovaya, 1976). The maximum binding of Cu(II), Co(II) and Ni(II) ions was found at pH 11–12 (Tolmachev, Lugovaya, Martirosyan, Zaboronok, & Valikhanovich, 1975b).

The optical activity dextran complexes with Cu(II), Co(II), Ni(II), Zn(II), and Mn(II) was investigated in the 300–600 nm range and was dependent on the pH. Complex formation involved the hydroxyl groups of C-2 and C-3 atoms of the dextran monomer and had no effect on the conformation of the macromolecules (Lugovaya, Tolmachev, & Il'enko, 1981). Cu(II) complexation with dextran by means of the hydroxy groups of D-glucopyranose units is also described in (Alekseev, Garnovskii, & Zhdanov, 1998). This was confirmed by the observation that protons are

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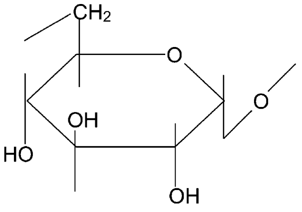
PII: S0144-8617(02)00056-5



Scheme 1. Monomer unit of dextran.

formed in the Cu(II) ion binding (Tolmachev, Lugovaya, Ishchenko, Valikhanovich, & Zaboronok, 1975a).

The goal of our work was to investigate the complexation level of copper(II) ions in dextran containing solutions at various pH values by means of DC polarography which allows rather simple and accurate determination of uncomplexed metal ions concentration.

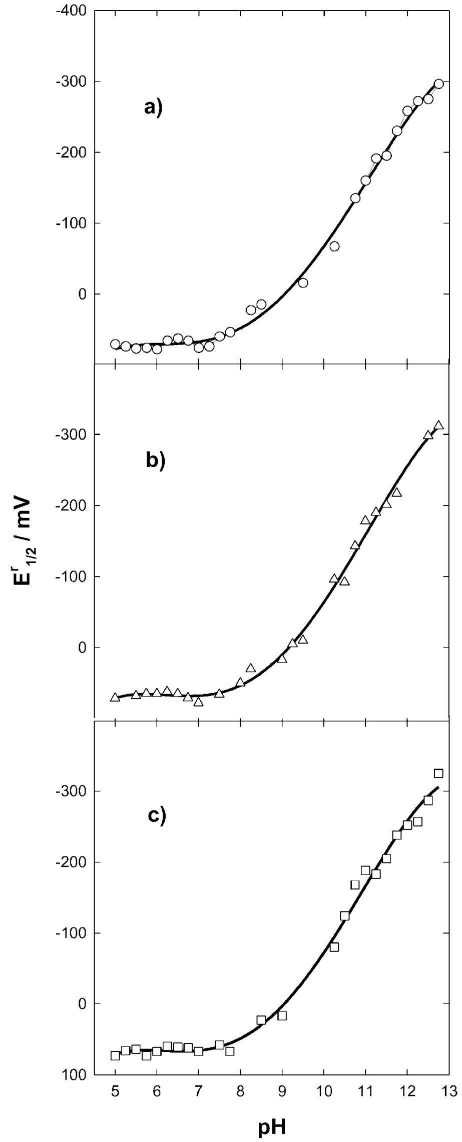


Fig. 1. Dependence of the reversible half-wave potential ($E^r_{1/2}$) of Cu(II) reduction on solution pH. $[Cu(II)]_0 = 0.5$ mmol l^{-1}; $[\text{dextran}]_0$ (g l^{-1}): (a) −10, (b) −20, (c) −30; $J = 0.1$.

2. Experimental

2.1. Materials

Analytical grade chemicals were used, and dextran was Dextran T70 from Amersham Pharmacia Biotech AB. $NaNO_3$ and NaOH solutions were used to keep ionic strength (J) of the solutions constant and normal to 0.1 mol l^{-1}.

