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Complexation of Arabinogalactan with Copper(II) Ions in Aqueous Solutions

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Abstract—Complexation of Cu(II) with arabinogalactan as influenced by solution pH was studied by spectrophotometry and the method of dialysis equilibrium. Copper ions form complexes with arabinogalactan in a wide pH range, pH 5.0–12.5. Arabinogalactan forms two complex species with the metal. The composition and formation constant of the complex formed at pH < 10.8 were determined.

Coordination chemistry of carbohydrates is a relatively young but actively developing field of research; several reviews summarizing the results obtained have already been published [1, 2]. The major attention was given to complexation with mono- and oligosaccharides. Data on complexation of neutral polysaccharides with metal ions are few [2–4]. In particular, formation of compounds of dextran with a series of polyvalent metals was reported. The structures of the majority of complexes were not elucidated, but for some of them the formation conditions were studied and the complexation constants were determined.

Data on related compounds of arabinogalactan, a natural polysaccharide, are few [5, 6], although arabinogalactan shows promise for development of transport species of biogenic metals, as it exhibits valuable pharmacological properties [7, 8], including membranotropic behavior. Its metal derivatives may find wide use in medicine.

We prepared a series of metal-containing derivatives of arabinogalactan with copper, iron, cobalt, and nickel ions [9]. The specific polymeric nature of polysaccharides complicates elucidation of the structure of their metal complexes by such standard techniques of coordination chemistry as single crystal X-ray diffraction and vibrational spectroscopy. As applied to complexation of metal ions with polysaccharides, the richest structural information is furnished by ESR and UV spectroscopy, as these methods are sensitive to the features of the electronic structure of the complex. To prove the complexing power of arabinogalactan, we studied complexation of the arabinogalactan molecule with copper ions by spectrophotometry and the method of dialysis equilibrium.

It is known that the complexation conditions are largely determined by the state of the ligand in solution. The complexing power of carbohydrates is attributed to the presence of diol fragments capable to bind metal ions in alkaline solutions via oxygen atoms, forming very stable diolate complexes. This, however, is not associated solely with ionization of hydroxy groups in alkalis, as alkali metal hydroxydes are not converted to alcoholates when treated with carbohydrates [11]. Nevertheless, it is believed [10, 11] that transition metals can promote ionization of the hydroxy groups of carbohydrates. It is known that some compounds containing a peptide, amino, or hydroxy group can undergo deprotonation in the presence of certain metal ions (with the formation of complexes) in the pH range in which no dissociation occurs in the absence of metal ions [10].

Determination of the equilibrium concentrations of free and bound copper ions in the presence of arabinogalactan by the method of dialysis equilibrium shows that copper binding depends on pH. At pH 4.8, the concentration of free copper ions remains equal to their total concentration in solution; hence, copper ions are not bound by the polymer. As the pH is increased from 4.8 to 6.5, the concentration of free copper ions gradually decreases from 4.68×10^{-3} M to zero. In the range of pH 6.5–12.5, free copper ions are not detected in the solution, but no copper hydroxide precipitate is formed. Therefore, it can be concluded that copper ions in this pH range are completely bound by the polymeric arabinogalactan matrix.

The complexation was monitored by electronic spectroscopy. Figure 1 shows the absorption spectra of aqueous solutions of reaction products obtained at a constant ratio of arabinogalactan and copper sulfate but at different pH values.

The absorption of solutions at pH 4.8 coincides with that of aqueous arabinogalactan solution, suggesting that arabinogalactan forms no complexes with Cu(II) at this pH. At pH > 4.8, absorption maxima appear in the UV (238 nm) and visible (700 nm) ranges, which unambiguously proves complexation of Cu(II) ions with arabinogalactan. As pH is increased from 4.8 to 6.5, the positions of the maxima do not change noticeably, but their intensity grows (Figs. 1, 2). In the range of pH 6.5–10.8, the absorption intensity remains constant, and at higher pH it starts to increase further. The increase in absorption in the range of pH 4.8–6.5 is consistent with the decrease in the concentration of free Cu(II) ions, revealed by the method of dialysis equilibrium. In solutions with the maximal optical density, free copper is absent. Thus, the increase in the absorption is attributable to increase in the content of bound copper. The position (λ_{max} 238 nm) and intensity (ε ~2500 l mol^{-1} cm^{-1}) of the UV absorption band suggest its assignment to a ligand-to-metal charge-transfer complex, and the weaker band (ε ~37 l mol^{-1} cm^{-1}) in the visible range (λ_{max} 700 nm) is probably due to a *d*–*d* transition [3].

