ION-EXCHANGE PROPERTIES OF AMMONIATED LIGNIN

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The oxidative ammonolysis of hydrolysis lignin from sunflower husks has given ion-exchange materials with amphoteric properties. The greatest total exchange capacity of the sample with respect to 0.1 N caustic soda solution amounted to 11.5 meq/g, and with respect to 0.1 N hydrochloric acid solution to 0.6 meq/g. The processes of ion exchange with heavy-metal cations are accompanied by complex formation. The bond of the metal cations with the lignin in the complexes is effected through nitrogen and the oxygen of a nonalcoholic group.

Lignin and its nitrogen-containing derivatives possess an adsorption capacity. However, this property of natural lignin does not appear in full measure, since the internal surface of its macromolecule is inadequately developed, which considerably lowers its reactivity [1].

The sorption properties of lignin and its derivatives depend to a considerable degree on the number of ionogenic groups and, in particular, of carboxy, alcohol, and amine groups in its macromolecule, these being responsible for the capacity of lignin for playing the part of a chelate sorbent [2] and of a complex-forming agent with heavy metals [3]. A rise in the amount of functional groups increases its absorption and ion-exchange capacities, and also its reactivity.

Investigations that we have performed on the transformation of hydrolysis lignin from sunflower husks in an aqueous ammoniacal medium in the presence of atmospheric oxygen [4] have shown that oxidative processes take place mainly in the direction of the addition of nitrogen and of an increase in the number of carboxy groups and of alcohol and phenol groups.

Lignin ammoniated in this way is used as a rust preventive [5, 6]. This has roused our interest in ammoniated lignin as an ion-exchange and, in particular, a cation-exchange, material.

To obtain cation-exchange materials possessing the maximum exchange capacity, samples of hydrolysis lignin were treated with a solution of NH_4OH by a method described previously [4] at various temperatures, and in the resulting sample of ammoniated lignin (AL) the total exchange capacities (TECs) with respect to 0.1 N NaOH solution were determined (Table 1).

A comparison of the TEC results with analyses of the reaction products for their active hydrogen contents shows their complete interchangeability: With an increase in the active hydrogen content the TEC rises, which indicates the participation of OH groups in ion exchange. This is also confirmed by a test of the TECs of samples methylated with dimethyl sulfate (Table 1).

The study of the properties of ion-exchange material also revealed its selectivity for the absorption of heavy-metal cations, especially Fe^{3+}.

Since the absorption of heavy-metal cations on an ion-exchange material depends greatly on the pH of the medium [7], we determined the dependence of the static exchange capacity (SEC) for the Fe^{3+} cation of the samples of ammoniated lignin obtained on the pH of the medium. As can be seen from Fig. 1, the absorption of Fe^{3+} increased only slightly with a rise in the pH from 0.1 to 2, rose sharply from 2 to 3, and then fell smoothly.

The results of determinations of the SECs of samples I-IV in the Na form with respect to 0.1 N $FeCl_3$ solution at pH 2.7 are given in Table 2, from which it can be seen that the SEC increases with a rise in the ammonolysis temperature.

A check on the reproducibility of the ion-exchange capacities of samples I-IV for Fe^{3+}

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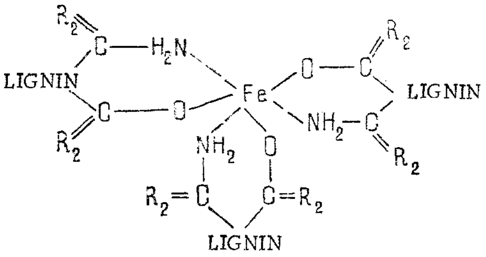
TABLE 1. Total Exchange Capacities of Samples of Ammoniated Lignin, meq/g

Sample	Temperature of synthesis, °C	TEC for 0.1 N NaOH	Active hydrogen content, meq/g	TEC for 0.1 N HCl	TEC of dimethyl sulfate-methylated samples for 0.1 N NaOH
I	Initial	4.8	4,8	0	0
II	50	5,0	5,1	0	0
III	100	6,5	6,4	0,1	0
IV	1[illegible]0	9,7	9,7	0,2	0
V	175	11,2	11,2	0,5	0
VI	200	11,5	11,6	0,6	0

after their regeneration showed a marked decrease in the SEC (Table 2). We assume that this phenomenon is explained by the formation of chelate compounds of the type of



or, in the general form, $Fe[(OR)_6]^{3-}$, where R is the lignin component. Heavy metals with complex-forming properties are capable of being absorbed by basic ion-exchange materials with the formation of stable complexes of the type of $(RNH_2)_2MeX_2$, $(R_2NH)_2MeX_2$, and $(R_3N)_2MeX_2$, which do not decompose when the anion-exchange materials are regenerated [8].

The presence in the ammoniated lignin of bound nitrogen, forming an anion-exchange group, also explains its complex-forming capacity.

To check this hypothesis we obtained samples of ion-exchange material from lignin at various temperatures, using in place of a 25% solution of ammonia a caustic soda solution of the same concentration. The SECs of these samples (VII–XI) in the Na form at pH 2.7 with respect to a 0.1 N solution of $FeCl_3$ before and after regeneration are given in Table 2. As can be seen from the Table, the change in the SECs was insignificant.

The process of absorption on anion-exchange materials may be accompanied by complex-formation not connected with ion exchange, and therefore we determined the SECs with respect to 0.1 N $FeCl_3$ solution of samples I–XI in the H form at pH 2.7 (Table 2). Under these conditions there was no absorption for the given ion. Consequently, the formation of stable complexes with Fe^{3+} ions is due to the presence of nitrogen in the ammoniated lignin molecule.

