

Studies on the Sulphonation of Lignin *

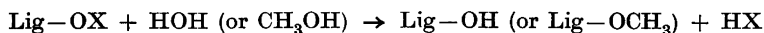
II. Sulphonation of Ethoxylated Lignin Sulphonic Acids of low Sulphur Content **

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In 1939 Kullgren made the important observation that strong pulp which had been successively washed with dilute hydrochloric acid and with distilled water on heating with distilled water yielded soluble lignin sulphonic acids¹. If the heating was carried out with methanol instead of water, soluble lignin sulphonic acids were also obtained which, however, showed an increased methoxyl content.

Strong sulphite pulp contains a small amount of solid, insoluble lignin sulphonic acids. When heated with water or methanol hydrolysis or methanolysis takes place with formation of soluble lignin sulphonic acids. Schematically the process may be represented in the following way:



(Lig-OX is the solid lignin sulphonic acid, X a lignin residue = Lig or a carbohydrate. Lig-OH and Lig-OCH₃ are the resulting soluble acids.)

The yield of soluble acids obtained in Kullgren's experiments was low.

Hägglund and Johnson applied the Kullgren process to sulphonated wood, obtained by heating wood with strong sodium sulphite solutions, and much larger yields of "low-sulphonated, soluble lignin sulphonic acids" were obtained². Such acids prepared by heating with water have been subjected recently to stepwise sulphonations with ordinary sulphite cooking acid³. It

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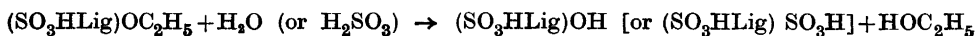
** Part 47 on the chemistry of the sulphite process by E. Hägglund and co-workers.

was found that for each sulphonic acid group introduced approximately one hydroxyl group capable of acetylation disappears.

We have refluxed sulphonated wood in "the hydrogen state" with absolute ethanol. The soluble lignin sulphonic acids obtained by this treatment were isolated by shaking the alcoholic solution with barium carbonate and they were obtained directly in a state of high "purity". As expected these acids were low-sulphonated and contained ethoxyl groups which could be split off by heating with mineral acids.

On heating with strong sodium sulphite solution of pH 5.45 (measured in the cold) some sulphonation took place but no ethoxyl groups were eliminated.

Heating with normal sulphite cooking acid furnished highly sulphonated products containing no ethoxyl groups. A corresponding amount of ethanol was found in the liquor. The "low-sulphonated, ethoxylated lignin sulphonic acids" apparently react in a way which is closely analogous to that of sulphonated wood and they may be regarded as simple, soluble models for the low-sulphonated, insoluble lignin sulphonic acids of sulphonated wood:



It should be noted that experiments closely analogous to those described in this paper were carried out fifteen years ago by Holmberg⁴. "Ethyl lignin" ("ethanol lignin") was subjected to the action of thioglycolic acid when normal lignin thioglycolic acids were obtained. Holmberg interpreted this result by assuming that ethanol lignin is a mixed ethyl-benzyl-ether which is cleaved by thioglycolic acid with the formation of ethanol and S-substituted thioglycolic acids. He also found that several ethyl ethers (ethyl α -phenethyl ether, ethyl benzhydryl ether) reacted similarly.

EXPERIMENTAL

Preparation of low-sulphonated, ethoxylated lignin sulphonic acids

In a rotating autoclave of stainless steel finely disintegrated, acetone-extracted wood (1.1 kg = 1.0 kg dry) was heated with a cooking acid as described in an earlier paper⁵. The acid was prepared in the following manner. Sulphur dioxide was passed into a solution of sodium hydroxide (583 g) in water (5 l) until pH 5.23 (20°) was reached. The sulphonated wood was washed very carefully with large amounts of distilled water and finally dried in the air. (Yield 910 g = 839 g dry).