As the pH was increased further from 10.8 to 12.5, the UV absorption maximum shifted to 250 nm, and the visible absorption maximum, to 625 nm (Fig. 1), which may be due to changes in the Cu(II) ligand surrounding. However, the identity of the IR spectra of arabinogalactan and its copper complexes suggests that formation of the new coordination cores in the range of pH 10.8–12.5 is not due to changes in the polysaccharide macromolecule, e.g., to appearance of carboxy groups as it was found in an experiment on complexation of dextran with copper ions [3]. Furthermore, Pyatnitskii [11] indicates that carboxy groups cannot participate in complexation in alkaline solutions. The changes observed at high pH are more likely due changes in the copper coordination number or to occurrence of intermolecular interactions; we wish to clarify this question in our further studies.

In this work, we studied the complex characterized by λ_{max} 238 nm. Its composition was determined spectrophotometrically by the method of molar ratios [12]. To this end, we measured the optical density of solutions with a constant concentration of Cu(II) ions and varied concentration of the polysaccharide. The experimental series was performed at pH 7–9. The dependence of the solution optical density on the ratio of arabinogalactan and Cu(II) ions is shown in Fig. 3. It is seen that the limiting optical density is attained at 6 : 1 ratio of arabinogalactan monosaccharide units to copper ions.

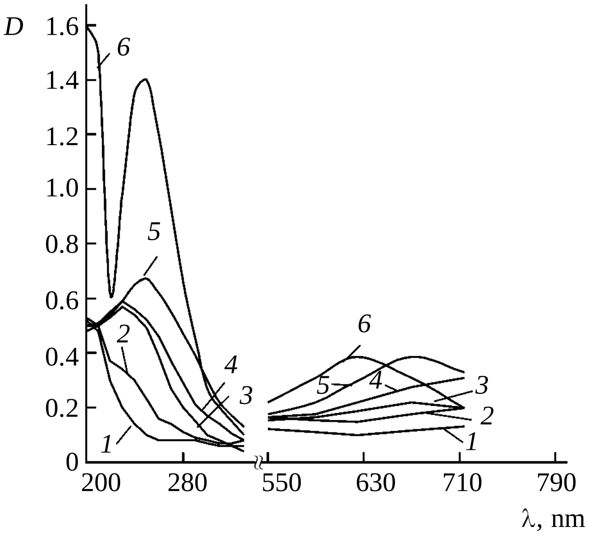

Fig. 1. Absorption spectra of aqueous solutions containing Cu(II) (c 4.68 × 10^{-3} M) and arabinogalactan (c 1.6%) as influenced by pH. pH: (*1*) 4.8, (*2*) 6.2, (*3*) 7.0, (*4*) 9.1, (*5*) 10.8, and (*6*) 12.5.

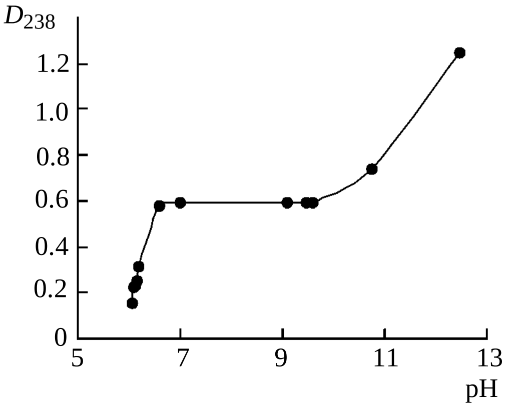

Fig. 2. Optical density D of a copper arabinogalactan complex as a function of solution pH.

Thus, in the polymeric complex, at optimal ratio of the components, there are six carbohydrate units of the polymer per copper ion. Molecular model studies [2] showed that, in complexation of carbohydrates with copper ion, a diol group of one monomeric unit is involved in the coordination. The carbohydrate unit acts a bidentate ligand forming a five-membered ring. Since in the structure of arabinogalactan the diol groups occur in the side chain only, their content is low. Thus, the major fraction (five of six) of arabinogalactan units are not involved in complexation, which may be due to the absence of diol groups and to the steric hindrance determined by the polymeric structure of the carbohydrate ligand.

