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Lignin. III. Fractional Precipitation of Barium Lignin Sulfonates from Water by Ethanol

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Introduction

Several investigations of the empirical composition of lignin sulfonic acids have been carried out by separating the acids or their salts into fractions which were then analyzed. Fractionation was conducted by Erdtman[1] with organic bases, by Racky[2] with hydrofluosilicic acid, by Lautsch and Piazolo[3] with benzacridine and by Schwabe and Hahn[4] with propanol. In all these cases, fractions were precipitated directly from sulfite waste liquor, and considerable departures from uniformity in composition within a particular series of fractions are apparent. Also there seems to be no clear evidence of fractionation on a basis of molecular size of lignin sulfonates. Since these departures might have resulted from the presence of non-lignin substances, it seemed that they might be eliminated by study of lignin sulfonates previously purified by dialysis.[5] Thus the present investigation has been carried out to effect a fractionation of non-dialyzable lignin sulfonates in order to study the uniformity of composition and the range of diffusion coefficients manifested by the several fractions.

Experimental

Preparation of Barium Lignin Sulfonate Solution.—Calcium sulfite waste liquor (from about 85% western hemlock and 15% white fir woods) from a commercial source was subjected to continuous countercurrent dialysis[5] against distilled water to yield an aqueous solution of purified non-dialyzable lignin sulfonates containing about 65% of the methoxyl originally present in the liquor. This calcium lignin sulfonate solution was evaporated under reduced pressure to a concentration of about 130 g. of total solids per liter. Calcium and other metallic ions were removed by cation exchange resin treatment (Ionex No. 2),[6] and the ash-free solution of lignin sulfonic acids was treated with barium carbonate in quantity just sufficient to neutralize the strong acids, as determined by conductometric analysis. A small precipitate of barium sulfate, probably resulting from cleavage and oxidation of small amounts of loosely combined sulfur dioxide, was removed by centrifugation. The aqueous solution of barium lignin sulfonates (121.9 g. of total solids per liter) was fractionally precipitated.

Fractionation Technique.—Fractionation was conducted in triplicate. Into each of three 250-ml. centrifuge flasks was placed 75 ml. of the solution of barium lignin sulfonate. With the flasks in a water-bath at 20.5 ± 0.1°, increments of absolute ethanol (*n*-propyl and isopropyl alcohols were found to be effective as precipitants at lower concentrations than ethanol, but yielded systems of two phases that were not easily separated) were added dropwise to each, with continuous stirring. The addition of each increment required about an hour, and stirring was continued for three hours more. The first increments were of 10 ml. each, this volume being increased to secure the later fractions. After a total of twenty-four hours in the thermostat for each precipitation, the solids were centrifuged from the solution, the solution decanted off, and the solids washed from the flasks with water. The weights of the flasks and contents at each step in the operations were taken. From these data the ethanol content of the solution as each fraction was precipitated was calculated. The final composition of the solution so estimated agreed within 0.1% with the figure obtained by analysis of the final solution by distillation and density determination.

Treatment of Fractions.—The solution of each fraction was evaporated under reduced pressure (about 40°) nearly to dryness, then redissolved in water, and again taken to dryness in a vacuum desiccator over calcium chloride. This repeated evaporation served to remove completely the ethanol, which if present would give rise to erroneously high results in the methoxyl determination. Drying was continued to constant weight in a vacuum oven at 60° and 15 mm. pressure (about four hours). The weights of the corresponding fractions from the triplicate experiments were nearly identical. Corresponding fractions were combined.

Characterization of Fractions.—Methods used for chemical analyses have been previously described.[5] Of the original total solids, methoxyl, sulfur and sulfated ash, 99.9, 97.4, 100.3 and 101.9%, respectively, were accounted for in the several fractions.

Extinction coefficients were calculated from absorption data secured from 3500 to 2400 Å, using a Beckman Quartz Spectrophotometer at minimum slit width. Silica cells with a 10-mm. light path were used. Absorption was measured at 50-Å. intervals for aqueous solutions of the barium lignin sulfonate fractions at two concentrations (1.00 and 5.00 mg. methoxyl per liter) buffered at *p*H 5.0 with 0.001 *M* acetate buffer.