Air-dry sulphonated wood (100 g) was slowly washed with 0.1 *N* hydrochloric acid (2.5 l) and finally with distilled water until the filtrate contained no chlorine ions. The material was then transferred into a wide glass tube and alcohol (95 %) slowly passed through from below in order to remove water. Finally absolute alcohol was passed in

until determinations of the specific gravity indicated that absolute alcohol was leaving the tube.

The material was immediately plunged into absolute alcohol (1.5 kg) and the mixture refluxed for two hours (calcium chloride tube). The alcoholic solution was rapidly removed by suction and the residue again heated with absolute alcohol (1 kg). The process was repeated twice. In this way three alcohol extracts (I—III) were obtained. They were immediately shaken with an excess of pure barium carbonate, suspended in a little water, in order to neutralise and precipitate the lignin sulphonic acids. The precipitates were separated by centrifuging and then shaken with water. The resulting solution was again centrifuged and then poured into eight volumes of methanol. The precipitate was collected and the dissolution-precipitation process repeated. The product was stirred with methanol and centrifuged, repeatedly stirred with ether and centrifuged, and finally spread on an inclined glass plate to ensure rapid drying. Yield from extract I 4.1 g (3.9 g dry), from II 2.5 g (2.4 g dry) and from III 2.0 g (1.9 g dry) barium lignin sulphonate. (Preparations I, II and III.) For the analyses, *cf.* Table 1.

Similarly extracted and sulphonated spruce wood (700 g air-dry) was treated in the same way with hydrochloric acid, distilled water and alcohol, and refluxed with absolute ethanol (4 hours). The precipitated barium salts were dissolved in water (1500 ml) and the solution concentrated to 300 ml by vacuum distillation. The solution was then freed from barium ions by a cation exchanger. The sulphonic acids were purified by two precipitations with 4,4'-bis-dimethylamino-diphenylmethane and converted into the barium salt as described earlier^{5,6}. Yield 27.2 g (25.5 g dry). Preparation IV. For analyses, *cf.* Table 1.

Sulphonation of low-sulphonated, ethoxylated lignin sulphonic acids

The barium salts I—IV (air dry, corresponding to 1.0 g dry salts) were dissolved in a small volume of water and the solutions freed from barium ions by passing through a cation exchanger. Calcium carbonate (0.715 g) was added to the filtrate (40 ml) and sulphur dioxide passed into the mixture until the "total amount of SO₂" was 5 g per 100 ml solution ("CaO" = 1.0, "SO₂" = 5). The solutions were heated in sealed tubes of Pyrex glass for 6 hours at 135°. After cooling, carbon dioxide was passed through the solutions to remove excess sulphur dioxide. The calcium ions were removed by passing through a cation exchanger, and the solutions were again treated with carbon dioxide and finally neutralised with barium carbonate. After filtration the solutions were concentrated to a small volume by vacuum distillation, centrifuged and precipitated by pouring into five volumes of alcohol. The precipitates were collected by centrifuging, carefully washed with alcohol and with ether as already described, and dried in the air.

The preparations are designated I S, II S, III S and IV S respectively. Yield of I S 0.77 g (0.74 g dry), of II S 0.80 g (0.77 g dry), of III S 0.82 g (0.78 g dry), and of IV S 0.79 g (0.75 g dry). For analyses, *cf.* Table 1.

Estimation of hydrolysable ethoxyl in the preparations I—IV

The preparations (250 mg) were dissolved in 10 ml water. 40 ml of 10 % sulphuric acid were added and the mixture refluxed for 30 minutes. 25 ml were then distilled off and potassium bichromate (3 g), followed by 98 % phosphoric acid (10 ml), was added to

Table 1. Analyses of the various lignin sulphonic acids.

