INTERMACROMOLECULAR REACTIONS OF LIGNOSULFONATE

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It is known that intermacromolecular reactions between synthetic polyelectrolytes form polyelectrolyte salt complexes [1]. We have studied the formation of a polyelectrolyte complex of a synthetic polymer with the macromolecules of a natural polymer — lignosulfonate (LS). The desirability of this type of investigations is connected with the use of mixtures of lignosulfonates with synthetic polyelectrolytes in the national economy [2].

The interaction of the product of the alkaline hydrolysis of the fiber Nitron [polyacrylonitrile] (HN) with samples of LS having various molecular masses was investigated by potentiometric titration. Mixing solutions of the two reactants produced a rise in the pH of the solution. This is connected with the occurrence of a reaction leading to the formation of salt bonds between the units of the LS and the HN, which is accompanied by the release of OH ions into the solution, as can be represented by the scheme:

$$(LS) - SO_3^{\dagger}Na^{+} + H_2N - C - (HN) + H_2O - (LS) - SO_3^{\dagger}N^{\dagger}H_3 - C - (HN) + Na^{+} + OH^{-}$$

Figure 1 shows curves of the potentiometric titration of mixtures of HN with various fractions of LS. The lignosulfonate samples were obtained by fractional precipitation with acetone from aqueous solution. The molecular masses of the fractions were determined by ultracentrifugation. It can be seen that the titration curves of the mixtures are located above the titration curve of HN, which corresponds to the scheme of complex-formation given above. It may be noted that on the curve of the potentiometric titration of a mixture of HN with the LS of a high-molecular-mass fraction (MM = 85,000) there are two points of inflection, while with a low-molecular-mass fraction of LS there is only one. Similar phenomena are known from the literature, and in these the first inflection on the titration curves relates to the formation of salt bonds between the macromolecules, and the second to the titration of the free basic groups of the HN. The presence of the second point of inflection can probably be explained by the appearance of steric hindrance when the reaction involves a high-molecular-mass fraction of LS, since the degree of branching of the lignosulfonate macromolecules increases with a rise in their molecular mass [3].

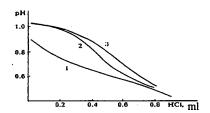


Fig. 1. Curves of the potentiometric titration of HN (1) and of HN—LS systems. Concentrations: HN 0.02%; LS 0.002%. Molecular masses of the LS: 85,000 (2); 4800 (3).

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Thus, we have shown the influence of the molecular weight of a lignosulfonate on the nature of the process of forming a polyelectrolyte complex with hydrolyzed Nitron.

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