[CONTRIBUTION FROM THE STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY]

The Solvent Properties of Liquids and Their Relation to the Solubility, Swelling, Isolation and Fractionation of Lignin

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The ability of solvents to dissolve or swell a variety of isolated lignins increases as the hydrogen-bonding capacities of the solvents increase and as their solubility parameters (after Hildebrand) approach a value of around eleven. Lower molecular weight lignin fractions are soluble in solvents with a wider range of solubility parameter and hydrogen bonding capacity than are the higher fractions. Earlier fractionations of ethanol and hydrol lignins are applications of this fact. Solubility trends in mixed solvents and within a homologous series of solvents are correlated with the same solvent properties. The yield of ethanol spruce lignin is substantially increased when the reaction is carried out in a better solvent system such as chloroform–ethanol. A threefold ethanolysis under mild conditions of acidity and temperature in this solvent mixture has given rise to a variety of products with widely different partition coefficients, solubilities and viscosities. The insolubility of lignin in wood and the heterogeneity and low molecular weight of its degradation products suggest the probability of a network structure or structures for lignin.

Although considerable data are available on the solubility of various isolated lignins, no general explanation of the subject seems to have appeared. Lignin solubility, compatibilities and swelling have therefore usually been investigated as isolated phenomena and similarities between many known lignin isolation methods have been obscured.[1]

This article suggests that the ability of solvents to dissolve or swell a variety of isolated lignins increases as the hydrogen-bonding capacities[2] of the solvents increase and as their solubility parameters[3] approach a value of around eleven. The lignins investigated, all of which conform to this pattern, include commercial pine kraft lignin,[4] commercial soda lignins,[5] ethanol maple lignin,[6] hydrol maple lignin,[7] ethanol spruce lignin,[8] "native" spruce[9] and aspen lignins.[10] The general similarity of the solubilities of these materials can be seen in Table I. The solubility of lignosulfonic acids, however, is completely altered by the introduction of the hydrophilic sulfonic acid group and is not comparable.

It is possible by mixing certain solvents with the lower alcohols to approximate the suggested conditions of maximum lignin solubility. If such a mixture is used as a solvent during alcoholysis, the yield of soluble alcohol lignin is markedly increased over that usually obtained.[1] The ethanolysis of sprucewood in chloroform–ethanol has been carried out as an example of this technique and will be described in detail later in this article.

Let us consider first the relationship of the solubility parameter of liquids to the solubility of lignin. Hildebrand has identified a constant which he calls the solubility parameter or δ-value with the square root of a substance's cohesive energy density. It is defined by the equation

$$\delta = (-E/v^1)^{1/2}$$

Where $-E$ is the energy of vaporization to the gas at zero pressure and v^1 is the molal volume of the liquid. Methods of calculation have been outlined and the values for many important solvents determined.[3] Polymers in general exhibit a maximum solubility in solvents with δ-values closest to their own.

In Table II a series of solvents with little or no hydrogen-bonding capacity is listed in order of increasing solubility parameter. The ethanol spruce lignin fractions in the table were obtained by partial precipitation with petroleum ether from dioxane solution. (There seems to be adequate evidence that differences in precipitability and viscosity in lignin fractions primarily reflect differences in molecular weight as is the case with other polymers.[6,11])

Clearly these lignin fractions are most soluble in solvents with δ-values around eleven, their solubilities decrease fairly regularly as the δ-value of the solvents decrease, and lignin fractions with increasing molecular weight are dissolved by solvents within a decreasing range of δ-values. Similar behavior has been observed with other polymers,[3,12] for example, natural rubber, thiokol, polyvinyl chloride, polystyrene and polyisobutylene.

For any considerable solubility of higher molecular weight lignin fractions, it is necessary to use solvents with some hydrogen bonding capacity or basic strength, but by comparing solvents of similar basic strength, it is possible to observe the same dependence of solubility on solubility parameter with higher lignin fractions. For example the solubility of any of the listed lignins in dioxane, acetone, methyl ethyl ketone and ether decreases essentially with decrease in solubility parameter of the solvent.

Gordy[2] has shown that when hydrogen-bonding solvents are mixed with heavy methanol (CH_3OD), a shift in wave length is observed in the oxygen–deuterium band of the infrared region of the

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[1] C. Schuerch, THIS JOURNAL, **73**, 2385 (1951).

