nitric acid for one-half hour at 50°. The reaction mixture was cooled and poured onto ice. The resulting solid was recrystallized from 95% ethanol to constant m. p., 134–135.5°.

Anal. Calcd. for $C_{14}H_8Cl_4N_2O_4$: N, 6.83. Found: N, 7.02.[6]

Tetranitro-*o,p'*-TDE.[7]—A mixture of 500 mg. of *o,p'*-TDE, 2.5 ml. of concentrated sulfuric acid, and 2.5 ml. of fuming nitric acid was heated on a steam-bath for one hour. The reaction mixture was cooled and poured onto ice. The resulting solid was recrystallized from acetone–ethanol to constant m. p., 183–185°.

Anal. Calcd. for $C_{14}H_8Cl_4N_4O_8$: N, 11.21. Found: N, 11.14.[6]

***o,p'*-TDE Olefin.**—A solution of 500 mg. of *o,p'*-TDE and 0.4 g. of potassium hydroxide in 20 ml. of ethanol was heated at reflux for three hours. The resulting mixture was poured into water. The mixture was extracted with ether, and the ether extract was washed with water and saturated salt solution and filtered. The ether was evaporated off, leaving a viscous oil. This oil, b. p. 160° (1 mm.), was distilled in a vacuum sublimation apparatus. The product remained as an oil after standing at room temperature for over a year.

Acknowledgment.—We are indebted to the Rohm and Haas Company for a generous supply of technical TDE mixture.

Summary

1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-TDE) has been separated from a mixture with its *p,p'* isomer by a procedure making use of the lowered reactivity with ethanolic sodium hydroxide of the *o,p'* isomer compared with the *p,p'* isomer.

Nitration and dehydrochlorination products of *o,p'*-TDE have been described. The rate constant for the reaction of *o,p'*-TDE with ethanolic sodium hydroxide has been determined.

BOULDER, COLORADO RECEIVED NOVEMBER 13, 1947

(6) The authors are indebted to Mr. Harlan L. Goering for the nitrogen analyses.

(7) The structure of this compound has not been proved, but it is presumably 1,1-dichloro-2-(2-chloro-3,5-dinitrophenyl)-2-(4-chloro-3,5-dinitrophenyl)-ethane.

[CONTRIBUTION FROM PULP MILLS RESEARCH PROJECT, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Lignin. I. Purification of Lignin Sulfonic Acids by Continuous Dialysis

BY QUINTIN P. PENISTON AND JOSEPH L. MCCARTHY

Introduction

Lignin sulfonic acids[1] have several times been separated from sulfite waste liquor and purified by metal or amine salt precipitations.[2] Although dialysis has been employed as a step in some of these procedures, and has been practically considered by Ogland,[3] no detailed study appears to have been made of the degree of purity and extent of recovery of the lignin sulfonic acids attainable by direct continuous dialysis of sulfite waste liquor. This easily conducted procedure was thought worthy of investigation both as a method for laboratory preparation of purified lignin sulfonic acids for research purposes and as a means of characterization of sulfite waste liquor components.

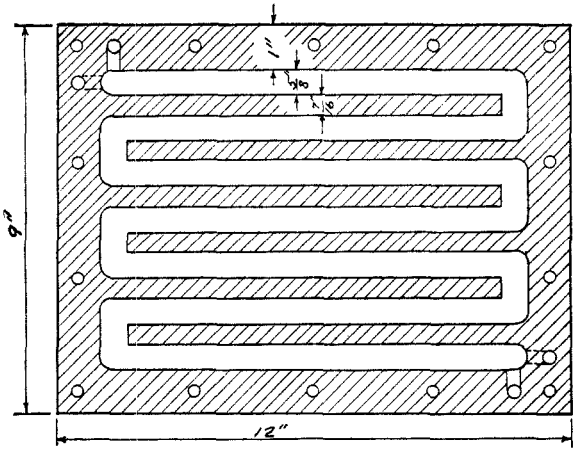


Fig. 1.—Dialyzer plate detail.

