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PREPARATION OF PHOSPHORIC—CARBOXYLIC CATION EXCHANGERS FROM WOOD CELLULOSE

E. E. Ergozhin,[1] N. A. Bektenov,[2]
A. K. Mekebaeva,[2] and N. N. Chopabaeva[1]

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Phosphorus-containing cellulose cation exchangers were synthesized by reaction of wood cellulose with orthophosphoric acid and the ternary polymer from glycidylmethacrylate, styrene, and maleic anhydride. The effects of the ratio of reactants, temperature, and duration of the reaction on the phosphorylation and exchange capacity of the modified cellulose material were studied.

Key words: wood cellulose; glycidylmethacrylate, styrene, maleic anhydride copolymer; phosphoric acid; phosphorus-containing cation exchanger; chemical modification; statistical exchange capacity.

Important problems of science and technology can be solved using synthetic polymeric ion exchangers. Preparation of these materials with rather high exchange capacities by sufficiently simple and inexpensive methods is essential for their application. Most known synthetic methods are multistep and complicated and require expensive and toxic reagents [1-3].

Sawdust from lumber mills is interesting as a cheap and available raw material for preparing sorbents. In contrast with several materials for producing various synthetic polymers, for example, petroleum, coal, and natural gas, the reserves of which are decreasing due to incessant consumption, cellulose from wood and other plant sources is a natural polymer, the supply of which can be renewed every year in any quantity according to demand with rational and judicious planning and use.

Natural cellulose contains several ionizable functional groups. Therefore, it acts as a weak ion exchanger [4]. Introducing various functional groups by esterification, alkylation, grafted copolymerization, and other methods can increase the exchange capacity.

The possibility of preparing cellulose cation exchangers by reaction of cellulose with various reagents has been reported [5, 6].

Our goal was to synthesize and study new phosphorus-containing cation exchangers from wood cellulose by chemical modification with orthophosphoric acid and the ternary copolymer from glycidylmethacrylate, styrene, and maleic anhydride (GMA-St-MA).

We used wastes from lumber mills of the Republic of Kazakhstan, pine sawdust of particle size 0.5-0.8 mm, to prepare the cation exchangers.

GMA copolymers containing reactive anhydride and epoxide groups were used because it was possible to synthesize highly stable ion exchangers with a practically unlimited set of functional groups by polymer-like conversions of their α-oxides and anhydrides.

The phosphoric and carboxylic groups were introduced into the natural biopolymer macromolecules by esterification of the wood cellulose with H_3PO_4 and further polymer-like conversion of the P–OH groups by the ternary copolymer GMA—St—MA according to Scheme 1.

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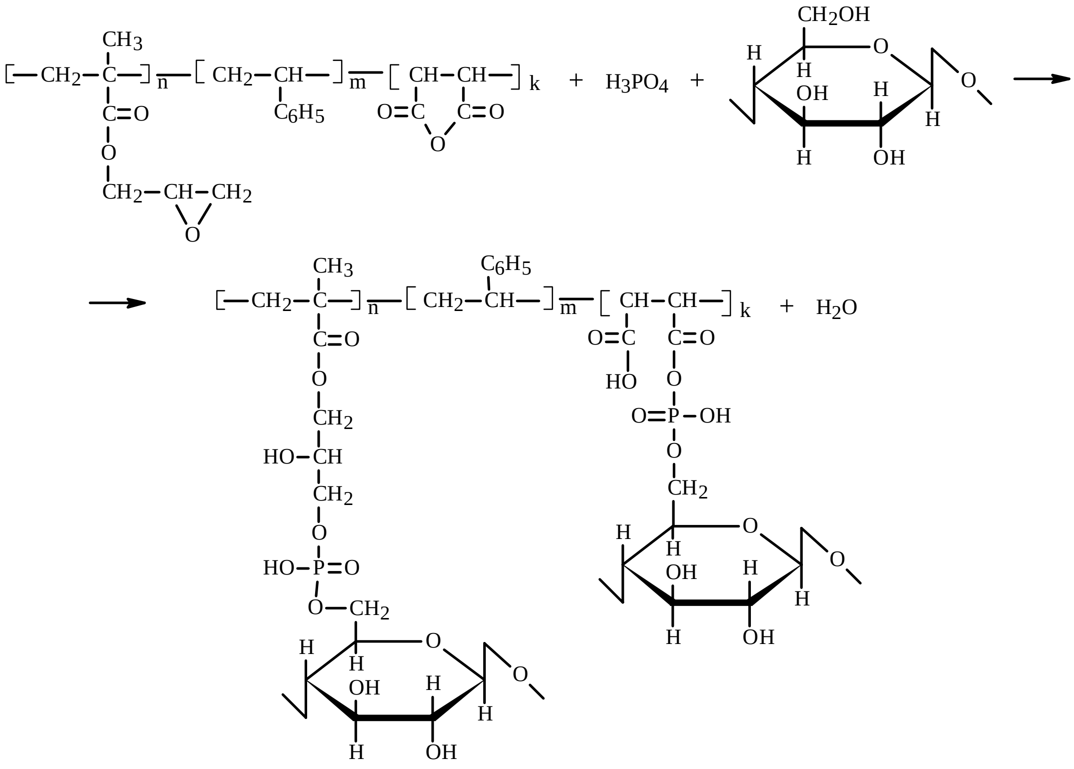
1) A. B. Bekturov Institute of Chemical Sciences, Ministry of Education and Science, Republic of Kazakhstan, 480100 Almaty, ul. Sh. Ualikhanova, 106, fax (83272) 91 57 65, e-mail: ics.rk@hotmail.com; 2) Abai Almaty State University, 480100 Almaty, ul. Kazybek bi, 30. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 234-237, May-June, 2003. Original article submitted January 6, 2003.