[2] W. Gordy, *J. Chem. Phys.*, **9**, 204, 215 (1941). See also ref. 3, chapter 10, and M. L. Huggins, *J. Org. Chem.*, 1, 407 (1936).

[3] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1951.

[4] "Indulin," described in Bulletin L-5 Industrial Chemical Sales Division, West Virginia Pulp and Paper Company, 230 Park Avenue, New York 17, N. Y.

[5] "Meadol" prepared from mixed hardwoods by Mead Corporation, Chillicothe, Ohio; and "Tomlinite" a soda lignin produced by Howard Smith Paper Company, Cornwall, Ontario.

[6] R. F. Patterson, K. A. West, E. L. Lovell, W. L. Hawkins and H. Hibbert, THIS JOURNAL, **63**, 2065 (1941).

[7] C. P. Brewer, L. M. Cooke and H. Hibbert, *ibid.*, **70**, 57 (1948).

[8] Experimental section of this paper.

[9] F. E. Brauns, THIS JOURNAL, **61**, 2120 (1939).

[10] M. A. Buchanan, F. E. Brauns and R. L. Leaf, *ibid.*, **71**, 1297 (1949).

[11] C. Schuerch, *ibid.*, **72**, 3838 (1950).

[12] G. Gee in "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946, p. 186 ff.

TABLE I

THE SOLUBILITY OF ISOLATED LIGNINS IN SINGLE SOLVENTS

Solvent	δ^a-Value, (cal./cc.)$^{1/2}$	$\Delta\mu$,^{b} microns	"Indulin" kraft^c pine	"Meadol" soda^c hardwood	Hydrol maple^c	Ethanol maple^c	Native spruce^c	Native aspen^c
Hexane	7.4	L	Ins	Ins	8	9	Ins	Ins
Ether	7.5	0.19	Ins	Ins	6	6	Ins	Ins
Carbon tetrachloride	8.6	L	Ins	Ins		Ins		Ins
Xylene	8.78	L	Ins					Ins
Butyl Cellosolve	8.9	H	Par	Par				
Diethylene glycol	9.1	H	Sol	Sol$^-$				
Ethyl acetate	9.1	0.12	Sli$^-$	Sli$^-$				
Benzene	9.15	L	Ins	Ins	7	7		
Methyl ethyl ketone	9.3	0.11^b	Par$^-$	Par$^-$				
Chloroform	9.3	..	Ins	Sli$^+$	4	4		
Chlorobenzene	9.5	0.02	Ins	Ins				
Carbon disulfide	10.0	L	Ins	Ins	Ins	Ins	Ins	Ins
Dioxane	10.0	0.14	Sol	Sol	3	3	Sol	Sol
Nitrobenzene	10.0	.04	Ins	Sli				
Acetone	10.0	.14	Par	Par	2	2	Sol	Sol
Methyl formate	10.16	*ca.* 0.12	Par$^-$	Par$^-$				
Acrylonitrile	10.5	*ca.* 0.08	Sli	Sli				
1-Nitropropane	10.7	L	Ins	Ins				
Pyridine	10.7	0.27	Sol	Sol	1	1	Sol	Sol
Methyl cellosolve	10.8	H	Sol	Sol	Sol	Sol	Sol	Sol
Nitroethane	11.1	L	Ins	Ins				
Butanol-1	11.4	H	Ins	Ins				
Propanol-2	11.5	H	Sli	Ins				
Acetonitrile	11.89	0.09	Sli	Sli$^+$				
Nitromethane	12.6	L	Sli$^-$	Sli				
Ethanol	12.7	H	Sli$^+$	Sli	5	5		
Ethylene glycol	14.2	0.31	Sol	Sol	Sol	Sol	Sol	Sol
Methanol	14.3	0.28	Par$^-$	Par$^-$				
Glycerol	16.5	H	Ins	Ins				
Water	23.4	H	Ins	Ins	9	8	Ins	Ins

[a] Values from ref. 3 except for glycol derivatives and glycerine, the calculations for which are in the Experimental section of this paper. [b] Numeral values from ref. 2 except those labeled "*ca.*" which are estimates from Gordy's data for analogous compounds. Where close analogies were not possible, H for high and L for low is used. The value for methyl ethyl ketone should perhaps be the same as that for acetone, *cf.* Gordy's results with D_2O in place of CH_3OD. [c] Ins = insoluble, Sli = slightly soluble, Par = partially soluble, Sol = soluble, numerals are in order of decreasing solubility for a given lignin.