Diffusion coefficients were determined by the solution-to-gel method of Felicetta, Markham, Peniston and McCarthy.[7]

Water Content of Fractions.—The water content of several fractions was estimated by measurement of the volume of water vapor evolved from a sample on heating at low pressure. The apparatus was a modification of that used by Browne and Houlehan,[8] and was so constructed that the evolved vapor could be condensed in an attached capillary tube, and its saturated vapor pressure, melting point and vapor density determined.

Discussion

A purified barium lignin sulfonate preparation has been fractionated by precipitation from aqueous solution by addition of increments of ethanol. Ten fractions were obtained at characteristic ethanol concentrations and the last was recovered from the remaining solution. Sufficient time was allowed at each solvent composition so that equilibrium in precipitation is believed to have been approximated. The several fractions were precipitated from solutions containing lignin sulfonates in rather high concentration in order to

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(1) Erdtman, *Svensk. Papperstidn.*, **45**, 374, 392 (1942).

(2) Racky, *Cellulosechem.*, **20**, 22 (1942).

(3) Lautsch and Piazolo, *ibid.*, **22**, 48 (1944).

(4) Schwabe and Hahn, *Holzforschung*, **1**, 42, 79 (1948).

(5) Peniston and McCarthy, THIS JOURNAL, **70**, 1324 (1948).

(6) Manufactured by the Dow Chemical Co., Midland, Mich.

(7) Felicetta, Markham, Peniston and McCarthy, THIS JOURNAL, **71**, 2879 (1949).

(8) Browne and Houlehan, *ibid.*, **35**, 649 (1913).

TABLE I

FRACTIONATION OF BARIUM LIGNIN SULFONATE[a]

Fraction	Cumulative % solids pptd.	Wt. % ethanol in solvent	Methoxyl, %	Sulfur, %	Sulfated ash, %	Carbon,[b] %	Hydrogen,[b] %	Diff. coeff. sq. mm./day
0	0	10.2	...	..	..	...	..	..
1	20.24	18.6	10.78	4.82	18.1	48.38	4.58	6.1
2	29.23	26.0	11.16	4.77	17.4	46.96	4.73	5.7
3	36.78	32.4	10.87	5.06	18.2	...	..	5.8
4	47.40	37.8	10.84	5.28	18.4	45.50	4.77	6.6
5	57.66	42.4	10.78	5.42	19.8	...	..	7.1
6	66.21	46.4	10.53	5.68	20.4	...	..	8.7
7	72.70	49.8	10.65	5.77	20.8	44.12	4.80	9.8
8	77.53	52.8	10.62	5.74	22.1	...	..	10.6
9	83.88	57.9	10.53	5.86	21.8	...	..	12.0
10	90.33	65.5	10.68	6.19	21.5	44.18	4.41	13.4
N	99.90	Not pptd.	10.59	5.67	20.3	44.55	4.58	16.7
Initial material		..	11.03	5.34	19.1	...	..	..

[a] Duplicate analyses for methoxyl, S, ash, C and H departed from the averages not more than 0.06, 0.05, 0.5, 0.10 and 0.06%, respectively, except fract. 6, methoxyl, 0.08%; fract. 2, S, 0.13%; and fract. 8, ash, 0.9%. Diffusion coefficient departed from the averages not more than 0.45 mm.^{2}/day. [b] Microanalyses by Microchemical Specialties Co., Berkeley, Calif.

provide adequate material for careful characterization, although sharpness of fractionation was probably thereby sacrificed.[9]

The analytical characteristics of the several barium lignin sulfonate fractions are found to be quite similar (Table I). These quantities, taken with the weights of the fractions, yield satisfactory material balances. Considering the precipitated fractions in order obtained, there is observed a trend of decrease in content of carbon and methoxyl, and of increase in content of sulfur and sulfated ash. These differences are not large and, while possibly affecting the precipitability of the barium lignin sulfonates, they are not believed to be controlling factors.