To study the complexation, we studied the pH dependence of the optical density of the complex at λ_{max} 238 nm. The complexation constant K_{eq} and the

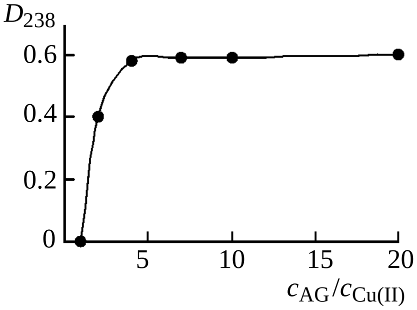

Fig. 3. Optical density *D* as a function of the ratio of arabinogalactan monomeric units and copper ions, $c_{AG}/c_{Cu(II)}$.

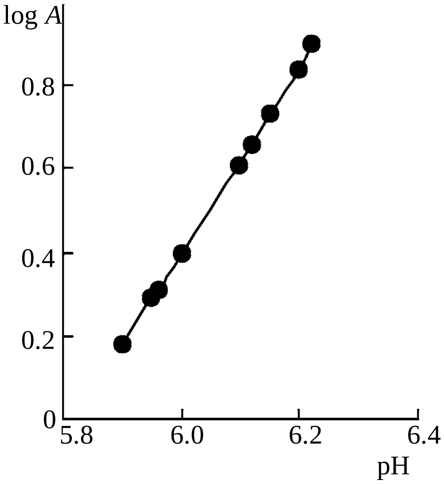

Fig. 4. pH dependence of the parameter log*A* characterizing formation of copper arabinogalactan complex ($n = 2$).

number of protons *n* released in the reaction were determined assuming the following scheme suggested for complexation of carbohydrates [3] [$R(OH)_3$ is the polysaccharide unit]:

$$R(OH)_3 + Cu^{2+} \rightleftarrows [CuR(O_3H_{3-n})]^{2-n} + nH^+.$$

The number of protons *n* was determined graphically [12] (Fig. 4) from the slope of the straight line given by the equation

$$\log K_{eq} = \log A - n\text{pH},$$

where $A = D/c_{AG}(D_{max} - D)$; D_{max}, solution optical density at complete binding of the Cu(II) ions in the complex (pH 6.5–10.8); *D*, optical density of the complex at pH < 6.5; and c_{AG}, arabinogalactan concentration, M.

According to the calculations, complexation of arabinogalactan with Cu(II) ion is accompanied by release of two protons. The equilibrium constant of the complexation was calculated by the formula $\log K_{eq} = \log A - n\text{pH}$ [3]. The mean K_{eq} value was 2.7×10^{-12}. It is close to the constant of Cu(II) complexation with dextran [3].

Thus, arabinogalactan forms complexes with copper ions at pH > 4.8. Binding of copper ions in a complex with arabinogalactan occurs in a wide pH range, 5.0–12.5. Arabinogalactan forms two complex species depending on pH. The complex having λ_{max} 238 nm is characterized by 6 : 1 ratio of the arabinogalactan units to Cu ions.

EXPERIMENTAL

Arabinogalactan was isolated from aqueous extract of *Larix sibirica* and purified by reprecipitation into ethanol. The weight-average molecular weight of arabinogalactan was 12 900, and its elemental composition was as follows: C 41.9; H 7.4; O 50.7; ash 0. Content of reductants 0.4%.

$CuSO_4 \cdot 5H_2O$, NaOH, and Na_2SO_4 were of chemically pure grade.

Complexation of arabinogalactan with copper was studied in aqueous solution at pH 4.8–12.5. A 1.6% solution of arabinogalactan was prepared; the required pH was adjusted with 0.1 M NaOH. The copper salt was added in an amount of 4.68×10^{-3} M, and the mixture was stirred for 30 min at 25°C. The pH of the resulting solutions was measured wth an EV-74 pH meter. The ionic strength (0.1) was supported by Na_2SO_4. The electronic absorption spectra of the solutions were recorded on a Specord UV-Vis spectrophotometer in the ranges 200–300 and 500–714 nm (cell thickness 0.5 mm and 2 cm, respectively). The IR spectra were taken on a UR-10 spectrophotometer (KBr pellets).

In studies by the dialysis equilibrium method, the solution was placed in a dialyzer with a membrane and equilibrated with an equal volume of water for 36 h. The free copper concentration in the dialyzate was determined spectrophotometrically (λ 425 nm) by the reaction with ammonium thiocyanate [13].

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