TABLE II

THE RELATION OF SOLVENT δ-VALUE AND LIGNIN MOLECULAR WEIGHT TO ETHANOL SPRUCE LIGNIN SOLUBILITY

Solvent	δ-Value, (cal./cc.)$^{1/2}$	Sample No.^{a} I 8	I 7	I 6N	I 6A	I 3N	I 3A	I 1A
Ligroin	*ca.* 7.3	Ins	Ins	Ins	Ins	Ins	Ins	Ins
Carbon tetrachloride	8.6	Ins$^+$	Ins	Ins	Ins	Ins	Ins	Ins
Benzene	9.15	Sli$^-$	Ins	Ins	Ins	Ins	Ins	Ins
Trichloroethylene	9.3	Sli$^-$	Ins	Ins	Ins	Ins	Ins	Ins
Chlorobenzene	9.5	Sli$^+$	Ins	Ins	Ins	Ins	Ins	Ins
Carbon disulfide	10.0	Ins	Ins	Ins	Ins	Ins	Ins	Ins
Nitrobenzene	10.0	Sol	Sol$^-$	Sol	Ins	Ins	Ins	Ins
Acrylonitrile	10.5	Sol	Sol	Sol	Sol$^-$	Sol$^-$	Sli	Ins
1-Nitropropane	10.7	Sol	Sol	Sli	Ins	Ins	Ins	Ins
Nitroethane	11.1	Sol	Sol	Sol	Par	Sli$^-$	Ins	Ins
Acetonitrile	11.9	Sol	Sol	Sol	Sol	Sol$^-$	Par	Ins
Nitromethane	12.6	Sol	Sol	Sol	Par	Sli$^-$	Ins	Ins

[a] Roman numeral I represents the first ethanolysis of spruce woodmeal reported in Experimental. Arabic numerals 1, 3, 6, represent the three main fractions obtained by fractional precipitation of lignin I from dioxane by petroleum ether. Fraction I 8 was recovered from chloroform–ligroin solution after the original precipitation of ligroin–insoluble lignin. Fraction I 7 remained in solution after the precipitation of I 1 to I 6. The samples are therefore arranged above in order of increasing molecular weight unless previous work (reference 6 and 11) is completely misleading. The letters A and N represent alkali-soluble and "neutral" fractions from the partitioning of fractions I 1, I 3 and I 6. Some difference in solubility is apparent between the subfractions I 3A and I 3N and between I 6A and I 6N.

spectrum. The shift in wave length ($\Delta\mu$) is proportional to the hydrogen-bonding capacity or basic strength of the solvent. Of the solvents[3] tested by Gordy, those having $\Delta\mu$ values of less than 0.14 micron are poor to mediocre lignin solvents, *i.e.*, nitro compounds, nitriles and esters. Those having $\Delta\mu$ values of 0.14 or higher *and solubility parameters around eleven* are good lignin solvents.

Table III lists seven solvents whose solubility parameters are between ten and eleven or close to the optimum value for lignin solubility. Their ability to dissolve lignin increases regularly from carbon disulfide, a poor lignin solvent, to pyridine, a powerful solvent, or in the order of increasing basic strength. The same effect is noticeable at other values of solubility parameter. Ether is, for example, a more powerful lignin solvent than carbon tetrachloride, xylene or benzene. The glycol ethers are excellent lignin solvents because of their hydrogen-bonding capacity although they vary rather widely in solubility parameter; other examples could be cited. Chloroform, the hydrogen of which has acidic properties, is a better solvent than chlorobenzene, a fact which suggests that lignin can act as a proton acceptor as well as donor.