Preparation	C	H	O	S	Ba	$\frac{\text{Ba}}{2\text{S}}$	O-alk ^{a)}	(C)CH ₃	OCH ₃ ^{b)} calc	OC ₂ H ₅ ^{c)} calc	OC ₂ H ₅ ^{d)} found	$\frac{\text{S}}{\text{OCH}_3}$ calc	$\frac{\text{OC}_2\text{H}_5 \text{ calc}}{\text{OCH}_3 \text{ calc}}$
I	50.65	4.88	28.65	4.72	11.1	1.10	15.28	1.96	12.04	4.70	4.47 4.62	$\frac{1}{2.63}$	$\frac{1}{3.7}$
I S	43.45	4.01	30.47	6.55 6.20	15.7	1.15	11.01	0.35	11.01	—	0.25	$\frac{1}{1.78}$	—
II	51.84	4.89	28.78	4.29	10.2	1.11	15.94	2.02	12.58	4.88	4.93	$\frac{1}{3.03}$	$\frac{1}{3.7}$
II S	45.20	4.07	29.18	6.15	15.4	1.17	11.56	0.30	11.56	—	0.23	$\frac{1}{1.94}$	—
III	52.86	5.03	28.68	4.25	9.18	1.01	15.63	2.05	12.22	4.95	5.28	$\frac{1}{2.97}$	$\frac{1}{3.6}$
III S	46.33	4.17	28.52	6.38	14.6	1.07	11.54	0.30	11.54	—	0.20	$\frac{1}{1.87}$	—
IV	51.35	4.96	29.41	4.28	10.00	1.09	16.02	1.65	13.30	3.95	4.12 3.93 3.68	$\frac{1}{3.21}$	$\frac{1}{4.9}$
IV S	46.56 46.37	4.68 4.54	27.57	6.20	15.15	1.14	11.43 11.54	0.27 11.54	11.43 11.54	—	0.16	$\frac{1}{1.91}$	—

a) Estimated according to the Vieböck method.

b) Calculated by subtracting OC₂H₅ calc. from O-alk.

c) Calculated by subtracting (C)CH₃ of resulphonated material from (C)CH₃ of the original ethoxyl-containing sulphonic acid salt.

d) By acid hydrolysis and oxidation of liberated alcohol with chromic acid (see experimental part).

the distillate. The mixture was refluxed for 5–10 minutes, 20 ml MgSO₄-solution added (cf. Clark ⁷) and the acetic acid formed isolated by steam distillation and estimated by titration with 0.04 N barium hydroxide. Indicator: phenol red (0.1 % in 90 % ethanol). For analyses, cf. Table 1.

Table 2. Composition of the preparations on the C_9 -basis.

Preparation	C	H	O	OCH ₃	OC ₂ H ₅ ^{a)}	SO ₃	Ba	$\frac{OC_2H_5^b)}{SO_3}$
I	9	7.84	2.1	0.96	0.3	0.37	0.20	1.4
I S	9	8.04	2.6	0.98	—	0.55	0.32	
II	9	7.52	2.2	0.99	0.3	0.33	0.18	1.5
II S	9	7.75	2.3	0.99	—	0.51	0.30	
III	9	7.75	2.1	0.93	0.3	0.31	0.16	1.1
III S	9	7.78	2.0	0.96	—	0.55	0.28	
IV	9	7.83	2.3	1.05	0.2	0.33	0.18	1.3
IV S	9	8.89	2.0	0.96	—	0.50	0.28	

a) Calculated on the basis of OC₂H₅ calc. in Table 1.

b) Quotient of OC₂H₅ in this table and the increase in SO₃ content caused by resulphonation.

Drying of the preparations prior to analysis

All preparations were dried at room temperature for three to four weeks in evacuated desiccators charged with sodium hydroxide, concentrated sulphuric acid and phosphorous pentoxide. As a check, it was shown that further drying at 50° over phosphorous pentoxide and paraffin did not result in any further loss of weight.

Sulphonation of preparation IV with cooking liquor of low acidity

An amount of preparation IV corresponding to 3.0 g "lignin" (Ba(SO₃)₂ subtracted) was dissolved in water and transformed into the free acid by passage through a cation exchanger. A solution of sodium hydroxide (6 g) in water (about 20 ml) was added to the filtrate and sulphur dioxide passed in until the solution showed a pH of 5.45. The volume of the solution was 50 ml. It was now heated in a sealed Pyrex tube for 6 hours at 135°. On cooling a jelly was formed, due to the salting out of the sodium salt of the lignin sulphonic acid. This was separated from the liquor by centrifuging. The jelly and the supernatant solution were investigated separately.