Before analysis, the fractions were dried to constant weight in a vacuum oven at 60° and 15 mm. pressure. These mild drying conditions were employed to avoid degradation of the material used for later characterization. To determine how much water might still be contained in the fractions, and if possible to differentiate between water of adsorption and of hydration, measurements of the vapor evolved on heating at reduced pressure were made on fractions 2, 4, 7 and N. The saturated vapor pressures of the condensed vapors from fractions 2 and 7 were determined at 0, 10 and 20° and found to be very close to those of water; the frozen condensate melted around -4 to $-5°$; and the vapor density, determined from the volume of evolved vapor and the weight of condensate, indicated molecular weights of the vapors from fractions 2 and 7 to be 16 and 17, respectively.

Similar measurements of vapor evolution from sodium tetradecane sulfonate hemihydrate supplied by Dr. E. C. Lingafelter, and from copper sulfate pentahydrate, showed stepwise evolution in four and one steps, respectively, characteristic of hydrates. The evolution of vapor from the barium lignin sulfonate fractions, however, proceeded without discrete steps. Instead, a more or less smooth curve was observed which may indicate evolution of water held by adsorption, or as a rather large number of hydrates, or both. The amount of vapor so liberated at 10 mm. was: at 117°, 3.08, 3.5, 3.67 and 3.8% from fractions 2, 4, 7 and N, respectively; and at 129°, 3.48, 3.9 and 4.1 from fractions 2, 4 and N, respectively. The amount of water evolved is nearly proportional to the number of sulfonate groups present. Thus, from 1.14 to 1.20 moles of water per sulfonate group was driven off at 117°, and from 1.29 to 1.32 moles at 129°. At 150° the amount is about 1.6 moles which appears to be nearly a limiting value. There is evidence of some decomposition at higher temperatures but over 80% of the gas evolved at 175° was re-adsorbed on cooling. From the known tendency of metal sulfonates to form hydrates and from the close proportionality between the water evolved and the amount of sulfonate present, it seems probable that the water is combined in a number of hydrates of differing dissociation characteristics.

For those fractions for which carbon and hydrogen analyses were available, the analytical data have been recalculated after subtraction of the indicated 1.6 moles of water per sulfonate group. A basis of nine carbon atoms was chosen because there now exists extensive evidence from degradation experiments[10] indicating that the structural units of gymnosperm lignins consist, in large proportion at least, of phenyl propane skeletons. The data when so calculated show that each fraction contains nearly an identical number of equivalents of barium and sulfur as expected for barium sulfonates, and that the degree of sulfonation of

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(9) Scott, *J. Chem. Phys.*, **13**, 178 (1945).

(10) (a) Freudenberg, *Ann. Rev. Biochem.*, **8**, 88 (1939); (b) Hibbert, *ibid.*, **11**, 183 (1942); (c) Erdtman, *Svensk. Papperstidn.*, **44**, 243 (1941); *Pulp Paper Mag. Can.*, **43**, 253 (1942); (d) Percival, *Ann. Repts. Progress Chem.* (*Chem. Soc. London*), **39**, 142 (1942); (e) Lewis and Pearl, U. S. Patent 2,433,227 (Dec. 23, 1947).

the several lignins is not quite the same. The first precipitated fraction is sulfonated to the extent of 0.37 mole per C_9 unit and the degree of sulfonation increases, reaching 0.52 in fraction 10. The difference in degree of sulfonation makes desirable a further recalculation of the data to a sulfur-free basis. This has been done by assuming that barium is exactly equivalent to sulfur and, for calculation purposes only, that each sulfonate group replaced a hydrogen atom in the original lignin.