2.2. DC polarography

The 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 measurements were made 10 min after mixing of the reactants to prevent alkaline cleavage of dextran (Hon & Shiraishi, 1986). The potential scanning rate was 100 mV min^{-1}. The capillary characteristics were as follows: $m = 2.95$ mg s^{-1}, $t = 3.73$ s. The reference electrode was an Ag/AgCl electrode filled with a saturated KCl solution (the results of polarographic investigations are given vs. this electrode). The solutions were deaerated by bubbling Ar through the solution.

The values of the actual half-wave potential $E_{1/2}$ were determined within ±1 mV from the plot of $\log(\bar{\imath}/\bar{\imath}_{\text{lim}} - \bar{\imath})$ against E. The values of the transition coefficient α and the reversible half-wave potential $E^r_{1/2}$ were calculated using the following method (Matsuda & Ayabe, 1959)

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

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

where $E'_{1/2}$ is the half-wave potential determined by extrapolation of the linear part of the graph $\log(\bar{\imath}/\bar{\imath}_{\text{lim}} - \bar{\imath})$ against E at sufficiently negative potentials, $E_{1/11}$ 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 (Heyrovsky & Kuta, 1966)

$$D^{1/2} = \frac{\bar{\imath}_{\text{dif}}}{607ncm^{2/3}t^{1/6}}, \tag{3}$$

where $\bar{\imath}_{\text{dif}}$ is the limiting diffusion current (μA), c is the total concentration of Cu(II) ions (mmol l^{-1}), m is the flow rate of Hg (mg s^{-1}), t is the time taken for the formation of drop (s).

The corrections for decrease in $\bar{\imath}_{\text{lim}}$ were made in calculation of $\Delta E^r_{1/2}$ in the case of complex formation (Heyrovsky & Kuta, 1966):

$$\Delta E^r_{1/2} = (E^r_{1/2})_{\text{kompl}} - (E^r_{1/2})_{\text{free}} - 2.303\frac{RT}{nF}\log\sqrt{\frac{\bar{\imath}_{\text{lim free}}}{\bar{\imath}_{\text{lim kompl}}}}, \tag{4}$$

Table 1
Average values of the diffusion coefficients (D) of Cu(II) ions in alkaline solutions of dextran ($8 < \text{pH} < 13$)

Dextran concentration ($g\ l^{-1}$)	$D \times 10^8$ ($cm^2\ s^{-1}$)
10	4.2
20	3.1
30	1.9

Concentration of free (uncomplexed) Cu^{2+} ions were calculated from $\Delta E^r_{1/2}$

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

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

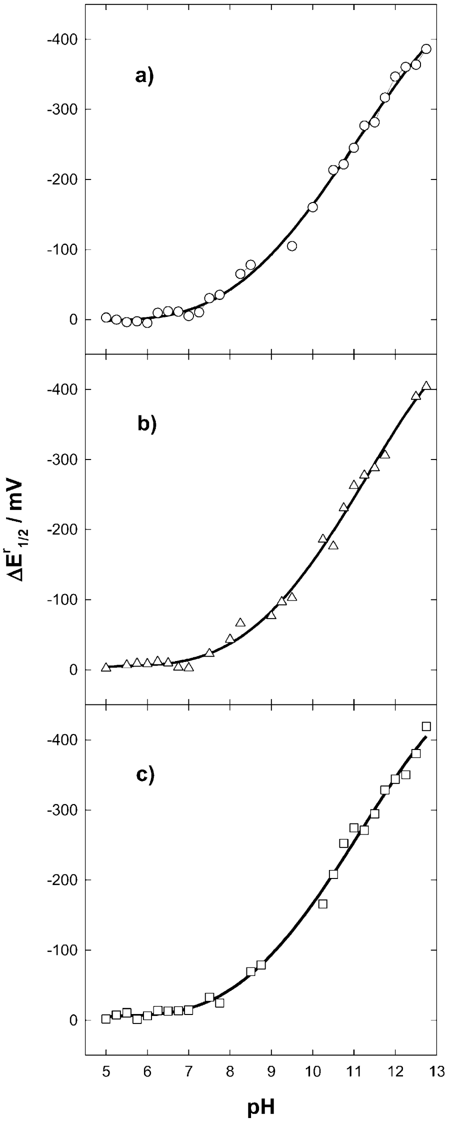


Fig. 2. Dependence of the reversible half-wave potential shift ($\Delta E^r_{1/2}$) of Cu(II) reduction on solution pH. $[\text{Cu(II)}]_0 = 0.5\ \text{mmol}\ l^{-1}$; $[\text{dextran}]_0$ ($g\ l^{-1}$): (a) −10, (b) −20, (c) −30; $J = 0.1$.