Experimental Part

Dialysis Apparatus.—To obtain a high ratio of membrane area to liquor volume and a close approach to true counter-current operation, a multicellular apparatus was constructed from $^1/_8$" × 9" × 12" plates of "Plexiglas." This material was chosen for its resistance to chemical attack, dimensional stability in water, workability, and transparency. The last quality is desirable since it aids detection of air blocks or other obstructions to flow. The cells consisted of zig-zag channels $^5/_8$" wide sawn in the "Plexiglas" plates. Both liquor and water plates were identical except for interplate connections. The design details are indicated in Fig. 1. Fifteen pairs of such plates were used, each pair being isolated by separator plates of $^1/_{16}$" "Plexiglas." Connections between cells were by means of ports grooved about half through the plates at the ends of the channels. The ports fed into holes which led through membrane and separator to the next appropriate cell. The entire assembly was held between $^1/_4$" stainless steel plates by means of 14 stainless steel machine bolts.

The total volume of the apparatus amounted to 2780 ml., and the total membrane area to 0.435 square meter. With no bulging of the membrane, the volumes in liquor and water channels were equal.

(1) Hagglund, "Holzchemie," Akademische Verlagsgesellschaft, m. b. h., Leipzig, 1939, 2nd. ed., Lithoprinted 1944 by Edwards Bros., Ann Arbor, Michigan.

(2) (a) E. G. King, F. Brauns and H. Hibbert, *Can. J. Res.* (B) **13**, 88 (1935); (b) G. H. Tomlinson and H. Hibbert, THIS JOURNAL, **58**, 340 (1936); (c) H. Erdtman, *Svensk. Papperstidn.*, **45**, 315–323 (1942); (d) W. Lautsch and Piazolo, *Cellulose chemie*, **22**, 48–54 (1944).

(3) N. J. Ogland, *Svensk. Papperstidn.*, **47**, 288–291 (1944).

Flows of both sulfite waste liquor and distilled water to the apparatus were from constant head reservoirs through small Alyea[4] flowmeters to open funnel receivers. Pressure on the two channels was independently controlled by adjustment of the height of inlet and outlet tubes. In operation the apparatus was placed with plates horizontal and both channels were filled with water using parallel upflow until all air bubbles were removed. Water was then switched from upflow to downflow and sulfite waste liquor was admitted in upflow in the other channel. Steady state operation was obtained over several days' operation without attention. The addition of small amounts of toluene to the input reservoirs was found effective to prevent growth of microorganisms in the apparatus. These if uncontrolled rapidly caused increase in porosity and failure of the membranes.

The membrane used in these studies was a denitrated nitrocellulose casing produced by the Sylvania Industrial Corporation and obtained from the Brosites Machine Company, New York; sample K 412, thickness (dry) 0.0032 inch.

Sulfite Waste Liquor Samples.—The compositions of sulfite waste liquor samples used in this study are shown in Table I. For sample B the alterations brought about by pretreatment before dialysis are indicated. Important differences between Samples A and B are: the higher amount of total reducing substances and fermentable sugar in Sample A, and the high values for total sulfur and loosely combined sulfur dioxide in Sample B. Both samples were obtained from commercial pulping operations using the same wood source: about 85% Western Hemlock and 15% White Fir. In the production of Sample B a much higher "free sulfur dioxide" concentration was present in the pulping liquor.