Scheme 1. Preparation of phosphoric—carboxylic acid cation exchangers from wood cellulose.

The effects of the ratio of reactants, temperature, and reaction time on the properties of the resulting compounds were studied to establish the optimum synthesis conditions for the phosphoric-acid cation exchanger.

Table 1 shows that the statistical exchange capacity (SEC) and phosphorus content in the reaction products increased as the temperature was increased from 20 to 80°C and the modification time increased from 2 to 8 h. The maximal P incorporation (11.5%) and, therefore, the highest capacity of the resulting P-containing cellulose cation exchanger, was 7.10 meq/g. It was achieved for a copolymer:phosphorylated wood cellulose mass ratio of 1:5.

IR spectroscopy was used to evaluate the structural changes after modification of the wood by orthophosphoric acid and GMA—St—MA. The spectrum of the unmodified wood has characteristic absorptions at 1200-1650 and 2900-3600 cm^{-1}. A band at 1500-1650 cm^{-1} is characteristic of benzene rings [7] in the lignin. Together with a strong band for =C–H stretches near 3030 cm^{-1}, it indicates the presence of aromatic rings. Stretching vibrations of C–H at 2950-2860 cm^{-1} are due to methylene and methine groups. Deformations of C–OH, CH, and CH_2 are found at 1300-1400 and 1425 cm^{-1}. The strong broad band at 3200-3600 cm^{-1} in the spectrum of starting cellulose is due to hydroxyl stretchings in H-bonds.

Changes due to incorporation of phosphoric acid into the wood occurred in the IR spectrum after modification of the wood. The most evident absorption changes caused by introducing phosphoric groups into the wood were observed at 420, 480, 520 (δ_{O-P-O}), 890 ($\delta_{P-OH\ \text{out-of-plane}}$), and 1220-1280 ($\delta_{P-OH} + \nu_{P=O\ \text{out-of-plane}}$). In addition to the appearance of these bands in the spectrum of the cation exchanger, absorptions of functional groups of the other modifying agent, GMA—St—MA copolymer, disappear. Bands at 760, 840, 910, 940, 1250, 3005, and 3065 cm^{-1} are missing from the spectrum. These correspond to stretches and deformations of C–O, C–C, and C–H bonds of the epoxy ring. Bands at 1848, 1790, and 1210-1310 are characteristic of C=O and C–O–C bonds of the anhydrides in GMA—St—MA. This is consistent with opening of three- and five-membered epoxide and anhydride rings of the ternary copolymer upon reaction with P–OH groups of the phosphorylated wood cellulose. The appearance in the IR spectrum of absorption bands at 1300-1400 cm^{-1} due to deformations of C–O and O–H on C=O indicate that carboxylic groups were formed by the modification (Scheme 1). These bands are partially masked by the absorptions of alcohol OH, methylene, and methine groups that are located in the same range.

TABLE 1. Preparation and Properties of Cellulose Phosphoric-Acid Cation Exchangers

Copolymer:phosphorylated wood cellulose ratio, mass frac.	Hardening conditions		SEC for NaOH (0.1 N), meq/g	P, %
	T, °C	τ, h		
1.0:0.2	80	6	3.45	6.90
1.0:3.0	80	6	4.90	8.55
1.0:5.0	80	6	7.10	11.15
1.0:8.0	80	6	5.80	10.25
1.0:5.0	20	6	4.58	8.25
1.0:5.0	40	6	5.72	9.32
1.0:5.0	60	6	6.05	10.15
1.0:5.0	100	6	6.65	10.45
1.0:5.0	80	2	4.15	8.12
1.0:5.0	80	4	6.45	10.39
1.0:5.0	80	8	6.85	10.81

Starting material, cellulose (sawdust), copolymer GMA—St—MA; H_3PO_4 linker.

