MODIFIED LIGNIN WITH ION-EXCHANGE PROPERTIES

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Polyfunctional ion-exchangers were synthesized by heterophase amination of α-oxide derivatives of hydrolyzed lignin with aliphatic di- and polyamines. Optimal conditions for their preparation were determined. Certain physicochemical properties were studied.

Key words: lignin, α-oxide derivative, polyamines, amination, ion-exchanger, static exchange capacity.

The goal of our work was to synthesize and investigate polyfunctional ion-exchangers based on lignin of cotton husks from Shymkent Hydrolysis Plant (SHP) by amination of its α-oxide derivatives by aliphatic di- and polyamines.

Lignin of cotton husks is waste from SHP, which specializes in the production of protein-feed yeast by biochemical processing of xylose obtained by hydrolysis of complex polysaccharides isolated from agricultural cultures.

The chemical composition of lignin from SHP cotton husks is as follows: basic components (%) (lignin, 72.0; cellulose, 14.50; extractable substances, 9.01; ash content, 3.43); functional groups (%) (OCH_3, 8.70; OH, 8.50; COOH, 1.27; CO, 5.18).

It was established previously that oxirane rings can be introduced into cotton-husk lignin by catalytic alkylation by the bifunctional glycidic oligomer ED-20 [1].

Epoxidized lignin was aminated by polyethylenimine (PEI), polyethylenepolyamine (PEPA), and hexamethylenediamine (HMDA) to produce aminoepoxide anion-exchanger. The influence of the nature and concentration of the aminating agent, temperature, and length of polymer-like transformations on the properties of the *N*-containing derivatives was studied to establish the optimal conditions for synthesizing the surface-modified natural polyelectrolytes.

Table 1 shows that the static exchange capacities (SEC) of the ion-exchanger weakly basic groups, total static exchange capacities (TSEC) of the samples, and the content of total and titrable nitrogen in them increased in proportion to an increased content of di- and polyamines in the starting reaction mixture. The capacity did not increase for esterified lignin to PEI, PEPA, and HMDA ratios greater than 1.0:1.50, 1.0:1.00, and 1.0:1.50 mass fraction. This is obviously due to total conversion of oxirane groups in the epoxidized polymer. Increasing the content of aminating agent further decreased significantly the yield of anion-exchangers. The decrease in exchange capacity of the ion-exchangers based on the low-molecular-weight diamine as its concentration in the system increased is probably due to the fact that the α-oxide ring was opened with a sufficient amount of HMDA mainly due to the primary or secondary amino groups and to a lesser extent the tertiary ones. This caused a regular decrease of the exchange capacity for the strongly basic groups.

Increasing the mass fraction of di- and polyamines in the system increased the swelling capacity for all anion-exchangers. This was seen in the increasing V_{sp} values, which characterize the volume of lignin amino derivatives at the swelling limit (Table 1). Such behavior of cross-linked polyelectrolytes is apparently due to fewer cross-links in them and the formation of poorly cross-linked aminopolymers [2, 3].

Varying the temperature and length of the modification of the glycidic derivative of hydrolyzed lignin could in certain instances improve the physicochemical properties, i.e., the quality of the synthesized anion-exchangers, and also establish the optimum conditions for performing the chemical transformations. Based on the results, anion-exchangers with high exchange capacity form upon lowering the reaction temperature to 40°C for all exchangers regardless of the nature of the amines used (Table 2). The TSEC of the lignin polymers aminated by PEI, PEPA, and HMDA reached 7.85, 5.55, and 3.50 mg-eq/g, respectively.

