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INTERACTION OF NITROLIGNIN WITH METAL IONS

A. M. Khvan and Kh. A. Abduazimov

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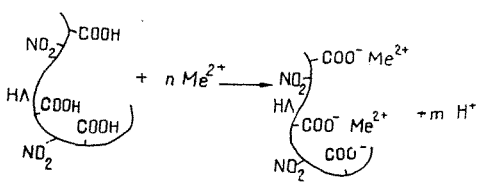
Lignin is a high-tonnage waste of the hydrolysis industry. All investigations of lignin and its derivatives are therefore connected with the necessity of solving the ecological problem of the practical use of these wastes. The most effective use of lignin requires an all-sided study of its reactivity with various reagents. We have studied the interaction of nitrolignin (NL) with metal ions (Me^{2+}) — Co^{2+}, Zn^{2+}, Mn^{2+}.

The interaction between nitrolignin macromolecules and metal ions is accompanied by a shift in the acid–base equilibrium in the system. This can well be seen from potentiometric titration curves (Fig. 1A) at various NL:Me^{2+} ratios. The NL—Me^{2+} titration curves are located below the nitrolignin titration curve. This indicates that the reaction between the NL macromolecule and metal ions proceeds by an electrostatic mechanism with the liberation of protons. As is known, nitrolignin is obtained from hydrolysis lignin with the aid of a mixture of concentrated H_2SO_4 and concentrated HNO_3 [1], and, therefore, not only nitration but also oxidation processes may occur. In actual fact the carboxy group content increases from 0.12 in hydrolysis lignin to 0.4 per phenylpropane unit in nitrolignin. In view of this, the interaction of NL with metal ions can be represented in the form:



It can be seen from Fig. 1B that the number of protons liberated when the reactants are mixed is proportional to the amount of metal added. It may be noted here that in the NL—Zn^{2+} system a metal ion replaces two protons over the whole range of ratios of the reactants that was used. In the NL—Co^{2+} system a metal ion replaces two protons only in the initial section of the curve, and with Mn^{2+} ions less than two protons are replaced over the the whole of the curve.

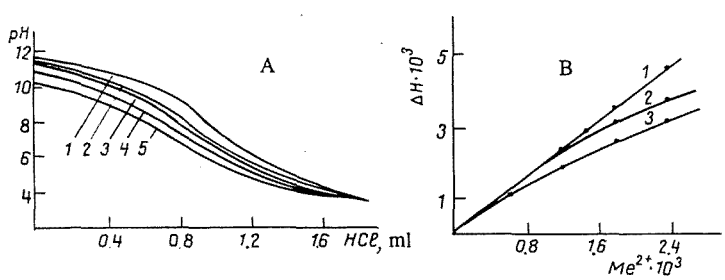


Fig. 1. A) Potentiometric titration curves for NL and NL–Co^{2+}. Concentrations (M): NL, 0.015; Co^{2+}, 0 (*1*), $0.65 \cdot 10^{-3}$ (*2*), $1.3 \cdot 10^{-3}$ (*3*), $1.9 \cdot 10^{-3}$ (*4*), $2.6 \cdot 10^{-3}$ (*5*); HCl concentration 0.2 N. B) Displacement of the titration curves of the systems NL–Zn^{2+} (*1*), NL–Co^{2+} (*2*), NL–Mn^{2+} (*3*).

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The literature contains descriptions of processes of the interaction of linear synthetic polymers with divalent metal ions in which a change in the dimensions of the macromolecules takes place [2]. We have shown by gel chromatography that different concentrations of the nitrolignin solution give different patterns of the gel chromatograms of the NL—Co^{2+}, Zn^{2+}, Mn^{2+} systems. Thus, at a high concentration (1%) of NL the NL—Me^{2+} gel chromatograms show a second peak relating to a fraction of higher molecular mass. This agrees with the literature and is explained by the fact that at a high concentration of the solution the macromolecules probably overlap one another and the metal ion binds two different lignin molecules, which lead to an increase in molecular mass. When lower concentrations of the solution of the mixtures were used, the gel chromatogram of the NL did not change on the addition of metal ions. This means that under these conditions each lignin molecule exists in the solution independently without overlapping another one, the metal ion reacts with the functional groups within a single molecule, and there is no increase in molecular mass. In contrast to linear polymers, in this case there is no decrease in the dimensions of the nitrolignin macromolecules, either. This result can be explained by the rigid reticular structure of the initial nitrolignin [3].

The agricultural use of nitrolignin in association with metal salts in the presowing treatment of cotton seeds gives positive results.

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