Chemistry of Natural Compounds, Vol. 32, No. 2, 1996

INTERMACROMOLECULAR REACTIONS OF NITROLIGNIN

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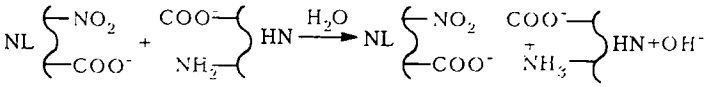
UDC 541.64

Interest in intermacromolecular reactions of lignin is dictated by the fact that the lignin–synthetic polymer system is widely used in the national economy, especially as a growth stimulator and fungicide, and the biological effect of these systems rises in the presence of trace elements [1-3]. In fact, the chemical processes taking place in these systems have scarcely been studied, although it is obvious that an investigation of the interactions on the basis of which biologically active preparations are obtained will permit a realistic approach to their synthesis and a more profound consideration of the mechanism of the biological effect.

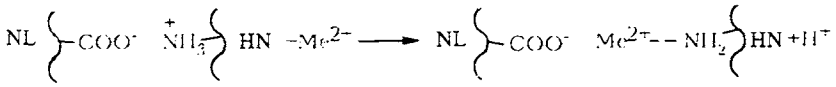
We have studied the interaction of nitrolignin with hydrolyzed Nitron (polyacrylamide) in the presence of Zn^{2+}, Mn^{2+}, and Co^{2+} ions by gel chromatography and potentiometric titration.

Figure 1 shows gel chromatograms of nitrolignin (NL) and of a solution of hydrolyzed Nitron (HN) with nitrolignin (HN–NL). (The NL was obtained by nitrating hydrolysis lignin, using the "wet" method [4], while the HN was the product of the five-hour alkaline hydrolysis of Nitron fiber with a 5% NaOH solution.) The mixture gave a second peak on the gel chromatogram corresponding to a higher molecular mass. This showed that there was an intramacromolecular interaction in the solution between the HN ad NL macromolecules.

The results of potentiometric titration are shown in Fig. 2. A comparison of the titration curves of HN and of a mixture of it with NL shows that, in the mixture, there was a shift of the acid-base equilibrium to the alkaline region. The observed rise in the pH of the mixture is connected with the occurrence of a reaction resulting in the formation of salt bonds between the NL and HN chains. The appearance of each salt bond is accompanied by the release of OH^- ions into the solution and the formation of an interpolymer complex:



The ternary systems HN–NL–Me^{2+} (Zn^{2+}, Mn^{2+}, Co^{2+}) were also investigated by potentiometry. The process taking place on the addition of the metal ions to a solution of the HN–NL complex can be represented in the following way:



It can be seen that the binding of the metal ions is accompanied by the liberation of protons into the solution and the formation of polymer-metallocomplexes.

Figure 3 presents curves of the potentiometric titration of the ternary systems HN–NL–Me^{2+}. It shows that on the addition of metal ions there is a shift of the titration curves into the acid region as the concentration of Me^{2+} ions in the solution is increased. This is explained by the fact that, by interacting with the metal ions, some of the carboxylate groups are excluded from the reaction forming the polymer-metallocomplex.

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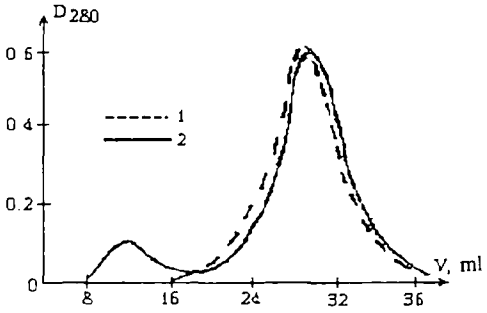

Fig. 1. Gel chromatograms of NL (*1*) and of the NL−HN system (*2*). Eluent, 0.2 N NaCl; sorbent, a mixture of Sephadexes G-75, G-100, and G-200 in a ratio of 50:25:25 (%).

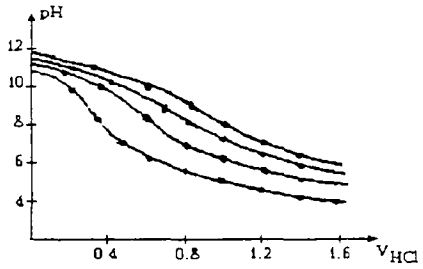

Fig. 2. Titration curves of NL (*1*) and of the NL−HN system. Concentration of HN 0.3%; NL:HN ratios 4.3 (*2*), 2.6 (*3*), 0.86 (*4*); HCl concentration 0.2 N.

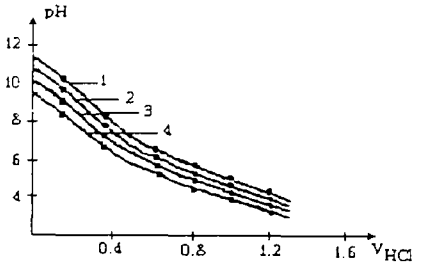

Fig. 3. Titration curves of the NL−HN−Mn^{2+} system. NL:HN ratio 2.6, (HN) = 0.3%; HN:Mn = 0.5 (*1*), 0.35 (*2*), 0.23 (*3*), 0.17 (*4*). The titration curves of NL−HN−Zn^{2+} and of NL−HN−Co^{2+} were similar. HCl concentration 0.2 N.

Thus, it has been shown that the processes in the HN−NL and HN−NL−Me^{2+} systems take place by a mechanism of electrostatic interaction.

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