TABLE I

COMPOSITION OF SULFITE WASTE LIQUOR SAMPLES

Sample	A	B original	B after ion exchange
*p*H	1.77	1.80	2.70
Total solids, g./l.[b]	115.4	121.6	95.9
Ash, g./l.	11.88	20.94	21.63[a]
CaO, g./l.	6.19	9.63	0.05
Free SO_2, g./l.[5]	0.6	8.04	4.02
Loosely combined SO_2, g./l.[5]	3.73	6.17	4.51
Sulfate, g. SO_3/l.[6]	1.14	1.10	0.76
Total sulfur, g. S/l.[7]	8.92	15.75	10.99
Methoxyl, g. OCH_3/l.[8,9]	7.84	8.09	6.16
Total reducing substance, g. glucose/l.	26.78	20.45	14.91
Fermentable sugar, g. glucose/l.[10]	19.05	12.45	...

[a] Sulfated ash. [b] Determined by drying *in vacuo* at 60° on quartz sand.

Method of Calculation of Dialysis Data.—To obtain samples representative of a given set of flow conditions the apparatus was allowed to operate for sufficient time to ensure a steady state condition. Usually a time equivalent to the passage of 2 liters of the more slowly moving fluid was allowed. Samples of dialyzed liquor and dialyzate were then collected over a measured time interval to determine output flow rates. Input flow rates were calculated from a total solids balance. Dialysis rate coefficients and amounts of substances transferred were then calculated from analyses of the effluent samples, the composition of the original liquor and the flow rates established from the total solids balance.

Results and Discussion

The isolation of pure lignin sulfonic acids from sulfite waste liquor by dialysis is dependent on two major factors. Firstly, the non-lignin components, being of relatively low molecular weight, diffuse more rapidly through the pores of the membranes than most of the lignin components, and secondly, the membrane behaves in some degree as an ultra-filter being substantially impermeable to particles above a certain size.

Schwabe and Hasner[11] have shown that for such low molecular weight non-electrolytes, as hexose sugars, the rate of diffusion is determined by Graham's law for certain membranes. With electrolytes in the presence of a high concentration of supporting electrolyte, presumably the dialysis rate is also inversely proportional to the square root of the molecular weight. This relationship has been used by Schwabe and Hasner for estimation of molecular weight of various lignin sulfonic acid preparations. In the absence of extraneous electrolyte, however, potential gradients as well as concentration gradients must be effective in determining the dialysis rate of electrolytic substances. According to Vinograd and McBain[12] the potential gradient in a mixture of electrolytes may be expressed as

$$\frac{d\psi}{dx} = \frac{RT}{F}\left[\frac{\Sigma u_+ G_+/n_+ - \Sigma u_- G_-/n_-}{\Sigma u_+ c_+ + \Sigma u_- c_-}\right]$$

where u_+, u_- are mobilities, G_+ G_- are ionic concentration gradients, c_+, c_- are concentrations and n_+, n_- are valences. An interesting consequence of this relation is that the presence of a high concentration of non-dialyzable high molecular weight lignin sulfonic acid anions should increase the rate of dialysis for low molecular weight anions in the mixture.

In order to aid in the interpretation of dialysis rate coefficients calculated for sulfite waste liquor components, two mixtures of pure substances have been dialyzed under similar conditions using the same dense membrane employed for the sulfite waste liquor experiments. Results with known aqueous mixtures of glucose and sucrose (Table II) dialyzed under four different flow conditions (Experiments 1–4) using newly installed membranes and, again after six weeks of continuous service in sulfite waste liquor dialysis (Experiments 5–8), show (a) that while the free diffusion rate for glucose is 1.37 times that for sucrose,[13] the ratio of dialysis rate coefficients now found for these substances is 1.64 indicating a filtering action by the membrane for molecules as small as sucrose; (b) that apparently the dialysis rate coef-

(4) H. N. Alyea, *Ind. Eng. Chem., Anal. Ed.*, **12**, 686 (1940).

(5) Method 0 403 sm-40, January 15 (1940); Technical Association of the Pulp and Paper Industry, New York.

(6) Q. P. Peniston, V. F. Felicetta and J. L. McCarthy, *Ind. Eng. Chem., Anal. Ed.*, **19**, 332 (1947).

(7) F. H. Yorston, Canadian Pulp and Paper Research Institute, Montreal, Canada, private communication.