TABLE III

THE EFFECT OF HYDROGEN BONDING CAPACITY ON LIGNIN SOLUBILITY

Solvents listed in order of increasing solvent power for lignins

		δ-Value, (cal./cc.)$^{1/2}$	$\Delta\mu$, micron
1	Carbon disulfide	10.0	Low
2	Nitrobenzene	10.0	0.04
3	Acrylonitrile	10.5	*ca.* 0.08
4	Methyl formate	10.16	*ca.* 0.12
5	Acetone	10.0	0.14
6	Dioxane	10.0	0.14
7	Pyridine	10.7	0.27

If a plot of solvent δ-value *vs.* solvent hydrogen-bonding capacity is made, good lignin solvents will be found in a roughly parabolic area, the apex of which will be at a solubility parameter of around eleven and a $\Delta\mu$ value dependent on the molecular weight of the lignin sample.[12a]

In a homologous aliphatic series such as the alcohols (and perhaps the nitro compounds) the solubility of lignin decreases abruptly with increasing hydrocarbon chain length, even when the solubility parameter is closer to a value of eleven in the higher members. The effect appears similar to the diluting of a good solvent with an aliphatic hydrocarbon, and the higher alcohols are poorer solvents than would perhaps be expected from their solubility parameter and the presence of a hydroxyl group in the molecule. The high association of pure alcohols frequently results in a lower solvent power than expected[2,8]; and the assumption that the molecules have a uniform force field around them, which is implied in the use of the δ-value, is clearly not true for molecules having non-polar and highly polar portions.[12]

Maple ethanol[6] and hydrol[11] lignins have been separated into fractions of differing viscosity and molecular weight by pouring solutions of the polymers into solvents of varying δ-value and basic strength. As would be expected from the foregoing discussion, water and petroleum ether have been found to dissolve primarily monomers; ether, benzene, ethanol and chloroform separately dissolve intermediate molecular weight fractions as well, while dioxane, acetone and (especially) pyridine are the best individual solvents for all molecular sizes. These separations again reflect the fact that low molecular weight lignin fractions dissolve in solvents with a wider range of solubility parameters, and a weaker hydrogen-bonding capacity than do the high molecular weight fractions.

Table IV lists the solubility of a soda lignin in mixed solvents. Whenever a hydroxylated solvent, such as water or the lower alcohols, is mixed with a solvent of lower hydrogen-bonding capacity and a δ-value of nine or greater, the solubility of lignin is greater in the mixture than in either solvent alone. In all cases the hydrogen-bonding capacity of the mixture is greater than that of one individual solvent and in most (though not all) cases the solubility parameter of the mixture is presumably closer to the optimum than with either solvent. The effect is noticeable even on the addition of water or alcohols to dioxane or acetone but is striking with a mixture of two poor solvents like nitroethane and butanol, or benzene and ethanol. The cellosolves, however, are such effective solvents that no qualitative improvement was noted on mixing them with other liquids. Solvents with δ-values less than about nine seem to act as simple precipitants and the solubility of lignin in mixtures which include them always appears to be less than in their absence.

Apparently the most extensive data on lignin solubility are contained in a list of about 170 liquids and 60 binary mixtures that have been tested as solvents for commercial pine kraft lignin.[4] These data show the same trend of dependence on δ-value and hydrogen bonding-capacity that has been outlined above and also show that the bulk of kraft lignin has a solubility comparable to the highest molecular weight fractions of ethanol and hydrol lignin. We have found no evidence that any other properties of the solvents are of comparable importance in determining lignin solubility.

Swelling experiments on insoluble Klason,[13a] Willstätter,[13b] periodate,[13c] and wood hydrolysis[14] lignins or—more pertinently—lignin in wood have in the present research not been carried out, but the swelling of cuproxam lignin increases in about the same order as the solubility of other lignins, *i.e.*, water < benzene < methanol < ether < acetone < pyridine[13d]; and moist phenol and formamide, both excellent solvents for other isolated lignins, are good swelling agents at least for periodate spruce lignin.[15] Similarly the position of maximum swelling of rubber when crosslinked by different methods and to different extents is at the same value of solubility parameter as is the maximum solubility of the native polymer.[12]

The insolubility of lignin as it exists in wood has received at one time or another most of the ex-

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(12a) NOTE ADDED IN PROOF.—A similar treatment of polymer solubility by H. Spurlin has just come to our attention in *J. Polymer Sci.*, **3**, 714 (1948).