2.3. VIS-spectrophotometry

The light absorption spectra were recorded with a Perkin Elmer Lamda 35 UV/VIS spectrometer at 20 °C in 1-cm thick quartz cells. The comparison solution was a background solution without Cu(II) addition.

2.4. pH-metric measurements

Measurements of the solutions pH and pH-metric titrations were carried out using of a Toledo Mettler *MP 220* pH-meter.

3. Results

The polarographic waves of Cu(II) reduction in dextran containing solutions are quasi-reversible and allow calculations of the reversible half-wave potential ($E^r_{1/2}$).

Three series of experiments with different dextran concentration (10, 20 and 30 $g\ l^{-1}$) and constant Cu(II) concentration (0.5 $\text{mmol}\ l^{-1}$) were made. No shift of the reversible half-wave potential ($E^r_{1/2}$) of Cu(II) reduction in the solutions was observed up to pH 6–7 (Fig. 1). The results obtained show that the complexation of Cu(II) ions begins at pH over 7 (Fig. 1); with a further increase in pH the $E^r_{1/2}$ shifts to more negative potentials and the solution becomes blue in color which is indicative of Cu(II) complex formation. It must be noted that the viscosity of the solutions under investigation remains nearly constant in each series in the pH range investigated while the height of the polarographic waves decrease sharply at pH 7.0–7.25 showing that complex compounds of large size had formed. For instance, the value of the limiting current of Cu(II) reduction in dextran solution of 10 $g\ l^{-1}$ is 3.1 μA at pH 5.00 whereas it decreases to 0.2–0.3 μA in the pH range 7.50–12.75. The mean values of the diffusion coefficients of Cu(II) ions in alkaline dextran solutions are given in Table 1.

The slope of the $\Delta E^r_{1/2}$–pH dependence in the pH range 7–8 is ca. 30 mV pH^{-1}, rises to ca. 60 mV pH^{-1} in the pH range 8–10 and reaches ca. 90 mV pH^{-1} at pH over 10 (Fig. 2).

The results of spectrophotometric investigations confirmed Cu(II) complex formation in alkaline dextran solutions. With increase in solution pH the light absorption maximum of Cu(II)–dextran solutions rises and shifts to shorter wavelength comparing with uncomplexed copper(II) (Fig. 3). To a considerable degree spectra changes at pH over 6. The light absorption maximum after the reaching of maximum value at pH 11.5 ($\lambda_{max} = 680$ nm) decreases with further increase in pH and shifts further to shorter wavelengths (Fig. 3).

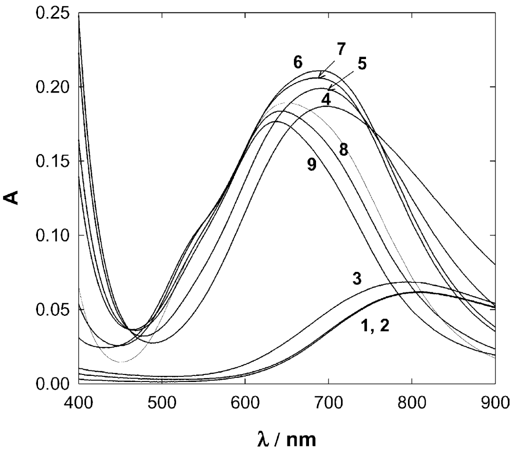


Fig. 3. Cu(II) light absorption spectra in dextran solutions. $[Cu(II)]_0 = 0.5\ mmol\ l^{-1}$; $[dextran]_0$ ($g\ l^{-1}$): (1) 0, (2–9) 20; pH: (1) 5.0, (2) 5.0, (3) 6.0, (4) 10.4, (5) 11.0, (6) 11.5, (7) 12.0, (8) 13.0, (9) 13.5; $J = 0.1$.