(8) E. P. Clark, THIS JOURNAL, **51**, 1479–1483 (1929).

(9) F. Viebock and A. Schwappach, *Ber.*, **63**, 2818 (1930).

(10) H. S. Daniels and J. L. McCarthy, unpublished method.

(11) K. Schwabe and L. Hasner, *Cellulosechemie*, **20**, 61 (1942).

(12) J. R. Vinograd and J. W. McBain, THIS JOURNAL, **63**, 2011 (1941).

(13) "International Critical Tables," Vol. V, p. 71.

TABLE II

DIALYSIS RATES FOR GLUCOSE–SUCROSE MIXTURES[a]

Experiment[c]		1	2	3	4	5	6	7	8
Liquid output, ml./hr.		672	499	296	139	445	316	166	66.7
Dialyzate, ml./hr.		612	422	256	125	359	213	144	78.1
Per cent. dialyzed	Glucose	43.0	47.7	55.7	73.5	51.6	51.2	71.6	87.3
	Sucrose	27.8	35.2	43.9	64.2	38.6	41.2	64.8	86.8
Dialysis rate[b] coefficients	Glucose	0.92	0.95	0.86	0.93	0.93	0.94	1.02	0.81
			Average 0.92				Average 0.93		
	Sucrose	0.56	0.55	0.53	0.54	0.57	0.56	0.64	0.58
			Average 0.54				Average 0.59		
	$\frac{K \text{ glucose}}{K \text{ sucrose}}$	1.64	1.72	1.62	1.72	1.63	1.68	1.60	1.40
			Average 1.67				Average 1.58		

[a] Original mixture: 20.0 glucose g./liter, 20.0 sucrose g./liter. [b] Grams transferred per square meter per hr. per gram per liter concentration difference (logarithmic mean). [c] Experiments 1–4 were carried out using new membranes; experiments 5-8 with membranes after six weeks of service in sulfite waste liquor dialysis.

TABLE III

DIALYSIS RATES FOR GLUCOSE AND SODIUM *p*-TOLUENE SULFONATE[a]

Experiment		1	2	3	4
Average solution rate, ml./hr.		104	215	327	558
Average water rate, ml./hr.		116	232	298	602
Per cent. dialyzed	Glucose	79.8	65.0	52.0	41.7
	Sodium *p*-toluenesulfonate	86.3	74.1	59.7	52.7
Dialysis rate coefficients	Glucose	0.79	0.86	0.85	0.88
	Sodium *p*-toluenesulfonate	1.06	1.22	1.26	1.39
	$\frac{K_{C_7H_7SO_3Na}}{K_{glucose}}$	1.34	1.43	1.49	1.59

[a] Original mixture: glucose 20.60 g./liter, sodium *p*-toluenesulfonate 22.84 g./liter.

ficients for these non-electrolytes, are not dependent on flow rate, and (c) that only a small change if any occurred in the porosity of the membrane during the entire period.

Similar experiments with known aqueous mixtures of glucose with sodium *p*-toluenesulfonate (Table III) showed that (a) although the two substances are of about the same molecular weight, the electrolyte dialyzed considerably faster than the non-electrolyte and (b) that the dialysis rate coefficient of the electrolyte increases with flow rate.

Since sodium *p*-toluenesulfonate is a salt of a relatively large organic anion, it might be expected that similar effects would occur in dialysis of sodium lignin sulfonates and low molecular weight non-electrolytic substances.

