*Chemistry of Natural Compounds, Vol. 37, No. 4, 2001*

# COMPLEXATION IN THE NITROLIGNIN— —PECTIN—COPPER ION SYSTEM

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UDC 547.64

*Potentiometric titration, spectrophotometry, and viscosimetry were used to study complexation of nitrolignin macromolecules, pectin, and their mixture with copper ions. The salt mechanism of formation of intramolecular polymer—metal complexes was established. Stability constants and extinction coefficients of the complexes were measured.*

**Key words:** macromolecule, nitrolignin, pectin, complexation.

One of the promising pathways for expanding the chemical industry and broadening the use of natural polymers is the development of new substances and the study of their chemical transformations [1].

We investigated complexation in the nitrolignin—pectin—$Cu^{2+}$ system. Reactions of the macromolecules nitrolignin (NL) and pectin (P) and the NL—P mixture with metal ions are accompanied by a shift of the acid—base equilibrium. This is manifested in the potentiometric titration curves at various reagent ratio. Titration curves of solutions containing $Cu^{2+}$ are located below those of solutions of NL and P and their mixture (Fig. 1). This indicates that complexation between NL and P and their mixture with $Cu^{2+}$ occurs through an electrostatic mechanism with release of protons, like the reaction of NL with $Co^{2+}$, $Zn^{2+}$, and $Mn^{2+}$ [2].

Figure 2 shows the shift of titration curves for the NL—$Cu^{2+}$, P—$Cu^{2+}$, and NL—P—$Cu^{2+}$ systems as functions of amount of added metal. It can be seen that two protons are released in the P—$Cu^{2+}$ system in the initial portion of the curve for each added $Cu^{2+}$. For the NL—$Cu^{2+}$ and NL—P—$Cu^{2+}$ systems, two-coordinate bonding of $Cu^{2+}$ in the complex is observed over the whole range of studied reagent ratio. We previously noted that complexation of NL with $Zn^{2+}$, like $Cu^{2+}$, releases two protons at all reagent ratios. However, $Co^{2+}$ only in the initial portion of the shifted titration curve binds into a two-coordinate complex. For $Mn^{2+}$, less than two protons are displaced per metal ion at any reagent ratio [2].

Both intra- and intermolecular complexation is possible for two-coordinate binding of metal ions by the macromolecules. Therefore, we used viscosimetry and ultracentrifugation to elucidate the nature of the interaction in the NL—$Cu^{2+}$, P—$Cu^{2+}$, and NL—P—$Cu^{2+}$ systems. It was determined that the value of the characteristic viscosity, which is known to be proportional to the size and molecular weight of the macromolecules [3], does not change for binding of NL by $Cu^{2+}$ and remains at 1.42 dl/g. Therefore, intermolecular binding of $Cu^{2+}$ is not evident in diluted solutions. For the P—$Cu^{2+}$ system with two-coordination complexation (P:$Cu^{2+}$ = 20:1), the value [η] decreases from 1.85 to 1.61 dl/g. This is consistent with intramolecular complexation. For NL—P—$Cu^{2+}$, the characteristic viscosity of the system is 2.07 dl/g, greater than [η] of the binary complexes NL—$Cu^{2+}$ and P—$Cu^{2+}$. This is consistent with an interaction involving both the NL and P macromolecules with formation of a ternary polymer—metal complex.

Ultracentrifugation data confirm the viscosimetry results. Thus, the molecular weights for the NL—$Cu^{2+}$ and P—$Cu^{2+}$ systems are 53,000 and 51,000, respectively both before and after complexation. Therefore, intramolecular complexation occurs. The molecular weight of the NL—P—$Cu^{2+}$ complex is 100,000. This agrees with results from viscometry and indicates formation of a ternary polymer—metal complex.

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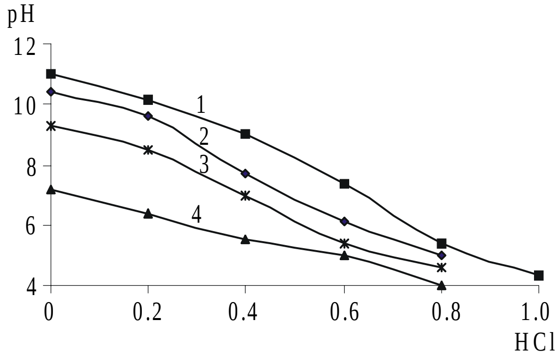

