[Contribution from Pulp Mills Research Project, Department of Chemistry and Chemical Engineering, University of Washington]

Lignin. II. Liberation of Phenolic Hydroxyl Groups by Alkaline Cleavage of Lignin Sulfonic Acids

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The conception of softwood lignin as a polymer of oxygenated guaiacyl propane structural units postulates the occurrence of one phenolic hydroxyl per methoxyl grouping. It has been concluded by most workers within the field that phenolic hydroxyl groupings occur in a free state in at least some structural units of the polymer. Thus, Tomlinson and Hibbert[1] have stated: "The fact that methylated (dimethyl sulfate and alkali) lignin sulfonic acids yield veratric aldehyde affords conclusive proof that the original lignin sulfonic acid contains a free phenolic hydroxyl group," and F. E. Brauns[2] has concluded, from diazomethane methylation studies, that: "...lignin sulfonic acid in addition to the sulfonic group has a free phenolic hydroxyl." Freudenberg and coworkers[3] have suggested that the phenolic hydroxyl group is bound in native lignins by an ether linkage to a secondary aliphatic hydroxyl and that this linkage is broken by sulfonation to yield a sulfonic acid and a free phenolic hydroxyl. From more recent investigations using a technique involving hydrazine reduction of toluene sulfonate esters of phenolic hydroxyl groupings to toluene sulfinate esters, Freudenberg and Plankenhorn[4] have concluded that there are present 0.075, 0.14, and 0.31 free phenolic hydroxyl groups per lignin structural unit in cuproxam lignin, hydrochloric acid lignin, and deacetylated acetic acid lignin, respectively.

To secure further information as to the status of the phenolic hydroxyl groupings in lignin sulfonic acids, conductometric titration studies have now been made of exhaustively dialyzed sulfite waste liquor solutions which, as is established in another communication,[5] consist of salts of lignin sulfonic acids of a high degree of purity.

Experimental Part

Conductometric titrations were conducted in 50% ethanol solution using carbonate-free sodium hydroxide. A 60-cycle Wheatstone bridge circuit with pointer type AC galvanometer was used. The titration cell, of 100-ml. capacity, was constructed with buret delivery tubes and glass stirrer mounted in the lid. This was connected by a ground glass joint to the body containing platinized electrodes. The cell constant was 0.492 cm.$^{-1}$.

Samples from alkali cleavage experiments were adjusted with dilute hydrochloric acid to *p*H 4. A measured excess of standard acid was then added and the samples were boiled to expel carbon dioxide and sulfur dioxide formed by desulfonation of the lignin sulfonic acid. After cooling in stoppered flasks, aliquots were titrated with 0.01 *N* iodine solution to determine residual sulfur dioxide. Weak acids, determined conductometrically on separate aliquots, were corrected for residual sulfite.

Potentiometric titrations were conducted using a Leeds and Northrup glass electrode *p*H electrometer.

Total solids and total sulfur recovery in the fractionation of alkali cleaved lignin sulfonic acid were corrected for sodium sulfate resulting from alkali neutralization by conductometric sulfate[6] determinations.

Other analytical procedures have been described in a separate communication.[5]

Extinction coefficients for the nitroso lignin test were determined using a Coleman Spectrophotometer.

Alkali cleavage experiments were generally conducted in glass apparatus under a reflux condenser using a nitrogen atmosphere. Some experiments were conducted using small stainless steel autoclaves in a constant temperature oil-bath.

The lignin sulfonic acid concentration was generally 20 g. per liter. Free lignin sulfonic acids were prepared from calcium or sodium lignin sulfonate solutions by treatment with an acid regenerated cation exchange resin (Amberlite IR 100).

Discussion

Typical results with untreated lignin sulfonic acid solutions are illustrated in Fig. 1, which shows comparative conductometric and potentiometric titrations on the same solution of lignin sulfonic acids. From the character of curves obtained, it is clear that only small amounts—certainly less than 0.2 mole per mole of methoxyl of weak acids with *pK* values between 4 and 10—can be contained. Since phenolic hydroxyl groups in lignin sulfonic acids, if free, should fall within this range, the absence, or presence in only low concentrations, of these groupings, is indicated.