The purification of lignin sulfonic acids by dialysis of sulfite waste liquor Sample A was investigated using five different liquid input flow rates corresponding to five different times for dialysis. Dialyzed liquors and dialyzates were analyzed for total solids, methoxyl, total reducing substances and sulfur. The analytical results and the amounts of each analytically determined constituent dialyzed are shown in Table IV as a function

TABLE IV

EFFECT OF DIALYSIS TIME ON LIGNIN SULFONIC ACID PURITY

Sulfite Waste Liquor Sample A

Experiment	1	2	3	4	5
Liquor input, ml./hr.	136	76.7	39.4	37.9	19.0
Water input, ml./hr.	270	273	275	265	256
Average liquor flow rate, ml./hr.	166	93.3	52.7	52.7	31.9
Average time in dialyzer, hours	8.37	14.90	26.7	26.7	43.5
Dilution ratio (liquor out/liquor in)	1.44	1.43	1.67	1.78	2.36
Composition of dialyzed liquor					
Total solids, g./l.	58.25	44.74	32.42	30.69	23.24
Methoxyl, g. OCH_3/l.	5.53	4.70	3.66	3.47	2.72
Total reducing substances, g./l.	7.15	3.23	1.07	0.82	0.48
Sulfur, g./l.	3.70	2.90	2.12	2.00	1.49
Composition of dialyzate					
Total solids, g./l.	20.43	16.40	9.76	9.77	5.02
Methoxyl, g. OCH_3/l.	0.49	0.44	0.30	0.34	0.20
Total reducing substances, g./l.	9.29	7.08	3.93	3.78	1.72
Per cent. of constituent dialyzed					
Total solids	27.4	44.5	53.1	52.8	52.5
Methoxyl	9.7	18.0	21.0	21.3	21.0
Total reducing substance	53.7	82.7	93.3	94.2	94.8
Sulfur	40.2	53.5	69.3	69.1	69.5
Methoxyl equivalent weight dialyzed solids	327	295	274	274	265

of the time of dialysis. Limiting values are approached by all constituents which are characteristic of the calcium salts of the purified lignin sulfonic acids. Interpreting the dialysis of methoxyl groups as proportional to that of lignin sulfonic acids, it appears that about 78% of the original lignin sulfonic acids in Sample A are retained by the membrane used irrespective of the time of dialysis. The remainder pass through the membrane at a rate not greatly lower than that for reducing substances and thus are apparently of lower molecular weight. From the above experiments with known substances and from the recent reports by Gralen[14] and by Pennington and Ritter[15] the molecular weight of lignin sulfonic acids pass-

(14) Nils Gralen, *J. Colloid Sci.*, **1**, 453 (1946).

(15) D. Pennington and D. M. Ritter, THIS JOURNAL, **69**, 665 (1947).

TABLE V

DIALYSIS RATES OF SULFITE WASTE LIQUOR COMPONENTS

Sulfite Waste Liquor B

	As calcium salts			As sodium salts			
Experiment	1	2	3	1	2	3	4
Average liquor flow, ml./hr.	49.6	100.8	179	41.05	65.6	122	179
Average water flow, ml./hr.	59.3	176.1	176	47.3	68.7	144	197
Dilution ratio	1.75	1.45	1.37	2.70	1.76	1.49	1.40
Composition of dialyzed liquor							
Total solids, g./l.	34.34	44.39	59.99	15.24	25.39	33.76	40.56
Reducing substances, g./l.	0.86	2.24	5.59	0.51	1.27	2.20	3.51
Methoxyl, g./l.	3.65	4.46	5.46	1.67	2.69	3.44	3.96
Total sulfur, g./l.	3.02	3.93	5.59	1.40	2.33	3.00	3.58
Free and loosely combined sulfur dioxide, g./l.	0.59	1.02	2.42	0.16	0.42	0.63	1.09
Methoxyl equivalent weight	292	309	342	283	293	304	317
Moles sulfur/mole methoxyl	0.80	0.86	0.99	0.81	0.84	0.84	0.88
Per cent. of constituent dialyzed							
Total solids	50.4	47.0	32.3	57.6	53.4	47.4	40.5
Reducing substances	86.7	82.9	59.2	88.0	83.6	76.3	67.8
Methoxyl	18.1	14.8	9.3	29.4	24.2	17.8	13.8
Free and loosely combined sulfur dixide	29.8	89.6	76.7	97.0	91.4	89.2	82.5
Dialysis rate coefficients							
Total solids	0.10	0.16	0.19	0.09	0.15	0.23	0.26
Reducing substances	.53	.56	.62	.36	.66	.70	.74
Methoxyl[a]	.10	.14	.15	.26	.30	.26	.25
Free and loosely combined sulfur dioxide	.63	.74	.93	1.00	1.15	1.33	1.45

