the radical and molecular reaction products we also used the methods of ESR and IR spectroscopies. The ESR spectra were recorded at 77 K on a EPR-21 radiospectrometer at a power of the UHF field of ~10^{-4} W, while the IR spectra were recorded on a UR-20 spectrometer. The concentrations of double bonds were determined with the aid of a ADS-4M double-bond analyzer, the working principle of which is based on the ozonization of isolated double bonds in organic substances.

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INTERACTION OF LIGNOSULFONATE WITH CERTAIN METAL IONS

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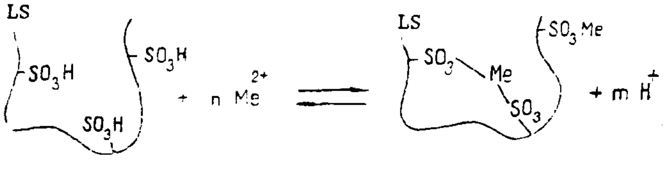
The reaction of lignosulfonate with the Co^{2+}, Ni^{2+}, and Cu^{2+} ions has been studied by the methods of gel chromatography, potentiometric titration, and UV spectroscopy. Lignosulfonate forms polymer-metal complexes with the metal ions over a wide pH range. In this process the size of the macromolecule scarcely changes, thanks to the reticular structure of the lignosulfonate. The capacity of lignin with respect to Cu^{2+} ions has been determined.

Interest in the investigation of the binding of metal ions by lignosulfonate is due above all to the availability of this material and the wide occurrence of such processes. An interaction of lignosulfonate with a metal is observed, for example, in the wood digestion process. The formation of metal complexes with lignin interferes with the bleaching of cellulose and increases the depth of color of the effluents. Its complex-forming properties also affect the biological activity of biostimulators from lignin. On the other hand, the products of the binding of metals by the lignin macromolecules may exhibit catalytic activity, a high foam-forming capacity, etc. [1].

We have studied the complex-forming capacity of lignosulfonates with the transition-metal ions Ni^{2+}, Co^{2+}, and Cu^{2+}.

The interaction between the lignosulfonate (LS) macromolecules and metal ions (Me) is accompanied by a shift in the acid-base equilibrium in the system according to the scheme shown below.



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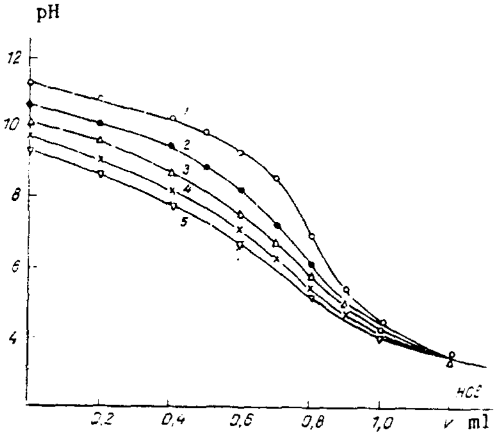

Fig. 1. Curves of the potentiometric titration of LS and of mixtures of LS with $Co(NO_3)_2$; concentration of LS 1.85%, $[Co(NO_3)_2]$: 1) 0; 2) $2 \cdot 10^{-3}$ M; 3) $4 \cdot 10^{-3}$ M; 4) $6 \cdot 10^{-3}$ M; 5) $8 \cdot 10^{-3}$ M.

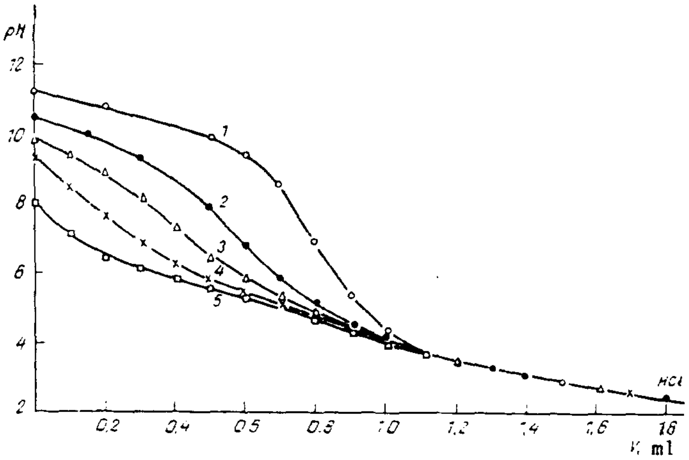

Fig. 2. Curves of the potentiometric titration of LS and of mixtures of LS with $CuSO_4$; concentration of LS 1.85%, $[CuSO_4]$: 1) 0; 2) $2 \cdot 10^{-3}$ M; 3) $4 \cdot 10^{-3}$ M; 4) $6 \cdot 10^{-3}$ M; 5) 10^{-2} M.

