NITROGEN- AND PHOSPHORUS-CONTAINING POLYAMPHOLYTE BASED ON LIGNIN

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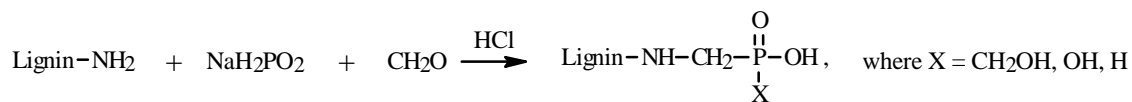
Nitrogen- and phosphorus-containing polycomplexant was synthesized using the Kabachnik—Fields reaction to modify the amino derivative of lignin. The kinetics of phosphorylation and the optimal conditions for preparing the amphoteric ion exchanger were investigated.
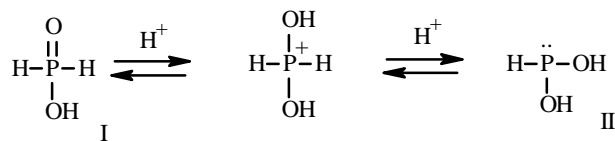
Polyampholytes containing phosphorus and nitrogen in addition to α-aminoalkylphosphorus groups are interesting as reagents with a high complexing ability. This is exceedingly promising for selective concentration of heavy metals and transition metals. The most accessible method for preparing them is phosphorylation of crosslinked aminocopolymers using the Kabachnik—Fields reaction [1-7].

The goal of our work was to synthesize new organophosphorus polycomplexant based on the amino derivative of lignin and to study its properties.

The method is based on simultaneous or successive treatment of an amino- and oxocompound (aldehyde or ketone) with trivalent P derivatives capable of two-fold tautomerism. The oxocompound was formaldehyde; the phosphorus component, hypophosphorous acid as the most reactive of all P(III) compounds; the amine, grafted aminocopolymer of lignin and epoxide resin ED-20 as shown below.

$$\text{Lignin}-\text{NH}_2 \ + \ \text{NaH}_2\text{PO}_2 \ + \ \text{CH}_2\text{O} \xrightarrow{\text{HCl}} \text{Lignin}-\text{NH}-\text{CH}_2-\overset{\displaystyle\overset{O}{\|}}{\underset{\displaystyle\underset{X}{|}}{P}}-\text{OH}, \quad \text{where X} = \text{CH}_2\text{OH, OH, H}$$

According to the literature [3-6], phosphorylation of an amino matrix in acidic medium in the nonpolar solvent ethyleneglycol can convert a large number of the amino groups due to a shift of the tautomeric equilibrium toward formation of the chemically active three-coordinate form of P (**II**) [8] and increase the affinity of nitrogen, which is protonated in acidic media, for the anion of the phosphorylating agent.

$$\text{H}-\overset{\displaystyle\overset{O}{\|}}{\underset{\displaystyle\underset{OH}{|}}{P}}-\text{H} \ \underset{\longleftarrow}{\overset{\text{H}^+}{\longrightarrow}} \ \text{H}-\overset{\displaystyle\overset{OH}{\underset{+}{|}}}{\underset{\displaystyle\underset{OH}{|}}{P}}-\text{H} \ \underset{\longleftarrow}{\overset{\text{H}^+}{\longrightarrow}} \ \text{H}-\overset{\displaystyle\overset{..}{P}}{\underset{\displaystyle\underset{OH}{|}}{}}-\text{OH}$$
$$\qquad\qquad\qquad\text{I}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{II}$$

Kinetic investigations [8] showed that compounds with P(O)H groups are slowly converted during the reaction from phosphoryl (**II**) into the highly reactive hydroxyl form (**I**), which is present under ordinary conditions in the equilibrium mixture in very low concentrations due to the instability of the P–O bond compared with the P=O bond in the phosphoryl group. In acidic medium, tautomeric conversion is catalyzed and shifts toward formation of **II**. The fraction of the intermediate highly reactive trivalent form increases.