4. Discussion

pH-metric titration of dextran solution with sodium hydroxide solution was carried out in the pH region 5–13. No jump was observed in the titration curves indicative of dextran deprotonation constant (pK_a) being higher than 12–13. This is in agreement with known pK_a values of some carbohydrates and polyhydroxylic alcohols, e.g. pK_a values of saccharose, β-cylodextrin and glycerol are 12.43 (Lygin & Ivanov, 1967), 12.2 (Li & Purdy, 1992) and 13.99 (Souchay & Shell, 1950), respectively. In the case of ligands mentioned the complexation of Cu(II) ions begins only in alkaline solution at pH over 10–11 when the appreciable amount of the deprotonized ligand form appears in the solution (Matsui & Kinugawa, 1985; Matsui et al., 1975; Norkus, Vaškelis, & Reklaitis, 1986a,b; Norkus, Vaškelis, & Reklaitis, 1988; Norkus, Vaškelis, Vaitkus, & Reklaitis, 1995a). Taking into account that pK_a value of dextran is in the same range as for saccharose, β-cylodextrin and glycerol, the complexation in Cu(II)–dextran system begins at lower pH limits—pH 7 (Figs. 1 and 2). Such unusual behavior of the system investigated could be explained by known metal ion-promoted deprotonation of alcoholic OH groups in aqueous solutions of low pH (Burger & Nagy, 1990; Buzas et al., 1998).

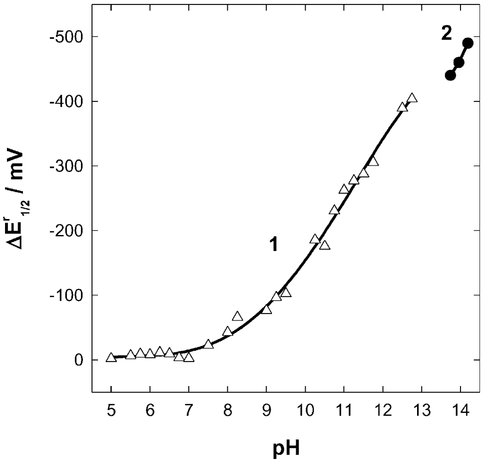


Fig. 4. Dependence of the reversible half-wave potential shift ($\Delta E^r_{1/2}$) of Cu(II) reduction on solution pH. $[Cu(II)]_0 = 0.5\ mmol\ l^{-1}$; $[dextran]_0$ ($g\ l^{-1}$): (1) 20, (2) 0; J: (1) 0.1, (2) 1.

Polarography allows the number of dextran monomer units ($C_6H_{10}O_5$) taking part in complex formation with one Cu(II) ion to be determined. It is known (Heyrovsky & Kuta, 1966) that in the case of two-electron Cu(II) reduction and 1:1 complex formation the $\Delta E^r_{1/2}$ value should shift at 29 mV to more negative potentials with a tenfold increase in ligand concentration at constant pH value. In our series the concentration of dextran monomer units increases from $0.062\ mol\ l^{-1}$ ($10\ g\ l^{-1}$) to $0.186\ mol\ l^{-1}$ ($30\ g\ l^{-1}$), i.e. threefold, and the shift of $\Delta E^r_{1/2}$ should be 14 mV. The results of the polarographic investigations confirmed the interaction of one Cu(II) ion with one dextran monomer unit—with the threefold increase in dextran concentration at constant pH values the $\Delta E^r_{1/2}$ value becomes more negative at 10–17 mV, and for instance, at pH 11.50 this shift is exactly 14 mV (cf. Fig. 2a and c).