[a] Based on assumption of 35% dialyzable methoxyl.

ing through the membrane is probably not greater than about 2000 and thus these may contain only up to about ten of the structural units postulated by Freudenberg[16] and Hibbert.[17]

The non-dialyzable lignin sulfonic acids may be characterized by a methoxyl equivalent weight (grams of total solids per 31.02 g. of methoxyl). This value for the solids remaining undialyzed was found to decrease with increasing time of dialysis, the data being representable by an equation of the form

$$\text{Methoxyl equivalent weight} = C + A/\text{Time}$$

where A and C are constants. Extrapolation with this relationship of the data to infinite time of dialysis (Fig. 2) suggests a value of about 250 as the methoxyl equivalent weight of the completely purified calcium lignin sulfonate from sulfite waste liquor Sample A. The mole ratio of sulfur, and of the copper reducing value calculated as glucose, to methoxyl in the dialyzed solutions is shown in Fig. 2 as a function of time of dialysis. Both quantities decrease rapidly with increasing purity and approach values of 0.5 mole of sulfur, and less than 0.04 mole of copper reducing groups, per mole of methoxyl, respectively. Thus the nondialyzable lignin sulfonic acids manifest approximately one sulfonic acid grouping for every two structural units. The rate at which the mole ratio of sulfur to methoxyl decreases with increasing purity appears to exclude the possibility that the sulfur-containing impurities can be entirely lignin sulfonic acid salts of higher sulfur content and suggests that they may be, in part, the sulfonic acid derivatives of sugars postulated by Hägglund and Urban[18] and recently studied by Adler.[19]

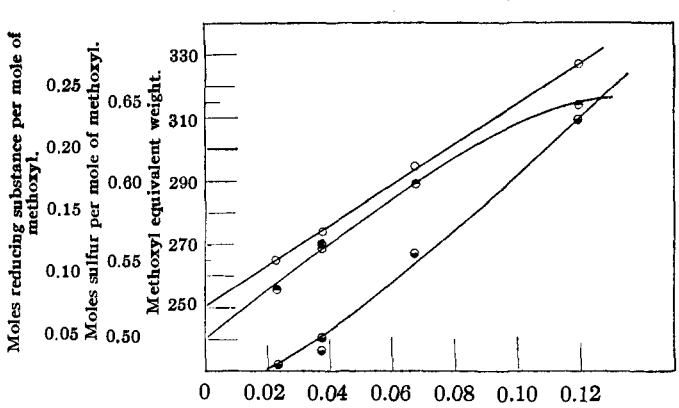


Fig. 2.—Calcium lignin sulfonate composition *vs.* dialysis time: ○, equivalent weight; ◒, sulfur; ◒, reducing substances.

To try to generalize the above trends, a series of experiments was conducted with calcium base sulfite waste liquor Sample B which differs from Sample A in that it was obtained from a separate commercial plant wherein the practice is to use a sulfite pulping liquor very high in concentration of sulfurous acid. In both cases, however, the wood used was the same, namely, about 85%

(16) K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 81 (1931).

(17) H. Hibbert, *ibid.*, **11**, 183 (1942).

(18) E. Hägglund and H. Urban, *Ber.*, **62**, 2046 (1929).

(19) E. Adler, *Svensk Papperstidn.*, **49**, no. 15 (Aug. 15, 1946).

Western Hemlock and 15% White Fir. Sample B, in its original form, and after conversion by ion exchange to sodium salts (Table I), was dialyzed at various flow rates. The dialyzed solutions were analyzed and dialysis coefficients were computed.