The clear solution was examined for free ethanol (steam distillation of the alkaline solution) but only traces were found. The jelly was dissolved in water and transformed into the barium salt in the usual way. The yield was 1.5 g (containing about 5 per cent moisture). The analysis of the dry preparation gave the following results:

Ba 11.49 (10.00), S 4.78 (4.28), O-alk 15.93 (16.02)
 "OC₂H₅ found" (*cf.* Table 1) 2.88 (3.95), (C)CH₃ 1.7 (1.65).

The figures in parentheses correspond to the analytical figures for preparation IV (*cf.* Table 1).

DISCUSSION

Table 1, column (C)CH₃, shows that all the ethoxylated low-sulphonated acids (I—IV) contain ethoxyl groups which are removed on resulphonation (I S—IV S). The small amount of (C)CH₃ remaining in the resulphonated preparations belongs to lignin. Column "OC₂H₅ found" shows that within the limits of experimental error all the ethoxyl groups introduced during the Kullgren process are hydrolysable with hot, dilute sulphuric acid. The small amounts found in the resulphonated products probably do not originate from ethoxyl groups.

The fact that the methoxyl and ethoxyl contents must be calculated by difference makes the relation between ethoxyl and methoxyl uncertain, but the last column of Table 1 shows that at any rate there is in the preparations I—IV about one ethoxyl group per four methoxyl groups.

In the resulphonation experiments a high sulphonation was not aimed at. A certain excess of "base" was present in the cooking liquors. As seen from the last column of Table 2 the amount of ethoxyl groups which has been split off apparently exceeds that of sulphonic acid groups which has been introduced during the resulphonation process. This may indicate that the hydrolysis of ethoxyl groups proceeds at a higher rate than the sulphonation under the conditions of acidity employed in the experiments. The result of the sulphonation of preparation IV at a higher pH (5.45 at room temperature) shows that scarcely any ethoxyl groups are removed when sulphonation is attempted under these conditions.

The results are quite consistent with the view that "genuine lignin" contains groups characterised by different reactivity. One type of group ("A") is directly available in the wood and may be sulphonated by hot cooking liquor of low acidity and high buffering capacity. This is accomplished more or less completely depending on the experimental conditions, *e. g.* the duration of the cook. Another type of group ("B") is not attacked under these conditions, or at least is attacked very slowly. The groups B are sulphonated only under more acid conditions and are presumably the groups connecting "lignin molecules" of the molecular size occurring in normal waste liquors with other similar lignin molecules (or with carbohydrates) to form the so-called "genuine lignin" of wood. (In stating this, of course, we do not overlook the possibility of secondary condensations with formation of lignin sulphonic acids of higher molecular weight.)

Much evidence can be brought forward in favour of the view that the groups A are of the benzyl alcohol type⁸, as first suggested by Holmberg⁹. The groups B may be of the benzyl ether type, as also indicated by the same

author¹⁰. It has been suggested that, alternatively, the groups B may possess a modified ether structure being of acetal or ketal¹¹ type. Experiments on the sulphonation of various benzyl ethers and compounds containing acetal or ketal groups with sulphite cooking acids of varying acidity are being carried out in order to throw more light on the nature of the groups B.

SUMMARY

Low-sulphonated, ethoxylated lignin sulphonic acids have been obtained from sulphonated wood containing free sulphonic acid groups by refluxing with ethanol. These acids have been subjected to resulphonation with sulphite cooking acid of varying acidity. If the acidity is low no elimination of ethoxyl groups takes place. If, however, the acidity is high the ethoxyl groups are split off and apparently more or less completely replaced by sulphonic acid groups. This provides a new indication of the presence of different groups in lignin characterised by varying reactivity to sulphite.

This work was originally planned during numerous discussions with Professor Erik Hägglund. It is a privilege that this paper is also included in his distinguished series of memoirs on the chemistry of the sulphite process.

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