(13) F. E. Brauns, "The Chemistry of Lignin," Academic Press, Inc., New York, N. Y., 1952; (a) p. 55; (b) p. 57; (c) p. 63; (d) p. 206; (e) p. 211; (f) p. 646.

(14) "The Madison Wood-Sugar Process," United States Department of Agriculture, Forest Service Report No. R 1617, Forest Products Laboratory, Madison 5, Wisconsin.

(15) Pulp and Paper Research Institute of Canada, Montreal, Canada, Fall Quarterly Report (1947).

TABLE IV

THE SOLUBILITY OF A SODA LIGNIN "TOMLINITE" IN MIXED SOLVENTS[a]

	δ-Value (cal./cc.)$^{1/2}$	Δμ, micron	Benzene	Chloroform	Chlorobenzene	Dioxane	Nitrobenzene	Acetone	Methyl Formate	Acrylonitrile	Methyl Cellosolve	Nitroethane	Butanol	Nitromethane	Ethanol	Water
Benzene	9.15	L	Ins													
Chloroform	9.3	..	Ins	Ins^{+b}												
Chlorobenzene	9.5	0.02	Ins	Ins	Ins											
Dioxane	10.0	H	Par	Sol	Par	Sol										
Nitrobenzene	10.0	0.04	Ins	Ins	Ins	Sol	Sli									
Acetone	10.0	0.14	Par^{-b}	Par	Sli	Sol	Sol	Sol^{-}								
Methyl formate	10.16	*ca.* 0.12	Sli	Sli	Sli	Sol^{-}	Sli	Sli^{+}	Sli^{+}							
Acrylonitrile	10.5	*ca.* 0.08	Sli^{-}	Sli	Sli^{-}	Par	Sli	Sli^{+}	Sli	Sli						
Methyl Cellosolve	10.8	H	Par	Sol	Sol	Sol^{-}	Sol	Sol	Sol	Sol	Sol					
Nitroethane	11.1	L	Sli^{-}	Sli^{+}	Sli	Sol	Sli	Sli	Sli^{-}	Sli^{-}	Sol	Sli^{-}				
Butanol	11.4	H	Par	Sol	Par^{+}	Par^{+}	Sol	Sol	Par	Sol	Sol^{-}	Sol	Ins^{+}			
Nitromethane	12.6	L	Sli	Sli	Sli	Sol	Sli	Sli^{+}	Sli	Sli^{-}	Sol	Sli	Sol	Sli		
Ethanol	12.7	H	Par^{+}	Sol	Sol	Sol	Sol	Sol	Par	Sol	Sol	Sol	Ins	Sol	Sli	
Water[a]	23.4	H	Ins	Ins^{+}	Ins	Sli[a]	Sli	Sol^{-}	Par	Sli	Sol	Ins	Ins	Ins	Ins	Ins

[a] Equal volumes of the two solvents used. The solubility of lignin in dioxane is, however, enhanced by small amounts of water. The solubility of lignin in water-immiscible solvents is little affected by the presence of water. [b] Plus and minus signs indicate solubilities somewhat greater or less than other cases described by the same word *i.e.*, insoluble, slight, partial soluble.

planations applicable to an organophilic polymer system interpenetrated with carbohydrate impurities. The correct interpretation of its insolubility is of importance in the choice of method of structure investigation. It appears pertinent, therefore, to review briefly the more frequent speculations in this field.

A highly crystalline structure is ruled out for lignin by X-ray diffraction studies.[13e] A chemical linkage to cellulose appears improbable since electron micrographs show lignin to have an amorphous granular structure that exhibits no intimate connection with cellulose,[16] and since the crystalline character of cellulose would seem to limit such a union to faults or fissures or on surfaces.[17] Such a superficial linkage, if it were to exist, is not sufficient reason by itself for lignin insolubility since the removal of carbohydrates by periodate oxidation and neutral hydrolysis leaves behind an insoluble lignin.[18] A linkage to the hemicelluloses also seems inadequate for these too are removed by periodate oxidation; most of the hemicelluloses are also removed by the peptizing action of dilute alkali in the cold while most of the lignin remains insoluble. It is improbable that lignin is inaccessible to swelling solvents since fine subdivision does not affect the yield of ethanol[19] or native[20] lignin, and wood density has little effect on the rate of alkaline pulping.[21] Lignin is apparently also accessible to sulfite liquor.[22] Excessive entangling with the carbohydrate fraction does not explain lignin insolubility since lignin shows no evidence of chain structure, and the known interpenetration of hemicelluloses with lignin[16] does not prevent their separation. The preceding analysis of lignin solubility suggests that there are no highly specific solvent requirements for lignin, but rather that its observed solubility behavior is that to be expected of an aromatic polymer with many hydroxyl groups.