TABLE 1. Effect of Ratio of Reagents on Composition and Physicochemical Properties of Lignin Anion-Exchangers ($T_{aminat.} = 80°C$, $\tau_{aminat.} = 3$ h, $T_{solidif.} = 80°C$, $\tau_{solidif.} = 10$ h, V_{sp} = specific volume)

[Epoxylignin]:[amine], mass fract.	SEC for 0.1 N, mg-eq/g		TSEC, mg-eq/g	N content, %		V_{sp}, mL/g	Yield, %
	HCl	NaCl		$N_{titr.}$	$N_{tot.}$		
PEI							
1.0:0.25	2.75	0.25	3.00	3.85	6.17	4.52	99.90
1.0:0.50	3.75	0.25	4.00	5.25	11.69	5.13	99.27
1.0:0.75	4.36	0.50	4.86	6.10	11.75	5.23	98.55
1.0:1.00	4.75	1.00	5.75	6.65	11.82	7.02	97.83
1.0:1.50	5.25	1.20	6.45	7.35	12.13	7.56	97.70
1.0:2.00	4.00	0.75	4.75	5.60	10.87	4.92	92.45
PEPA							
1.0:0.25	2.00	0.10	2.10	2.94	5.21	2.94	95.46
1.0:0.50	3.00	0.15	3.15	4.41	7.15	3.61	93.30
1.0:0.75	3.60	0.50	4.10	5.74	7.34	3.87	92.15
1.0:1.00	3.70	0.40	4.10	5.74	7.98	4.12	87.71
1.0:1.50	3.70	0.00	3.70	5.18	7.17	4.92	75.00
HMDA							
1.0:0.25	1.20	0.50	1.70	2.38	2.97	2.13	100.0
1.0:0.50	1.93	0.30	2.23	3.12	3.91	2.78	100.0
1.0:0.75	2.30	0.20	2.50	3.50	4.52	3.50	100.0
1.0:1.00	2.80	0.15	2.95	3.85	4.87	4.50	100.0
1.0:1.50	3.50	0.00	3.50	4.90	5.43	5.00	98.27
1.0:2.00	3.55	0.00	3.55	4.97	5.45	5.75	92.78

Increasing the reaction temperature to 100°C reduced the capacities of the polyelectrolytes based on the high-molecular-weight amines PEI and PEPA and had practically no effect on the ion-exchange properties of the anion-exchangers based on the diamine. These differences are due to the nature of the modifying agents. Apparently surface-bound epoxide rings react preferentially at elevated temperatures with active hydrogen of hydroxyls of lignin rather than with NH groups of the polyamines due to the poorer steric availability of the latter and the slow segmental mobility of their macromolecules caused by the linked structure.

The reduced yields and nitrogen contents in the reaction products from PEI and PEPA as the temperature was increased from 40 to 100°C confirmed this hypothesis. Under the given temperature conditions, amination was completed in 1 h for HMDA and PEPA and in 2 h for PEI. This also was due to the molecular-weight characteristics of the amines. Increasing the reaction time further did not change the exchange capacity, composition, or yield of the anion-exchangers (Table 2).

Potentiometric experiments were performed to determine the degree of dissociation of the amino groups in the lignin structure. Figure 1 shows that the shape of the pH curves of the cross-linked polyelectrolytes was determined by the nature of the aminating agent and the concentration of their functional groups. The flat nature of the curves was consistent with polyfunctional anion-exchangers based on lignin amino derivatives. The lack of sharp inflection points did not allow the quantity of primary and secondary amino groups to be reliably estimated. Average values of apparent dissociation constants were calculated from the single inflection point corresponding to amino groups of different basicity. For lignin with PEI, PEPA, and HMDA groups, pK_b values were 6.76, 6.20, and 6.27, respectively. The small difference in the pK_b values suggested that the amino groups were ionized practically simultaneously. The resulting values agreed with those in the literature and indicated that the lignin ion-exchangers were moderately basic ($K_b \approx 10^{-3}$-10^{-5} M, pK_b = 3-5) [4-7] and contained primary ($-NH_2$), secondary (=NH), and tertiary (N≡) amino groups and some quaternary alkylammonium groups ($-N≡$) bonded to the aliphatic chain of the matrix.