Analysis of the solid phase of the ion-exchange material after its regeneration for its content of nitrogen and of Fe^{3+} ions makes it possible to state (Table 3) that in the complex obtained with the ligand–metal (1 : 1) composition, the Fe^{3+} cation is bound to the nitrogen by one valence.

The second functional group participating in the formation of the stable chelate must be assumed to be an OH group. The protection of various OH groups by the corresponding reagents (acetic anhydride and dimethyl sulfate [9], and a mixture of methanol with HCl [10]) showed that this was a benzyl alcohol group. IR spectroscopy confirmed these conclusions. A comparison of the relative optical densities of samples of ammoniated lignin after their regeneration (Table 3) shows an increase in the intensity of absorption of the 1660 cm^{-1} band due to CO groups [11], while the 1710 cm^{-1} band which is characteristic for COOH and CO groups and also the 1365 cm^{-1} band corresponding to phenolic OH groups [12] did not change their intensities.

EXPERIMENTAL

The samples of hydrolysis lignin were prepared by a method described previously [4] be-

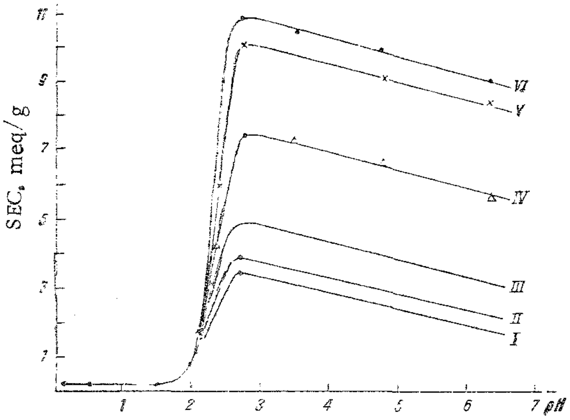


Fig. 1. Dependence of the static exchange capacity of samples I-VI on the pH of the medium.

fore further treatment. Samples II-VI were obtained from the lignin in an autoclave by the action of 25% aqueous ammonia solution, and VII-XI by the action of a 25% caustic soda solution at temperatures of 50, 100, 150, 175, and 200°C, respectively, for 5 h. Then the samples were washed with 15 volumes of 5% HCl and with distilled water to neutrality and the absence of Cl^-. They were converted into the Na form by treatment with an excess of a 5% solution of NaOH and were washed to neutrality. The TECs were determined by potentiometric titration [7] on an LPU-01 instrument with a glass electrode.

The SECs of the ion-exchange materials in the Na form were determined with respect to 0.1 N solutions of $FeCl_3$ and $CaCl_2$ by the static method [7] after contact for three days. The ion-exchange material was regenerated with 5% HCl until Fe^{3+} ions were absent. The amount of Fe^{3+} in the equilibrium solution was determined by a colorimetric method with sulfosalicylic acid [13].

The amount of Fe^{3+} was calculated from a calibration graph plotted with allowance for additions to the working solution in order to maintain the pH of the medium.

The nitrogen content of the solid phase of the ion-exchange material after its regeneration was determined by the Kjeldahl method, and the amount of Fe^{3+} by a colorimetric method [13] after the mineralization of the samples.

IR spectra were recorded on an IR-10 spectrophotometer in KBr tablets (3 mg of substance and 300 mg of KBr), and relative optical densities were calculated by the method of Karklin' and Érin'sh [14]. Table 3 gives the mean values of three measurements. As internal standard we took the 1510 cm^{-1} frequency corresponding to the vibrations of the benzene nucleus [15]. The base line was drawn through the minima at 1800 and 700 cm^{-1}.

TABLE 2. Equilibrium Exchange Capacities of Samples and the Results of Analyses of the Solid Phase after the Regeneration of the Ion-Exchange Material

Sample	Method of synthesis	Temp. of synthesis	SEC, meq/g			Solid phase, %	
			Na-form	Na form after regeneration	H form	nitrogen unsaponifiable by 35% HCl	Fe^{3+}
I	Initial	—	3,5	1,1	2,4	0,7	0,72
II	25% ammonia	50	3,9	1,2	2,7	0,85	0,83
III	„	100	5,0	1,4	3,7	1,12	1,10
IV	„	150	7,6	2,1	5,4	1,64	1,63
V	„	175	10,2	2,4	7,8	2,34	2,36
VI		200	10,9	2,8	8,2	2,52	2,50
VII	25% caustic soda	50	3,5	3,4	0	0,2	0
VIII	„	100	4,9	4,8	0	0,1	0
IX	„	150	7,9	7,9	0	0,1	0
X	„	175	10,8	10,7	0	0,1	0
XI	„	200	13,6	13,4	0	0,1	0

TABLE 3. Relative Intensities of the Absorption Bands in the IR Spectra of the Initial Hydrolysis Lignin (1), That Treated with Ammonia at 200°C (2), and the Solid Phase after Regeneration (3)

Frequency, cm^{-1}	Sample		
	1	2	3
1710	0,47±0,03	0.51±0,04	0,53±0,04
1660	0,51±0,03	0.67±0,02	0,76±0,02
1600	0,80±0,03	0.99±0.03	1.08±0,02
1510	1,00	1.00	1 00
1365	0,87±0.03	0,86±0,02	0.87±0,03

SUMMARY

1. Ion-exchange materials possessing amphoteric properties have been obtained by the oxidative ammonolysis of hydrolysis lignin.

2. The process of ion exchange with Fe^{3+} cations is accompanied by the formation of chelate compounds.

3. The bond of the metal ion with the ion-exchange material is effected through nitrogen and the oxygen of a benzyl alcohol group.

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