In the case of constant ligand concentration and increase in solution pH the $\Delta E^r_{1/2}$ value should shift to more negative potentials due to the increase in equilibrium concentration of deprotonized form of the ligand taking part in the complex formation reaction. According to (Heyrovsky & Kuta, 1966) in the case of 1:1 complex formation this shift should be $29\ mV\ pH^{-1}$.

In our experiments this tendency is observed only at pH 7–8 (Fig. 2). At higher pH values $\Delta E^r_{1/2}$ shifts ca. $60\ mV\ pH^{-1}$ (pH 8–10) and ca. $90\ mV\ pH^{-1}$ at pH over 10. The results obtained can be accounted for by the participation of OH^- ions, present in the solution bulk, in the complex formation reaction. Taking into account that Cu(II) complex formation occurs with participation of the hydroxyl groups from the C-2 and C-3 atoms of the dextran monomer unit (Lugovaya et al., 1981) four free sites are left in the Cu(II) coordination sphere to coordinate OH^- ions. Participation of OH^- ions in Cu(II) hydroxycomplex formation with polyaminopolycarboxylic and polyaminopolyhydroxylic compounds (Norkus & Pauliukaitė, 2000; Norkus, Vaškelis, Žakaitė, & Reklaitis, 1995b), saccharose (Norkus et al., 1988; Norkus et al., 1995a) and glycerol (Norkus et al., 1986a,b; Norkus et al., 1995a) in alkaline medium is known.

Thus, we can conclude that Cu(II) forms three different complexes with deprotonized dextran monomer units in the system under investigation—$CuDx^+$ (where Dx^- is deprotonized dextran monomer unit) at pH 7–8, CuDx(OH) at pH 8–10 and $CuDx(OH)_2^-$ at pH over 10.

The changes of Cu(II)–dextran spectra with increase in solution pH confirm formation of different kinds of complex species (Fig. 3). The calculated molar extinction coefficient of Cu(II)–dextran complex where $CuDx(OH)_2^-$ units

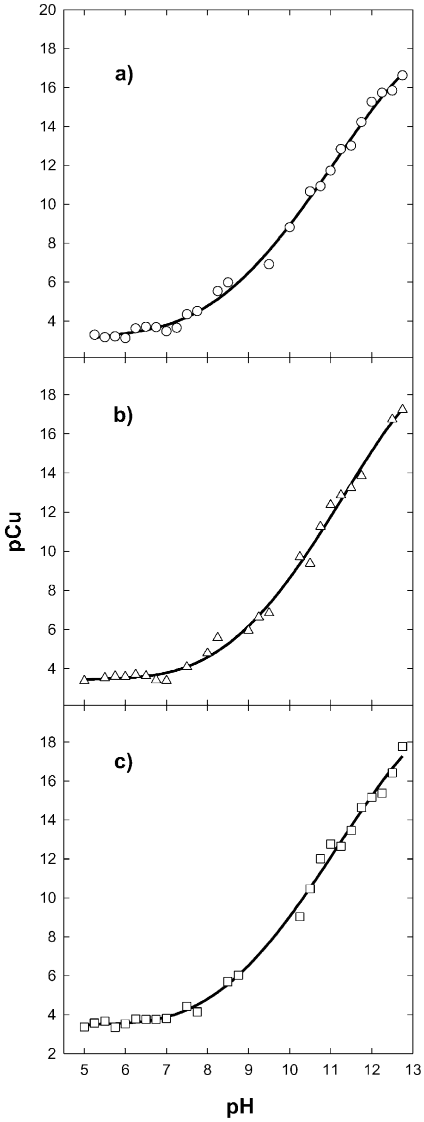


Fig. 5. Dependence of pCu on solution pH calculated from polarographic data. $[Cu(II)]_0 = 0.5$ mmol l^{-1}; $[\text{dextran}]_0$ (g l^{-1}): (a) −10, (b) −20, (c) −30; $J = 0.1$.