TABLE 1. Effect of Aminolignin Phosphorylation Conditions on Composition and Ion-Exchange Properties of Crosslinked *N*- and *P*-Containing Polycomplexant

Aminophosphorylation conditions			SEC for 0.1 N solutions, mg·eq/g			TEC, mg·eq/g	P, %	$N_{titr}/N_{element}$, %
Aminolignin:NaH$_2$PO$_2$: CH$_2$O:HCl ratio	T, °C	τ, h	HCl	NaOH	NaCl			
1:2:2:1	80	5	3.00	3.75	0.7	7.45	9.68	4.20/10.32
1:4:4:2			1.75	5.40	0.7	7.85	15.09	2.45/8.97
1:10:10:4			1.50	5.60	0.7	7.80	15.28	2.10/8.57
1:4:4:2	40	0.5	3.65	3.25	0.8	7.70	7.70	5.11/11.90
		1.0	3.20	3.75	0.8	7.75	9.40	4.48/10.45
		2.0	2.72	4.25	0.8	7.77	10.77	3.81/9.84
		3.0	2.63	4.32	0.8	7.75	10.90	3.68/9.99
1:4:4:2	60	0.5	2.60	4.50	0.8	7.90	11.80	3.64/9.52
		1.0	1.90	5.10	0.8	7.80	13.76	2.66/8.90
		2.0	1.65	5.25	0.8	7.70	14.35	2.31/8.99
		3.0	1.70	5.25	0.8	7.75	14.77	2.38/8.88
1:4:4:2	80	0.5	1.70	5.25	0.8	7.75	14.45	2.38/8.93
		1.0	1.50	5.50	0.8	7.80	15.11	2.10/8.17
		2.0	1.30	5.60	0.8	7.70	15.22	1.82/8.23
		3.0	1.34	5.52	0.8	7.66	15.17	1.88/8.19
1:4:4:2	100	0.5	1.55	5.40	0.8	7.75	15.06	2.17/8.33
		1.0	1.30	5.60	0.8	7.70	15.40	1.82/8.22
		2.0	1.33	5.62	0.8	7.75	15.34	1.86/8.17
		3.0	1.35	5.60	0.8	7.75	15.22	1.89/8.20
Starting aminolignin	-	-	6.75	-	1.00	7.75	-	10.85/13.09

Table 1 shows that increasing the solution acidity and the mass fraction of the modifying agents, formalin and NaH$_2$PO$_2$, causes a gradual increase of the capacity of acids and decreases the capacity of basic groups. The latter is due to the decrease in the amount of titratable N atoms in aminolignin during its condensation with aldehyde and sodium hypophosphite. A polyampholyte with a high cation-exchange capacity was formed with a four-fold excess of the *P*-containing component and formaldehyde. The residual content of active N in the amino derivative, which decreased from 10.85 to 2.10%, indicated that the amino groups were mostly phosphorylated by NaH$_2$PO$_2$ in acidic medium (Table 1). Incomplete conversion of the NH groups in the aminophosphine was apparently due to partial suppression of the di-addition reaction by formation of the Zwitter ion and the insufficient swelling of the hydrophilic copolymer of lignin with grafted aminoepoxy groups in ethyleneglycol, which is less polar than water. This decreases the diffusion of the reagents into the polymer.

The condensation kinetics at various temperatures also indicated that the primary and secondary amino groups in the lignin were more reactive. The process had a fast rate at low temperatures. Thus, 11.80% P was introduced at 60°C after 30 min; 13.76%, after 1 h. The P content in the polymer and the static exchange capacity (SEC) of the ion exchanger for NaOH solution (0.1 N) were 14.45-15.11% and 5.25-5.60 mg·eq/g, respectively, at 80°C and 0.5-1 h. The total exchange capacity (TEC) and capacity of strongly basic groups did not change during the modification.

Table 2 lists the chemical composition of aminolignin and its *P*-containing derivative prepared under the optimal conditions with a biopolyer:NaH$_2$PO$_2$:CH$_2$O:HCl mass ratio of 1:4:4:2, 80°C, and 1 h. Acidic aminolignin groups, carboxyls, hydroxyls, and methoxyls were not involved in the polymer-like conversions. The high content of alcohol OH groups in the amino derivative was due to their formation during synthesis of aminolignin via amination of epoxylignin by polyethyleneimine (PEI). As a result, α-oxide rings were opened to form hydroxyls.