Fig. 1

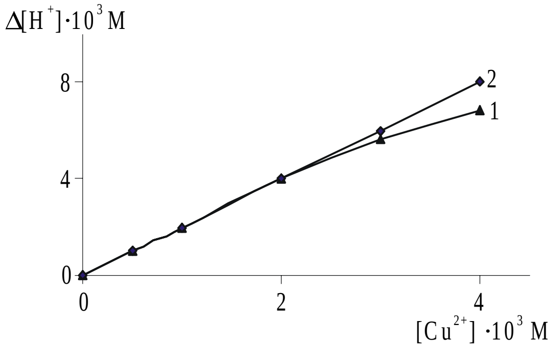

Fig. 2

Fig. 1. Potentiometric titration curves for P—NL—$Cu^{2+}$. [P] = [NL] = $1\cdot 10^{-2}$ M (1), [$Cu^{2+}$] = $5\cdot 10^{-4}$ M (2), $1\cdot 10^{-3}$ M (3), $2\cdot 10^{-3}$ M (4), $5\cdot 10^{-3}$ M (5). [HCl] = 0.1 M.

Fig. 2. Shift of titration curves for P—$Cu^{2+}$ (1), NL—$Cu^{2+}$ and NL—P—$Cu^{2+}$ (2).

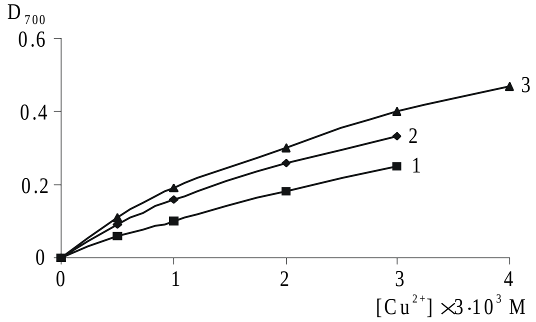

Fig. 3. Optical density of solutions of complexes P—$Cu^{2+}$ (1), NL—$Cu^{2+}$ (2), and NL—P—$Cu^{2+}$ (3) as a function of $Cu^{2+}$ content. [P] = [NL] = $3\cdot 10^{-2}$ M.

Figure 3 presents results from a spectrophotometric study of complexes in the visible region. It was found that the optical density of the complexes as a function of the amount of $Cu^{2+}$ tends to reach saturation. However, the complexes become insoluble in all systems before saturation is attained. We note that the volume of the ternary complex per $Cu^{2+}$ is greater than that of P—$Cu^{2+}$ and NL—$Cu^{2+}$ separately. This enables the polymer—metal complexes with a large metal content to be obtained in soluble form. The extinction coefficients of the complexes calculated from the initial portion of the curves at $\lambda$ = 700 nm are $E_{NL\text{-}Cu^{2+}}$ = 48.6, $E_{P\text{-}Cu^{2+}}$ = 23.3; and $E_{NL\text{-}P\text{-}Cu^{2+}}$ = 58.3. The fact that the magnitude of $E_{NL\text{-}P\text{-}Cu^{2+}}$ differs from the extinction coefficients of the binary systems again suggests the formation of a ternary complex.

Atomic absorption was used to determine the equilibrium concentration of free uncomplexed $Cu^{2+}$. Using these data we determined the stability constants of the complexes as $K_{st\ NL\text{-}Cu^{2+}} = 9.3\cdot 10^3$, $K_{st\ P\text{-}Cu^{2+}} = 2.5\cdot 10^4$, and $K_{st\ NL\text{-}P\text{-}Cu^{2+}} = 2.98\cdot 10^4$.

Thus, formation of binary $Cu^{2+}$ complexes with NL and P is shown to have an intramolecular nature whereas a ternary NL—P—$Cu^{2+}$ complex forms through an electrostatic mechanism. Stability constants and extinction coefficients of the complexes are determined.

## EXPERIMENTAL

NL was prepared from hydrolyzed lignin by a wet method [4].

Apple pectin had 43% esterification (calculated by the literature method [5]).

The concentration of the starting NaOH solution was 0.1 M; of $CuSO_4$, 0.1 M.

Potentiometric titration was performed using a pH-340 potentiometer with a glass electrode as the reference electrode and AgCl as the measurement electrode. The accuracy of the measurements was 0.005 pH units. The measurement temperature was 20°C. The concentrations of NL and P solutions was 0.01 M.

Spectrophotometric measurements were made on a KFK-3 (Russia) photoelectrocolorimeter at $\lambda_{max}$ = 700 nm. The cuvette thickness was 1 cm. Solutions of the corresponding macromolecules with $Cu^{2+}$ were used as references.

Viscosimetric measurements were made using an Ubbelohde viscometer at 20°C in 0.1 M aqueous NaCl with $\tau_0$ = 2.07 s.

Atomic absorption analysis was carried out by a standard method on a Perkin—Elmer (USA) 3030 B atomic-absorption spectrometer at 3248 nm with a propane—air background deuterium correction.

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