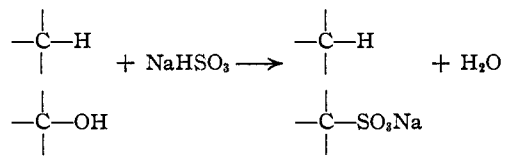
Results (Table V) indicate that dialysis coefficients of electrolyte components of sulfite waste liquor are higher when in the form of sodium salts than as calcium salts. This might be expected from activity considerations.

By extrapolation to infinite time of dialysis of data secured using the sodium salts, it is estimated, on a methoxyl basis, that about thirty-five per cent. of the weight of the original lignin sulfonic acid present in Sample B will dialyze through the membrane, compared to about 22% for Sample A. This evidence for the presence of a larger proportion of lower molecular weight lignin sulfonic acid molecules in the sulfite waste liquor Sample B may correlate with the higher sulfurous acid concentration during the sulfite pulping procedure in this case.

Following completion of these experiments, non-dialyzable sodium lignin sulfonates were prepared by dialyzing Sample B as the sodium salt using a very low flow rate. Also at the conclusion of the above described studies on Sample A, non-dialyzable calcium lignin sulfonates were secured similarly and these were converted to sodium salts by ion exchange. Purified lignin sulfonates A and B were recovered by evaporation to dryness at reduced pressure and then carefully dried under vacuum below 60°. According to Purves[20] erroneous carbon and hydrogen values may result if high temperatures are used. The composition of the two dry samples was found to be

	Sample A (%)	Sample B (%)
Carbon	52.1	50.5
Hydrogen	4.18	3.96
Sulfur	6.66	7.38
Sodium	4.63	4.88
Methoxyl	12.8	12.5

Differences in degrees of sulfonation of these purified non-dialyzable sodium lignin sulfonates can be taken into account to permit comparison of the two samples by calculation of the above analytical data to a sulfur and ash free basis. For such a computation, the mechanism of sulfonation may be postulated either as replacement of one hydroxyl grouping, or else one hydrogen atom, of the lignin for each sulfonic acid grouping becoming attached to the lignin. We have based our calculations on the hydroxyl replacement mechanism, *i. e.*



which yields the following carbon–hydrogen–oxygen–methyl ratios from the experimental data for the average unsulfonated lignin structural unit containing ten carbon atoms

Sample A	$C_{9.00}H_{7.20}O_{2.75}$ $(OCH)_{0.94}$
Sample B	$C_{9.00}H_{7.00}O_{2.84}$ $(OCH_3)_{0.95}$
"Theoretical"	$C_{9.00}H_{7.00}O_{2.75}$ $(OCH_3)_{1.00}$

The "theoretical" ratio given may be secured by assuming that the lignin polymer consists of "*n*" guaiacyl oxygenated propane structural units with the empirical formula $C_{10}H_{10}O_3$ and "3*n*" units with the empirical formula $C_{10}H_{10}O_4$.

Mr. Vincent F. Felicetta's analytical assistance is appreciated.

Summary

1. Lignin sulfonic acids may be isolated in a high degree of purity in about 65 to 80% yield by exhaustive continuous dialysis of sulfite waste liquor.

2. The dialyzable lignin sulfonates are believed to be of molecular weight of less than 2000 and appear to vary in amount depending upon conditions obtaining during the pulping process.

3. Two non-dialyzable lignin sulfonate samples from different commercial sources are found to have nearly the same empirical composition when calculated to a sulfur and ash free basis, and this composition is in agreement with the concept of lignin as a polymer of guaiacyl oxygenated propane structural units.

SEATTLE, WASHINGTON RECEIVED JULY 24, 1947

(20) C. B. Purves, P. F. Ritchie and W. J. Wald, THIS JOURNAL, 69, 1371 (1947).