Consequently, the formation (breakdown) of the polymer-metal complex (PMC) can be studied by the method of potentiometric titration. Figures 1 and 2 show curves of the potentiometric titration of the LS–Co^{2+} and LS–Cu^{2+} systems at various ratios of the components. The titration curves for the LS–Ni^{2+} system are similar to those for the LS–Co^{2+} system. It can be seen that the titration curves for the LS–Me mixtures are located below the titration curves for lignosulfonate. This indicates that the reaction between the LS macromolecules and the metal ions takes place by a mechanism of electrostatic interaction with the liberation of protons by the scheme given above.

The results presented also show that the binding of metals into PMCs takes place over a wide pH range.

It can be seen from Fig. 3 that the number of protons liberated when the reactants are mixed is proportional to the amount of metal added.

In the LS–Ni^{2+}, Co^{2+} systems, a metal ion displaced one proton over the whole range of Me/LS ratios investigated. The situation was different in the LS–Cu^{2+} system. When the concentration of copper ions in the system was low (initial section of curve 3 in Fig. 3), for each Cu ion bound two protons were liberated. It is obvious that under these conditions either intra- or intermolecular binding of the macromolecules of the lignosulfonate by copper ions took place. With a subsequent increase in the concentration of Cu^{2+} ions in the system the number of H^+ ions liberated for each additional metal ion decreased.

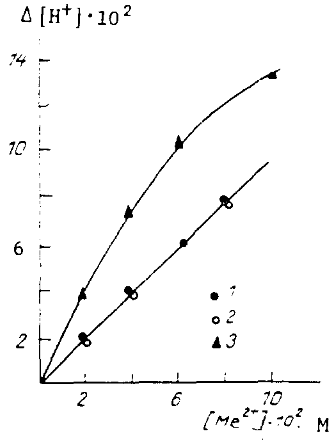

Fig. 3

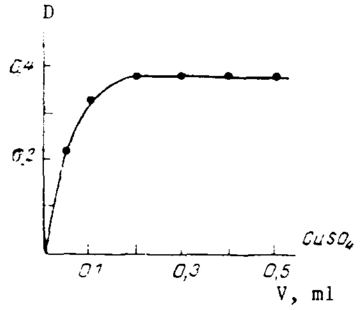

Fig. 4

Fig. 3. Dependence on the amolunt of metal ions of the number of protons liberated when the reactants are mixed (pH 8): 1) LS—$Ni(NO_3)_2$; 2) LS—$Co(NO_3)_2$; 3) LS—$CuSO_4$.

Fig. 4. Dependence of the optical density in the LS—$CuSO_4$ system on the $CuSO_4$ content, pH 8, ℓ = 1 cm, λ_{max} = 420 nm. $[CuSO_4]$ = 0.2 M. [LS] = 1.85%.

As a rule, in the process of binding macromolecules their dimensions change [2]. However, the results that we obtained from the gel chromatography of the lignosulfnonate before and after complex-formation showed that the size of the LS did not change on the binding of copper ions.

The fact that as a result of complex-formation no increase was observed in the size of the macromolecule unambiguously demonstrates that, under the conditions of the experiment, there was no intermolecular binding of the lignin by the copper ions. This was to be expected, since fairly dilute solutions of LS were used with $[\eta]\cdot C < 1$.

Thus, in the LS—Cu^{2+} system, binding takes place intramolecularly, and the fact that the size of the lignin macromolecule does not decrease can be explained by the rigid reticular structure of the LS [3]. It is probable that only those functional groups that are already sufficiently close in the initial lignosulfonate are bound by the copper ions, so that this does not lead to an additional contraction of the macromolecule.

Since the lignosulfonate macromolecule possesses a reticular structure, it is obvious that not all the functional groups are accessible for metal ions. It follows from Fig. 4 that saturation sets in as early as a Cu^{2+}/LS ratio of 6.95:1 (by weight).

EXPERIMENTAL

The optical density of the complex of lignosulfonate with copper ions was recorded on SF-26 spectrophotometer at λ_{max} 420 nm. An aqueous solution of lignosulfonate was used as the comparison solution. The optical pathlength was 1 cm.

The potentiometric titration of the LS-Me systems was conducted with the aid of a pH 340 potentiometer, using a glass electrode as the sensitive element. The accuracy of measurement was 0.05 pH unit.

Gel chromatography was performed in a column (1.1 × 42 cm) filled with type Sephadex G-200 gel. The eluent used was 0.5 M aqueous NaCl solution.

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