predominate (pH 11.5) is equal to 41 l mol^{-1} cm^{-1} ($\lambda_{max} = 680$ nm). The decrease in light absorbance at higher solution pH (>12) could be attributed to decomposition of Cu(II)–dextran dihydroxycomplex and its conversion to $Cu(OH)_4^{2-}$. Decomposition of Cu(II) complexes and formation of tetrahydroxycuprate(II) was observed previously in strongly alkaline solutions of nitrilotriacetate (Norkus & Vaškelis, 1994), ethylenediaminetetracetate (Norkus, Vaškelis, & Žakaitė, 1996), diethylenetriaminepentaacetate (Norkus & Vaškelis, 1995), hydroxyethylenediaminetriacetate, triethylenetetraminehexaacetate and ethylenedioxydiethylenediaminetetracetate (Norkus & Pauliukaitė, 2000).

To confirm the decomposition of Cu(II)–dextran complex in strongly alkaline solutions the polarograms of Cu(II) reduction in strongly alkaline solutions in the absence of dextran were recorded. Fig. 4 presents an additional evidence of Cu(II)–dextran complex conversion to $Cu(OH)_4^{2-}$—the values of $\Delta E^r_{1/2}$ of Cu(II) reduction in the presence of dextran approximate to that of $\Delta E^r_{1/2}$ in the absence of dextran when $Cu(OH)_4^{2-}$ complex predominate in solution (Norkus & Pauliukaitė, 2000; Norkus & Vaškelis, 1994; Norkus et al., 1996).

The pCu values were calculated from the polarographic data. The concentration of free Cu(II) ions in dextran containing solutions decreases gradually to pH 9. With further increase in solution pH the concentration of free Cu(II) ions decreases sharply and diminishes by 14 orders of magnitude at pH 12.75 comparing with that at pH 7 (Fig. 5).

When comparing the results obtained with complexation of Cu(II) ions with other ligands it may be mentioned that complexing ability of alkaline dextran solutions is similar to the ligands forming Cu(II) complexes of medium stability with the stability constants in the range 10^{15}–10^{17}.

Unsubstituted carbohydrates are only weak acids ($pK_a > 12$), but it is possible to reduce the basicity of the alkoxo group by the introduction of electron withdrawing substituents (Hegetschweiler, 1999). In our case, we have unsubstituted dextran and its coordination with copper(II) ions in neutral and weak alkaline solutions is quite unexpected. In general, such a behavior is not typical of sugars or other carbohydrate polymers, for instance, no Cu(II) complex formation was observed at pH 7–11 when investigating complexation level of copper(II) ions in hydrolyzed cellulose pulp at different pH values (Norkus, Vaičiūnienė, Virbalytė, Vuorinen, & Heikkilä, submitted).

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 (Gyurcsik & Nagy, 2000). However, deprotonated carbohydrate and polyols represent rather strong and efficient metal binding agents (Burger & Nagy, 1990).

Thus, the occasion for Cu(II)–dextran complex formation in neutral and week alkaline solutions might be the known metal ion-promoted (Burger & Nagy, 1990; Buzas et al., 1998) deprotonation of the alcoholic hydroxy groups of dextran.

The further polarographic experiments concerning dextran interaction with some other heavy metal ions in the wide pH range could contribute to this topic.

5. Conclusions

1. Complexation of Cu(II) ions in dextran containing solutions begins at pH over 7.
2. Formation of three different complexes with deprotonized dextran monomer units is suggested—$CuDx^+$ (where Dx^- is deprotonized dextran monomer unit) at

pH 7–8, CuDx(OH) at pH 8–10 and $CuDx(OH)_2^-$ at pH over 10.

3. Decomposition and conversion of Cu(II)–dextran complex occurs at pH over 12–13.
4. Concentration of free Cu(II) ions in dextran containing solutions diminishes in 14 orders of magnitude at pH 12.75 comparing with that at pH 7.

Acknowledgements

J. V. is grateful to Lithuanian State Science and Studies Foundation for the award of a fellowship.

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