TABLE 2. Physicochemical Properties of Ion-Exchangers Based on Hydrolyzed Lignin as Functions of Temperature and Length of Amination of Its α-Oxide Derivative ($T_{solifid.}$ = 80°C, $\tau_{solifid.}$ = 10 h)

| [Epoxylignin]:[amine], mass fract.	Amination conditions		SEC for 0.1 N, mg-eq/g		TSEC, mg-eq/g	N content, %		Yield, %
	T°, C	τ, h	HCl	NaCl		$N_{titr.}$	$N_{tot.}$	
PEI								
1.0:1.50	40	3	6.75	1.10	7.85	10.99	12.90	100.00
	60	3	6.00	1.00	7.00	9.80	12.60	99.64
	80	3	5.25	1.00	6.45	9.03	12.13	97.70
	100	3	5.00	1.00	6.00	8.40	11.92	95.73
	40	1	6.00	0.90	6.90	9.66	12.67	97.88
		2	6.75	1.00	7.75	10.85	12.84	100.0
		4	6.75	1.00	7.75	10.85	12.89	100.0
PEPA								
1.0:0.75	40	3	4.95	0.60	5.55	7.77	8.96	90.50
	60	3	3.96	0.50	4.46	6.24	7.42	91.30
	80	3	3.60	0.50	4.10	5.74	7.34	92.15
	100	3	3.30	0.40	3.70	5.18	6.59	90.07
	40	1	4.95	0.60	5.55	7.77	8.91	90.13
		2	4.95	0.60	5.55	7.77	8.95	90.20
		5	4.95	0.60	5.55	7.77	8.99	90.70
HMDA								
1.0:1.50	40	3	3.50	0.00	3.50	4.90	5.40	98.11
	60	3	3.50	0.00	3.50	4.90	5.41	98.24
	80	3	3.50	0.00	3.50	4.90	5.43	98.27
	100	3	3.58	0.00	3.58	5.01	5.50	98.39
	40	1	3.50	0.00	3.50	4.90	5.42	98.20
		2	3.50	0.00	3.50	4.90	5.46	98.25
		5	3.50	0.00	3.50	4.90	5.48	98.28
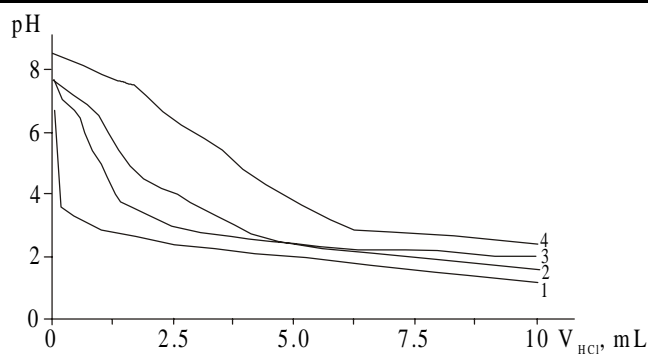
Fig. 1. Plots of pH of starting lignin (1) and that modified with HMDA (2), PEPA (3), and PEI (4).

Thus, polyfunctional anion-exchangers with high ion-exchange capacities were synthesized by heterophase amination of α-oxide derivatives of cotton-husk lignin from SHP by aliphatic di- and polyamines. This enabled multi-ton wastes of the hydrolysis industry to be recycled and used in progressive sorption technologies.

EXPERIMENTAL

Lignin from cotton husks from SHP was extracted with alcohol:benzene (1:2, v/v) for 4 h, then with alcohol (95%) for 4 h in a Soxhlet apparatus, and then with distilled water for 1 h on a water bath [8]. A highly dispersed preparation with a large internal surface area was prepared by activating extracted lignin by grinding in a mortar with a small amount of distilled water until a homogeneous paste formed and was diluted with a 10-fold excess of water. After individual large particles settled, the upper layer with suspended fine particles was decanted onto a filter and pulled through. The precipitate on the filter was slowly washed with 1,4-dioxane and then ether to remove water from it, dried in vacuo, and stored in a desiccator [9].