However, free phenolic hydroxyl groups do exist in lignin sulfonic acids which have been subjected to an alkaline environment. Such conditions may arise during methylation reactions which have been used to indicate the presence of free phenolic groups[1] and have been found by Karrer and associates,[7] to lead to rapid cleavage of some anthocyanins to simple phenolic substances. Treatment of lignin under more strongly alkaline conditions and at higher temperature yields products which are precipitable with carbon dioxide and thus presumably phenolic in character and under these conditions lignin sulfonic acids yield vanillin and other phenolic substances.

When the lignin sulfonic acid preparation described in Figure 1 was treated with 5% sodium hydroxide at 100° for several time periods, the reaction products showed the conductometric titra-

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(1) Tomlinson and Hibbert, This Journal, **58**, 350 (1936).

(2) Brauns, *Paper Trade Journal*, **111**, no. 14, 33–39, Oct. (1940).

(3) Freudenberg, Meister and Flickinger, *Ber.*, **70**, 500 (1937).

(4) Freudenberg and Plankenhorn, *ibid.*, **75**, 857–867 (1942).

(5) Peniston and McCarthy, This Journal, **70**, 1324 (1948).

(6) Peniston, Felicetta and McCarthy, *Ind. Eng. Chem., Anal. Ed.*, **19**, 332 (1947).

(7) Karrer and co-workers, *Helv. Chim. Acta.*, **10**, 67, 729 (1927); **12**, 292 (1929); **15**, 507 (1932).

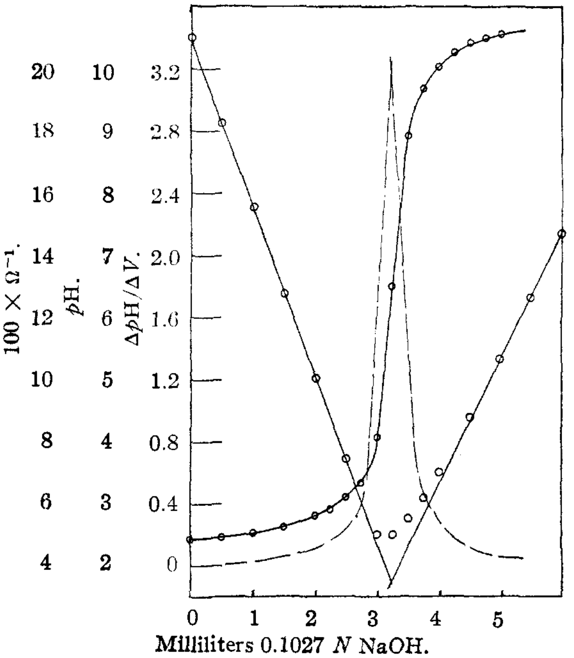

Fig. 1.—Potentiometric and conductometric titrations of lignin sulfonic acid showing low weak acid content: 1.0 ml. NaOH = 0.164 mole of acid per mole of OCH_3.

tion curves given in Fig. 2. After sodium hydroxide addition equivalent to the midpoint of the indicated weak acid lines, all solutions were found to be approximately *p*H 9, indicating that the ionization constants for the acids titrated are in the expected range for phenolic hydroxyl groups. From the above and similar studies on different lignin sulfonic acid preparations, it is concluded that treatment in five per cent. sodium hydroxide solutions at 100°, causes liberation in about two hours of about 0.67 mole of phenolic hydroxyl per mole of methoxyl. Following this there is a more gradual formation of weak acid groups which continues with the time of cleavage.

The rate of the initial phenolic hydroxyl liberation appears to be approximately proportional to the alkali concentration. Thus in aqueous solutions 1% in sodium hydroxide, the rate is found to be roughly one-fifth of that observed in solutions 5% in sodium hydroxide. Also, at the lower alkali concentration, the more gradual acid formation is not discernible. Thus there may be two reactions involved or two different groupings cleaved by the alkaline treatment.