The empirical composition of the several lignin fractions on an anhydrous, and also sulfur-free and ash-free basis is found to be nearly uniform (Table II) in spite of the accumulation of error in the hydrogen and oxygen data.[11] This composition is in general agreement with that reported by Wald, Ritchie and Purves[12] for pine lignin *in situ*, by Brauns[13] for "native" spruce lignin and by Racky[2] for some of his fractions of lignin sulfonic acids from spruce (Table II).

TABLE II

ESTIMATED EMPIRICAL COMPOSITION OF LIGNINS

Lignin	Composition
Fr. 1	$C_9\ (OCH_3)_{0.85}\ H_{7.9}\ O_{2.4}$
2	$C_9\ (OCH_3)_{0.91}\ H_{8.4}\ O_{2.7}$
4	$C_9\ (OCH_3)_{0.92}\ H_{8.8}\ O_{2.7}$
7	$C_9\ (OCH_3)_{0.93}\ H_{9.1}\ O_{2.5}$
10	$C_9\ (OCH_3)_{0.93}\ H_{7.9}\ O_{2.2}$
N	$C_9\ (OCH_3)_{0.91}\ H_{8.4}\ O_{2.6}$
Pine,[12] *in situ*	$C_9\ (OCH_3)_{0.91}\ H_{7.8}\ O_{2.0}$
Spruce,[13] "native"	$C_9\ (OCH_3)_{0.89}\ H_{8.7}\ O_{2.6}$
Spruce,[a] from LSA	$C_9\ (OCH_3)_{0.93}\ H_{8.4}\ O_{2.2}$

[a] Calculated by us to a nine-carbon atom basis from data on lignin sulfonic acids (LSA) given by Racky[2] in his Table 2 using the average composition of his fractions 2, 3, 7 and 9 which were very similar.

The similarity of ultraviolet absorption spectra found for the fractions is in agreement with the uniformity of chemical composition. Extinction coefficients (cm.$^{-1}$ per mg. of methoxyl per liter) obtained in aqueous solutions containing 5.00 mg. of methoxyl per liter were 0.259, 0.243, 0.241, 0.231, 0.227 and 0.241 at 2800 Å., and 0.222, 0.210, 0.205, 0.192, 0.187 and 0.194 at 2650 Å. for fractions 1, 2, 4, 7, 10 and N, respectively.

Diffusion coefficients are found to increase markedly throughout the series of fractions. If molecular weights are calculated on the basis of spherical particles, a range from 100,000 to 4,000 is indicated although the actual molecular weights are probably somewhat lower judging from the few frictional ratios for lignins which have been reported.[14] It thus appears probable that the molecular size of the lignin sulfonates controls the order of precipitation although the latter may be influenced by degree of sulfonation. The characteristics manifested by the lignin sulfonate fractions seem to be in accord with those expected for fractions secured from a polymeric series.

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Summary

1. A lignin sulfonate preparation purified by dialysis has been precipitated as a barium salt from aqueous solution by ethanol to yield a number of fractions which have been characterized by chemical analyses, ultraviolet extinction coefficients and diffusion coefficients.

2. When results of the chemical analyses are calculated to an anhydrous, sulfur-free and ash-free basis, the fractions are found to be of nearly uniform composition.

3. Diffusion coefficients of the several fractions are found to increase progressively in order of precipitation and indicate a corresponding decrease in molecular weights over a wide range.

4. The uniformity of chemical composition and of ultraviolet absorption spectrum and the regular trend in diffusion coefficients indicate the polymeric character of lignin sulfonic acids.

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(11) The analytical margins of error in Table I, increased by the assignment of hydrogen and oxygen to methoxyl, sulfonate and hydration groups may amount to as much as 0.75 atom of hydrogen and 0.4 atom of oxygen in the C_9 formulas of Table II.

(12) Wald, Ritchie and Purves, THIS JOURNAL, **69**, 1371 (1947).

(13) Brauns, *ibid.*, **61**, 2120 (1939).

(14) (a) Gralen, *J. Colloid Sci.*, **1**, 453 (1946); (b) Olleman, Pennington and Ritter, *ibid.*, **3**, 185 (1948).