The chemical composition of the hydrolyzed lignin was determined by a known method [8-10].

The glycidic derivative of hydrolyzed lignin with 4.79% epoxide groups was synthesized by esterification of lignin with a solution of epoxide resin ED-20 (25%) in DMF in the presence of triethylamine (TEA) catalyst at a 1.0:1.5 mole ratio for 1 h at 100°C [1]. Esterified samples were purified of unreacted compounds by extraction with benzene in a Soxhlet apparatus for 5-6 h and aminated by PEI, PEPA, and HMDA for 1-5 h at 40-100°C. Esterification and amination were carried out in a three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Polymers were solidified in ceramic crucibles in a muffle furnace.

PEI (Fluka AG) of molecular weight (MW) $30 \cdot 10^3$-$40 \cdot 10^3$ and PEPA (Nizhnii-Tagil plastic plant) of MW 265 were stored over granulated KOH; HMDA, in an air-tight vessel; and were used without additional purification. Ion-exchangers were prepared as before for the experiments [11].

The V_{sp} values were determined by placing a weighed portion of air-dried anion-exchanger (OH-form) in a volumetric cylinder with a ground-glass stopper and 0.1-mL markings, compacting by tapping on a wood surface, and treated with distilled water [11]. The cylinders were kept vertical for 24 h and then stood up vertically. The volume of the swelled polymer in them was determined. The V_{sp} values were calculated from the volume ratio of swelled sample (V_s, mL) to the mass of dry polymer (m, r):

$$V_{sp} = V_s/m$$

The SEC was determined by storing an accurately weighed portion of anion-exchanger (OH-form, 1 g) in HCl (100 mL, 0.1 N) for 24 h and titrating an aliquot of the solution (25 mL) with NaOH solution (0.1 N) with methylene blue indicator [11]:

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

where V is the volume of NaOH solution (0.1 N) consumed in the titration (mL) and m is the weight of anion-exchanger (g).

Potentiometric titration of anion-exchangers was performed using the method of separate weights. For this, polymer (0.1 g) in the OH-form (calcualted for dry compound) was treated with HCl (50 mL, 0.1 N), the amount of which was varied from 0 to 15 mg-eq/g of ion-exchanger in the range 0.2-0.5 mg-eq/g. The ionic strength of the solution was maintained by adding the calculated amount of NaCl solution (0.1 N, $\mu = 1$). After equilibrium was established (10 d), the pH of the aqueous solutions was measured with an S20-K ion-meter (Mettler-Toledo) equipped with an InLab413 universal combination electrode (three in one) that combined a measuring electrode, reference electrode, and temperature sensor in a single polymeric unbreakable body. A potentiometric titration curve was constructed in coordinates of pH and amount of titrant (mL) using the results. The composition and amount of functional groups in the polymer was found from inflection points on the titration curve.

Apparent dissociation constants of ionizable groups of the anion-exchangers (pKα) were determined from the potentiometric titration data [6, 11]. The degree of their neutralization by the working solution (α) was calculated after determining the content of functional groups for each titration point. It was kept in mind that in the absence of acid $\alpha = 0$ and at the neutralization point $\alpha = 1$. Therefore, there is a direct relationship between the amount of added acid and α. Curves of the function pH = $f[\log(\alpha/(1 - \alpha))]$ were constructed from the found values of α and the pH values corresponding to them. Extrapolation of the linear function to $\log[\alpha/(1 - \alpha)] = 0$ ($\alpha = 0.5$) defined pK in the Henderson-Hasselbach equation:

$$pH = pK + m \log[(1 - \alpha)/\alpha],$$

where pK is the dissociation constant of the functional groups, m is an empirical coefficient of inter-unit interaction of the polymer chain, and α is the degree of neutralization of the active groups.

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