IR spectroscopy and elemental and functional analyses confirmed that the modified lignin contained aminomethylphosphinic acid (Table 2). The strength of the bands at 984 and 1362 cm^{-1}, which correspond to stretching and deformation vibrations of P–OH (940-1020 cm^{-1}), alcohol OH (1100-993 and 1360-1260), and CH bonds in methylenes (1360-1280) increased in the spectrum of the phosphorylated aminopolymer compared with that of the starting amino derivative.

TABLE 2. Analytical Data for Aminolignin and Its *P*-Containing Derivative

| Lignin derivative	Content, %								
	N	P	OCH₃	OH_alcohol		OH_phenolic	OH_total	COOH	CO
				primary	secondary				
Aminolignin	13.09	-	5.71	1.62	18.92	1.24	21.78	1.48	2.69
Polyampholyte	8.17	15.11	5.68	8.86	18.77	1.23	28.86	1.51	2.65
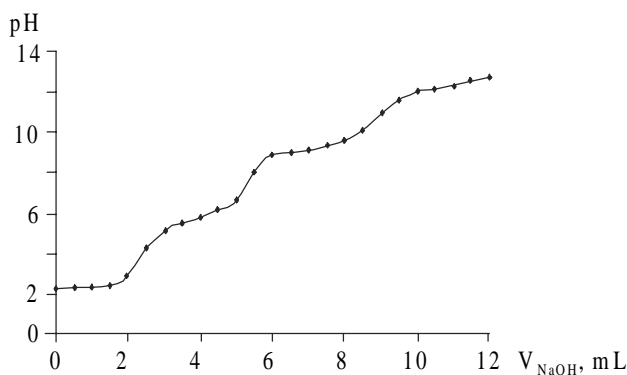
Fig. 1. pH titration of phosphorylated lignin amino derivative.

The C–O band in ether groups at 1190 cm^{-1} became sharper because of overlap of the P=O absorption, the location of which agreed with literature data and corresponded to P=O in phosphinic groups (1190-1200 cm^{-1}) [9, 10]. The spectrum lacked bands characteristic of P–H groups at 2350-2440 cm^{-1}. The increased number of primary OH groups in phosphorylated aminolignin from 1.62 to 8.86% compared with the starting polymer indicated that the *P*-acid group contained CH$_2$OH groups. Therefore, the ionizable group of the synthesized polyampholyte had the structure of α-aminomethylhydroxymethylphosphinic acid, NH–CH$_2$P(O)(OH)(CH$_2$OH).

The betaine-like Zwitter-ionic structure is typical for aminophosphoric polyampholyte. Figure 1 shows the potentiometric titration curve of the ion exchanger. Three distinct inflections were observed and corresponded to equivalence points of phosphoric acid, phenols, and NH$^+$ groups. It can be seen that the –PO$_2$H group ionizes first (pH 3-5). Protons are cleaved from betaine N atoms at more basic values (pH 6-9). Phenol hydroxyls in lignin dissociate last at higher pH values (10-12) than the betaines (Scheme 1).
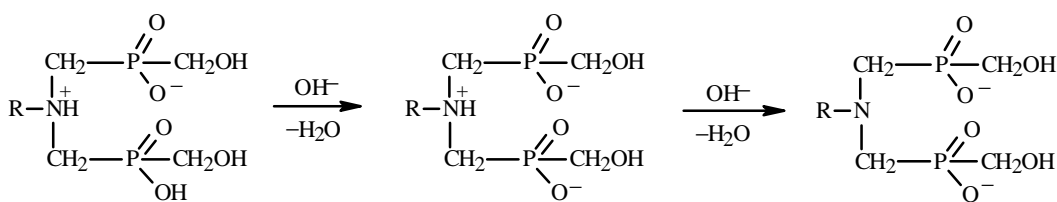
Scheme 1