There remains then only the most obvious explanation of lignin insolubility: that lignin has a three dimensional structure. The solution of a network polymer requires a fragmentation by chemical reaction, as does lignin. Fragments obtained by random cleavage would be expected to be of various sizes,[6,7] relatively low molecular weight,[13e] chemically heterogeneous,[11,23] and in part non-linear.[24] This is the case with all isolated lignins. In addition in one isolation method the known chemical changes occurring on the lignin can be written as a balanced equation of solvolysis.[1] While a lignin carbohydrate complex cannot be completely excluded, it does not appear to be a complete explanation for the insolubility of lignin and the independent evidence for cross linked structure(s) seems impressive.

One attack on the lignin problem has been the search for a method of isolating the material chemically unchanged. If however lignin is three-dimensional, it is of equal importance to have available a method of degradation of proven and preferably uncomplicated mechanism. In this connection, a study of the acid-catalyzed solvolysis of lignin under conditions advantageous for its solution may have some merit: Only two reagents are required, making it perhaps possible to interpret the reaction mechanism more readily. The hypothetical reaction previously mentioned can serve as a theoretical basis of investigation. There are probably no important methods of dissolving lignin which do not require the action of either hydrogen or hydroxyl ions.

Cyclization[25] and intermolecular condensations[26]

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(16) K. Mühlethaler, *Biochim. et Biophys. Acta*, **3**, 15 (1949).

(17) C. B. Purves in E. Ott's, "Cellulose and Cellulose Derivatives," Interscience Publishers, Inc., New York, N. Y., 1943, p. 101.

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

(19) W. B. Hewson, J. L. McCarthy and H. Hibbert, *ibid.*, **63**, 3041 (1941).

(20) F. E. Brauns and H. Seilen, *Tappi*, **35**, 67 (1932). The authors list this fact and others as evidence of a lignin–carbohydrate linkage or a condensed lignin structure.

(21) G. L. Larocque and O. Maass, *Can. J. Research*, **B15**, 89 (1937).

(22) J. M. Calhoun, F. H. Yorston and O. Maass, *ibid.*, **B17**, 121 (1939).

(23) H. Pauly, *Ber.*, **67**, 1177 (1934).

(24) H. Staudinger and E. Dreher, *ibid.*, **69**, 1729 (1936).

(25) H. Richtzenhain, *ibid.*, **83**, 488 (1950).

(26) K. A. West, W. L. Hawkins and H. Hibbert, THIS JOURNAL, **63**, 3038 (1941).

have received considerable attention as side reactions occurring during alcoholysis and are important complications which require further assessment. If occurring to only a small degree they may not vitiate structural conclusions. It is perhaps pertinent that eugenol has been found extremely resistant to acid-catalyzed condensation with aliphatic and aromatic aldehydes[27] and that monomers isolated from lignin resist resinification by ethanolysis when present in high dilution.[26] A repolymerization reaction must be dependent on the square of the substrate concentration, while depolymerizations need not be. The lignin concentration in the following preparations was about 1% or less and repolymerization should therefore be minimized.

For exploratory work the ethanolysis reaction was chosen and of the variety of solvent mixtures superior to pure ethanol, the combination of chloroform and ethanol was used. A series of standard ethanolyses was first carried out,[6] with varying proportions of chloroform in the solvent mixture. Extent of delignification was measured by Klason lignin determinations. A typical delignification maximum was observed at close to an azeotropic mixture of the two solvents (Table V). Under conditions which gave about 30% delignification with ethanol as solvent, chloroform–ethanol (80:20) gave about 75% delignification.