The liberation of phenolic hydroxyl groups in lignin sulfonic acid should result in its increased reactivity in chemical reactions dependent on the presence of active nuclear hydrogen. After alkali treatment there should be evident increased ease of oxidation and of halogenation, increased reactivity in condensation reactions, *e. g.*, with formaldehyde, and in substitution reactions such as coupling with diazonium salts or reaction with nitrous acid. Two such reactions have now been studied in comparison with titration data for the amount of weak acid liberated in alkali cleavage.

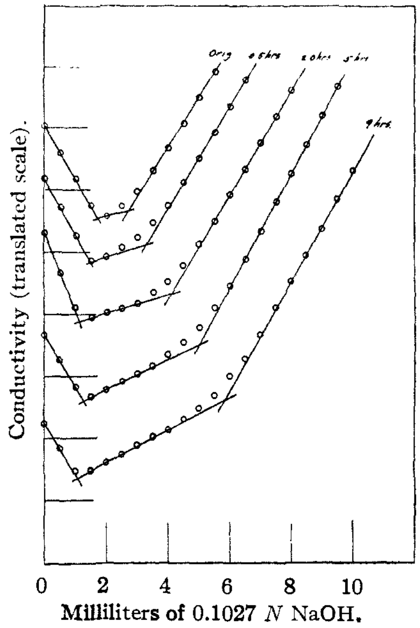

Fig. 2.—Conductometric titrations of L. S. A. after alkali cleavage.

Pearl and Benson[8] have developed a procedure for determination of lignin sulfonic acid in sea water utilizing the color formed by reaction with nitrous acid presumably forming a nitroso lignin. Mr. William G. Westover,[9] in collaboration with H. K. Benson and the authors, has studied the effects of alkali cleavage on the color developed in this reaction.

Pennington and Ritter[10] have recently investigated oxidation of various phenolic substances with periodic acid and have found that substances with guaiacyl nuclei with free phenolic hydroxyl groups are readily oxidized with accompanying demethylation. Dr. Pennington has examined a series of our alkali cleavage samples using the periodate oxidation technique.

Results of the three characterizations of the same series of alkali treated lignin sulfonic acid samples are shown in Fig. 3, in which the conductometric moles of weak acid per mole of methoxyl, the increase in extinction coefficient at 4700 Å. for the nitrous acid reaction product, and the moles of periodate consumed per mole of methoxyl, are each plotted as ordinates against the time of alkali cleavage as abscissa. The three quantities show pronounced increases during the early stages of treatment, indicating an increase in concentration of free phenolic groups. After two hours of treatment, however, there is no further increase in periodate consumption, or in the extinction coefficient, while a continued gradual increase in weak

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(8) Pearl and Benson, *Paper Trade J.*, **111**, no. 18, 35–36 (1940).

(9) Westover, B. S. Thesis, University of Washington, 1946.

(10) Pennington and Ritter, THIS JOURNAL, **69**, 187 (1947).

acids is still apparent. It is believed, therefore, that for the experimental conditions used liberation of phenolic groups is substantially complete in two hours, and that generation of other acidic groupings is probably responsible for the subsequent gradual rise in titratable acids. Ritter and Pennington[10] have observed that pure guaiacyl type phenolic substances in general consume three moles of periodate per mole of methoxyl. This would imply that in alkali cleavage under conditions used only two thirds of the potential phenolic hydroxyl groups have been liberated and suggests the possibility that a different type of linkage exists for the remaining third. A similar result is obtained by linear extrapolation to zero time of the gradual weak acid increase. On this basis the amounts of phenolic hydroxyl liberated in the first two hours are in close agreement as determined by periodate consumption or titration (Fig. 3a).