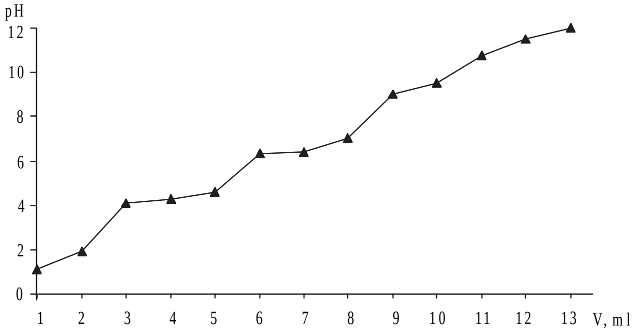


Fig. 1. pH-Titration of phosphoric-acid cation exchanger from wood cellulose and GMA—St—MA ternary copolymer.

Potentiometric titrations of the specimens were performed to prove the formation of acid esters and to determine the type of functional groups in the modified wood that impart to it the cation-exchange properties. The resulting pH curve (Fig. 1) is consistent with the presence of three inflection points, indicative of the presence of several types of ionizable groups. The apparent acid-dissociation constants of the functional groups that were calculated using the Henderson—Hasselbach equation [2] were 3.7, 5.8, and 7.5. The large difference in the $pK\alpha$ values leads to the conclusion that the functional groups ionize sequentially. The $pK\alpha$ values agree with those in the literature [3, 8, 9] and correspond to carboxylic ($pK\alpha$ = 4.9-6.0) and the first and second dissociation constants of phosphoric acid ($pK_{\mathrm{I\ P–OH}}$ = 3.2-3.9; $pK_{\mathrm{II\ P–OH}}$ = 7.2-7.9). The wood probably contains phenols in addition to these functional groups. Therefore, the break in the potentiometric-titration curve seen at pH > 9 (Fig. 1) may be due to dissociation of hydroxyls belonging not only to phosphoric and carboxylic acids but also phenols.

The modified specimens are chemically stable to agressive media, which indicates that the modified wood cellulose behaves differently in acid, base, and oxidant solutions. The chemical stability of the modified wood is [SEC in NaOH (0.1 N), meq/g]: starting 7.10; after treatment with NaOH (5 N), 7.00; H_2SO_4 (5 N), 6.95; HNO_3 (1 N), 7.02; and H_2O_2 (10%), 6.9.

The greatest loss of capacity was observed in H_2O_2. Apparently this is due to degradation of the functional groups (loss of carboxylic groups, loss of phosphorus via hydrolysis of ester and polyphosphate chains) responsible for ion exchange.

Thus, cation exchangers prepared by chemical modification of wood cellulose by phosphoric acid and the ternary copolymer GMA—St—MA are singly and doubly substituted esters that contain two types of functional groups of different acidity (medium- and weak-acid: P–OH, COOH, and R–OH) and are stable in mineral acids, bases, and oxidants.

EXPERIMENTAL

Wood cellulose was modified by H_3PO_4 (75%) ($\rho = 1.4$ g/cm^3). The natural biopolymer macromolecules were esterified by the literature method [6].

The ternary copolymer GMA—St—MA was prepared by radical polymerization in C_6H_6 containing initiator ($5 \cdot 10^{-3}$ M) at 60°C in sealed ampuls of molybdenum glass under an inert atmosphere (Ar). The copolymer was purified of unreacted monomer by reprecipitation twice from acetone in diethylether. Specimens were dried at room temperature in a vacuum chamber.

Phosphorylated wood celluose was transformed chemically with GMA—St—MA in a three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel. The flask was charged with the calculated amount of copolymer solution. The viscous phosphorylated wood cellulose was gradually added dropwise with vigorous stirring while the temperature was raised from 30 to 60°C. After the reaction was complete, the resulting gel was loaded into a porcelain dish and solidified in a drying chamber at 60-100°C for 2-8 h. The synthesized P-containing cellulose cation exchangers were washed repeatedly with solvent, extracted in a Soxhlet extractor to remove unreacted reagents, and dried to constant mass in vacuo at 25-30°C. The physicochemical properties were determined using standard methods [1-3].

IR spectra of the studied compounds were recorded on a Specord-80M spectrophotometer in KBr disks.

The potentiometric titration of modified wood specimens was carried out using individually weighed samples and keeping the ionic strength constant [1-3]. The pH of the solution was monitored using an EV-74 universal ionomer equipped with glass and silver-chloride electrodes.

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