CHANGE IN THE ACID-BASE PROPERTIES OF LIGNIN CHROMOPHORES ON PHOTOEXCITATION

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The excitation by light of solutions of lignin and a number of model compounds leads to a change in the redox properties of the chromophoric groupings that can be recorded from the change in the photopotential [1, 2]. In addition to this, the acid-base properties of many phenols may change [3].

In view of the wide pH range at which lignified materials undergo treatment in technological processes, and also the fact that the photochemical transformations of lignin are induced by the excitation of definite groups [4], it is necessary to have information on the change in acid-base properties of the lignin chromophores on passing from the ground to the excited state.

The determination of the thermodynamically based pK values of the phenolic elements in lignin is associated with great difficulties, since it is complicated by the macromolecular structure of the lignin (by the influence of intramolecular hydrogen bonds [5, 6], by polyelectrolyte effects [7, 8] etc.). Consequently, for lignin in this case it is more appropriate to speak of the effective pK values.

Since lignin possesses fluorescent properties in alkaline solutions [9], we have performed an estimate of pK^*_{eff} of the excited state from the change in the intensity of fluorescence as a function of the pH. To determine pK_{eff} of the ground state of lignin we used the spectrophotometric method with a control for the change in the optical density of the solution at λ 345 nm (region of absorption of phenolic elements with a conjugated carbonyl group in the α position to the phenol ring).

For the measurements we used solutions of lignin with a concentration of 0.2 mM. In order to increase the solubility of the lignin at low pH values, a weighed sample was dissolved in a mixture of 15 ml of 0.2 N NaOH + 10 ml of C_2H_5OH, and 1 ml of this solution was taken and was made up in a measuring flask to the 25-ml mark with a buffer having a predetermined pH (from 6.0 to 13.4). The differential UV spectra of the solutions were taken on

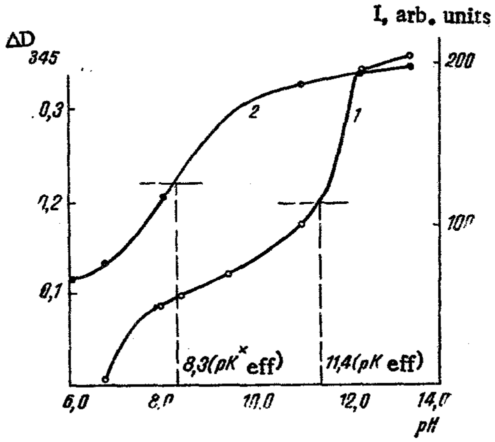

Fig. 1. Dependence of the optical density (1) and of the intensity of fluorescence (2) of solutions of lignin on the pH (C_l = 0.2 mM).

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a SF-16 spectrophotometer (relative to a solution of lignin with pH 6.0). The intensity of fluorescence was determined on an apparatus based on an ISP-51 spectrograph with a FÉP-1 attachment. As the source of excitation we used a LGI-21 nitrogen laser (λ_b = 33.5 nm).

Figure 1 shows the dependence of the changes in optical density (curve 1) and of intensity of fluorescence (curve 2) on the pH. The phenolic elements of the lignin in the excited state have more pronounced acidic properties. The value of pK^*_{eff} for the excited state is 8.3, while for the ground state it is 11.4.

Thus, the change in pK_{eff} for the phenolic elements of lignin on passing from the ground to the excited state is 3.1 units.

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