The increase in extinction coefficient for the products of reaction with nitrous acid agrees reasonably well with the assumption that light absorption of the lignin polymer is due to two typical groupings, *i. e.*, structural units with free phenolic hydroxyls, and those remaining as phenolic ethers. The observed extinction coefficient, "K_{obs}," should thus be expressible as a sum of two terms as

$$(C_1 + C_2)K_{obs.} = K_1C_1 + K_2C_2 \qquad (1)$$

where "C_1" and "C_2" represent the molar concentrations of free and combined phenolic hydroxyl groupings per mole of methoxyl, and "K_1" and "K_2" represent the extinction coefficients associated with these respective groupings. If the concentrations of free phenolic hydroxyl found experimentally by periodate oxidation be taken as C_1, then C_2 may be regarded as the difference between unity and C_1. Using values found experimentally by the nitroso technique for the total extinction coefficient, K_{obs}, then the individual extinction coefficients, K_1 and K_2, may be evaluated by simultaneous solution of Equation 1 using data derived from samples hydrolyzed for two different time intervals. Taking K_1 and K_2 as 76 and 20, respectively, calculation of the terms $K_1C_1 + K_2C_2$ as compared to $(C_1 + C_2)K_{obs}$ shows (Table II) satisfactory correlation of the results of the periodate oxidation method with those of the nitroso method except for the original sample in which some phenolic hydroxyl may have been liberated under the alkaline conditions obtaining during the carrying out of the nitroso method.

The liberation of phenolic hydroxyl groups by mild alkaline treatment of lignin sulfonic acid necessarily brings about other changes in molecular structure. If all of the structural units of the lignin polymer are joined together by non-cyclic ether linkages (such as in Formula I), simple cleavage of these ethers would result in conversion of the polymer to the monomer. However, if furan or pyran rings are involved (such as in Formula II), reduction in molecular weight would require not only liberation of the phenolic hydroxyl but also rupture of carbon to carbon bonds.

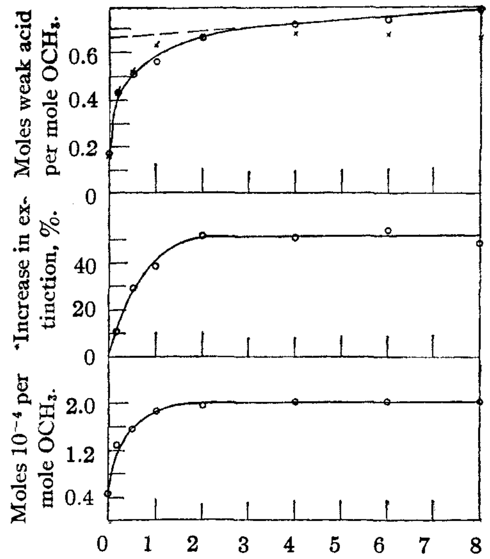
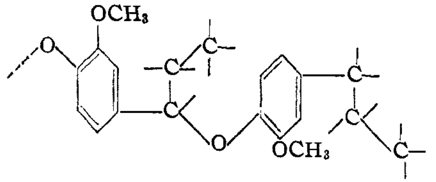


Fig. 3.—Phenolic hydroxyl liberation by alkali cleavage.

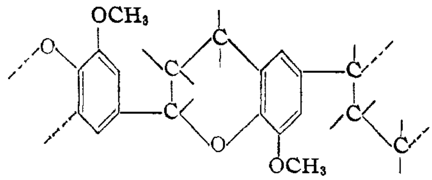
TABLE I

CORRELATION OF EXTINCTION COEFFICIENTS WITH AMOUNT OF FREE PHENOL

Time, hr.	C_1	C_2	K_1C_1	K_2C_2	$(K_1C_1 + K_2C_2)$	$(C_1 + C_2)\cdot K_{obs}$
0	0.16	0.94	12.2	18.8	31.0	38.0
0.167	.43	.57	32.7	11.4	44.1	42.1
0.50	.52	.48	39.5	9.6	49.1	49.2
1.00	.63	.37	47.9	7.4	55.3	52.8
2.00	.66	.34	50.1	6.8	56.9	57.8
4.00	.68	.32	51.6	6.4	58.0	57.2
6.00	.68	.32	51.6	6.4	58.0	58.5