The apparent dissociation constants calculated from the pH-curves of the crosslinked polyelectrolytes were pKα_1 = 3.2, pKα_2 = 7.75, and pKα_3 = 10.98 for P–OH, HN$^+$, and Ar–OH groups, respectively. The significant difference between the found pKα values of the active groups suggested that the polymer functional groups were successively ionized and deprotonated. The values were in good agreement with the literature. Thus, pKα of P–OH, HN$^+$, and Ar–OH in soluble low-molecular-weight aminophosphinic complexants and *N*- and *P*-containing chelating styrene sorbents with α-aminomethylphosphinic acid groups fall in the ranges 3.70-4.61, 7.58-7.60, and 10.84-11.25, respectively [3, 4, 11, 12]. The starting hypophosphorous acid is a rather strong acid with pKα = 1.07 [8, 13]. Addition of phosphinic groups to the high-molecular-weight organic matrix decreases its strength by two orders of magnitude. However, it is still impossible to confirm that the acid function is weak in

the lignin polyampholyte. According to the accepted classification [14], phosphorylated aminolignin is a moderate strength cation exchanger (pKα 3-5).

Thus, the investigations enabled a convenient method for preparing a crosslinked *P*- and *N*-containing polyampholyte to be developed. It has α-aminomethylphosphinic acid groups. The aminocopolymer of lignin and formaldehyde reacts with sodium hypophosphite in the presence of HCl in ethyleneglycol. The amino groups are mostly converted to iminophosphoryl groups under the derived optimal conditions to form a sorbent with increased ion-exchange ability. This opens broad possibilities for using it for selective extraction of ions of transition, nonferrous, rare, and other heavy metals with similar properties.

EXPERIMENTAL

The amino derivative was synthesized by catalytic alkylation of cotton-husk lignin using the diglycidyl ester of dihydroxydiphenylpropane followed by amination of the α-oxide derivative with PEI [15, 16]. Tables 1 and 2 give the properties. Phosphorylation of aminolignin was carried out in a three-necked flask equipped with a mechanical stirrer, an immersion thermometer, and a reflux condenser at 40-100°C for 0.5-5 h. The SEC of *N*- and *P*-containing polyampholyte for basic and acidic groups was determined by separate titration of the OH- and H-forms of the ion exchanger by HCl or NaOH solutions (0.1 N), respectively, in the presence of methylene blue indicator [17]. The equation is,

$$SEC = (100 - 4V)/10m,$$

where V is the volume of NaOH or HCl solution (0.1 N) consumed in the titration (mL) and m is the sample weight (g).

The SEC of strongly basic groups was established by storing an accurately weighed portion of ion exchanger in the OH-form (1 g) in NaCl solution (100 mL, 0.1 N) for 12 h and titrating an aliquot of the solution (25 mL) with HCl solution (0.1 N) [17]. The equation is,

$$SEC = 4V/10m,$$

where V is the volume of HCl solution (0.1 N) consumed in the titration (mL).

Potentiometric titration of the complexant in the H-form was carried out using separate portions at constant ionic strength in the solutions, the pH of which was monitored with an S20-K ion meter (Mettler Toledo, Switzerland) equipped with a universal combination electrode [18]. The apparent ionization constants of the functional groups (pKα) of the polyampholyte were estimated based on the pH-curves obtained.

The P content was found by organic microanalysis on a POCH instrument for microdetermination of C and H. The amount of N was found by pyrolysis of a sample in a closed volume followed by chromatographic measurement of N.

The content of functional groups in the modified lignins was determined by known methods [19]. Primary OH groups and total aliphatic OH groups were determined using phthalate; secondary OH groups, from their difference; methoxyls, by the Zeisel—Veiboeck—Schwappach method; carbonyls, by forming oximes; total number of acid, carboxyl, and phenol groups, by chemisorption.

The structure of aminophosphorylated lignin was established by IR spectroscopy. Spectra were recorded on a Nicolet 5700 FT-IR spectrophotometer in the range 400-4000 cm^{-1}. Samples were prepared as KBr disks (200 mg + 1 g sample).

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