TABLE V

VARIATION IN YIELD OF ETHANOL LIGNIN IN DIFFERENT CHLOROFORM–ETHANOL SYSTEMS[a]

No.	Ethanol, %	Pulp, yield, %	Klason lignin content of pulp, %	Original lignin dissolved, %
I	10	77.2	21.2	41
II	15	57.3	16.1	66
III	20	51.4	12.0	77
IV	40	59.2	18.3	60
V	50	62.7	21.0	52
VI	80	69.6	24.5	38
VII	100	73.3	25.8	32

[a] Norway spruce wood meal heated 49 hours at 64° with 1.76% hydrogen chloride.

It also seemed of interest to determine whether lower concentrations of mineral acid were feasible for ethanolysis. In a preparative experiment, therefore, the concentration of hydrogen chloride was decreased from 1.75% used in the previous series to 0.7% (0.2 *N*). Following reaction, the lignin was isolated by filtering off and washing the wood pulp, washing the combined chloroform liquors with water, drying, concentrating *in vacuo* and precipitating into petroleum ether. Three consecutive ethanolyses of 40-hours duration were required to give a total yield of 73% delignification (Table VI). The rate of delignification was obviously substantially lowered by a decrease in hydrogen ion concentration.

Although these products were obtained by reaction at a temperature about 15 degrees lower than usual, and at about one-third the concentration of mineral acid, the heterogeneity of the products was as great as that of any other lignin preparation. Table VI summarizes the data obtained on the ligroin insoluble material obtained by this three-step ethanolysis. The following points seem of interest:

The viscosities of the lignin solutions were low and the plot of the ratio of specific viscosity to concentration $(N_{sp})/(c)$ against concentration was linear over the range studied from 1.5 to 4 g. per 100 ml. The intrinsic viscosity of the ligroin-insoluble products increased from the first to the second to the third ethanolysis. The first ethanolysis also gave rise to the largest quantity of ligroin-soluble material. An analogous result has been observed with sulfite pulping, another acid-catalyzed lignin depolymerization. Cooks which remove only small amounts of lignin produce soluble lignosulfonic acids of low molecular weight, while waste liquors from cooks removing large proportions of the lignin contain largely sulfonic acids of high molecular weight.[28]

The values of the constant k' calculated from the equation

$$\frac{n_{sp}}{C} = [n] + k'[n]^2C$$

were not the same for the three products as would be expected in a homologous series[29] but were nearly the same for the first and third ethanolysis, markedly greater for the second.

The proportion of "neutral"[23] and alkali-soluble material was determined in each fraction by a three stage (four separatory funnel) countercurrent extraction between aqueous ethanolic alkali and ethanolic chloroform. The fraction subjected to ethanolysis for the longest period of time and having the highest viscosity also had the highest proportion of alkali-soluble material. This result is not consistent with a single structure for lignin in which the phenolic oxygens form a portion of a linear unbranched chain free of heterocyclic rings [13f] but is consistent with almost any more complicated system.

The three main products were fractionated according to molecular weight by partial precipitation, similar fractions were recombined to give larger quantities and the different molecular weight bands were distributed between alkali and chloroform. Even when comparing fractions subjected to ethanolysis for the same length of time, the lower molecular weight fractions had higher proportions of "neutral" material than the high molecular weight fractions (Table VI). This result was obtained with samples I and II but could not be confirmed with sample III, for the highest molecular weight fraction precipitated from chloroform–ethanol on the addition of the aqueous ethanolic alkali and set to an insoluble product. Apparently higher dilution and a better aqueous solvent system is required for the partitioning of higher molecular weight fractions in order to avoid insolubilization. The observed concentration of the so-called "neutral" fraction in the lower molecular weight por-