I. Non-cyclic lignin structure



II. Cyclic lignin structure

To investigate alteration in molecular size and other changes associated with the alkaline treatment, a fractionation of lignin sulfonic acid after five hours of treatment with 5% sodium hydroxide solution at 100°, has been conducted. Fraction A, which is first apparent after about three hours of treatment and increases with time of the alkali reaction, is insoluble in water under neutral conditions and after its separation, the remaining soluble Fraction B was dialyzed exhaustively following the same procedure and with the same membranes initially used for preparation of the lignin sulfonic acids from sulfite waste liquor. The non-dialyzable residue (Fraction B-1), the dialyzate (Fraction B-2), and Fractions A and B were then analyzed to determine total material, methoxyl and sulfur balances.

TABLE II

FRACTIONATION OF ALKALI CLEAVED LIGNIN SULFONIC ACIDS

Fraction	Fraction A	Fraction B	Fraction B-1	Fraction B-2
Per cent. of total material	19.1	68.5	32.4	32.3
Per cent. of total sulfur	10.0	58.5	21.5	31.9
Per cent. of total methoxyl	22.5	72.3	36.0	29.7
Extinction coefficient	43	61	49	73

Although considerable material losses occurred particularly in isolation of the peptizable Fraction A, results (Table II) show insoluble Fraction A to be strongly desulfonated (from about 0.50 in the lignin sulfonic acid before alkaline cleavage, to about 0.22 mole of sulfur per mole of methoxyl in Fraction A). The soluble non-dialyzable residue Fraction B-1 is desulfonated to a lesser degree (0.43 mole of sulfur per mole of methoxyl) while the soluble dialyzable Fraction B-2 retains practically the same proportion of sulfur as the original lignin sulfonic acid (0.54 mole of sulfur per mole of methoxyl). Extinction coefficients indicate that a considerable proportion of the phenolic hydroxyl groups remains combined in Fractions A, B, and B-1, while in the dialyzate Fraction B-2 all phenolic hydroxyl groupings appear to be free. That about one-third of the lignin sulfonic acid is readily dialyzable after alkali cleavage whereas the original material had been isolated as a non-dialyzable residue using the same membrane material, appears to demonstrate a substantial decrease in molecular weight for this fraction. Other indications of reduced molecular weight in cleavage products have been obtained from observations of a reduction in specific viscosity.

The liberation of only two-thirds of the potential phenolic hydroxyl groups of lignin sulfonic acid by alkali treatment and the apparent simultaneous formation of sulfonated fragments of lower molecular weight suggest that more than one type of linkage between structural units must exist in the lignin polymer.

The authors are indebted to Mr. Vincent F. Felicetta for analytical assistance.

Summary

1. Examination of a sample of purified lignin sulfonic acids by conductometric and potentiometric titration methods has indicated the absence, or the presence in only low concentrations, of free phenolic hydroxyl groupings in the material as it exists in sulfite waste liquor.

2. By mild alkaline hydrolysis of purified lignin sulfonic acids, weakly acidic groupings are formed which show a *pK* value of about 9 and are regarded as phenolic hydroxyl groupings.

3. Periodate oxidation studies, and the extent of "nitroso-lignin" formation, as well as conductometric analyses, indicate phenolic hydroxyl liberation by mild alkaline treatment of lignin sulfonic acids.

4. From periodate oxidation values and also conductometric titrations apparently only about 0.67 mole of phenolic hydroxyl per mole of methoxyl are liberated by alkali treatment under the conditions used. The presumed remaining phenolic groups (0.33 mole per mole of methoxyl) thus appear to be bound in a more stable type of linkage.

5. Alkaline hydrolysis of lignin sulfonic acid brings about a decrease in molecular weight of some fractions of the acids, and this and other evidence indicates that more than one type of bond serves to combine structural units in lignin sulfonic acid.

SEATTLE, WASHINGTON RECEIVED JULY 24, 1947