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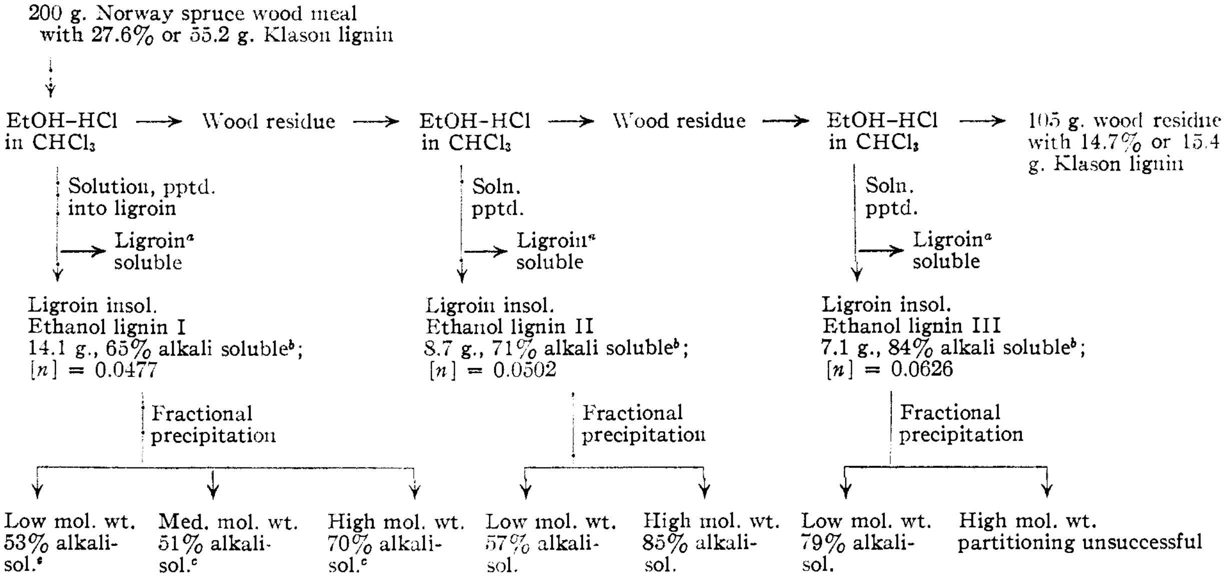
(27) A. Michael and J. P. Ryder, *Am. Chem. J.*, **9**, 130 (1887).

(28) H. Erdtman, *Svensk Papperstidn*, **45**, no. 16, 315 (1942); *Bull. Inst. Paper Chem.*, **13**, 79 (1942-1943).

(29) C. E. H. Bawn, "The Chemistry of High Polymers," Interscience Publishers, Inc., New York, N. Y., 1948, p. 166.

TABLE VI

SPRUCE ETHANOL LIGNIN PREPARATION



[a] The "ligroin soluble" fractions were combined and weighed 11.0 g. Total yield of all products was 56.3 g. of lignin from 55.2 g. originally present in the wood. [b] Per cent. alkali soluble was calculated as % recovered in separatory funnels A and B divided by total recovery, and the quotient multiplied by 100 (see Experimental). [c] Weighting these results by quantity of fraction recovered gave a total % alkali solubles equal to 57% or slightly lower than that found on the unfractionated material (65%).

tions of spruce ethanol lignin is the reverse of the distribution obtained with maple hydrol lignin. Whether this difference is due to extent or method of degradation, difference in wood source or some other reason must await further investigation.

The fact that previously maple ethanol lignin has been obtained in higher yield than spruce ethanol lignin[30] is apparently due to the greater solubility of the former in ethanol. The greater solubility is to be expected of a more heterogeneous polymer even if of the same molecular weight and need not at present be ascribed to a greater tendency of spruce ethanol lignin to repolymerize.

Experimental

Solubility Tests.—Small samples (0.1 g.) of lignin were shaken at room temperature with 10 ml. of individual or mixed solvents (1:1 by volume) and observed for depth of color of solution and for the presence of undissolved material. The results in some cases indicate less solubility than recorded in reference 4 and in general minimize the solubility of the lignin samples in order to emphasize differences between solvents.

Ethanolysis with Different Solvent Proportions.—Five-gram samples of air-dried Norway spruce meal (40–80 mesh, ethanol–benzene extracted) were sealed in tubes with 40 ml. of chloroform–ethanol in various proportions containing 1.76% hydrogen chloride. The tubes were rotated in a 64° oil-bath for 49 hours. The wood residues were filtered off, washed four times with about 50 ml. of their own solvent mixtures, and the liquors and washes made up to 100 ml. The liquors from tubes 1 to 3 (with high chloroform content) were clearly the darkest. The wood residues varied in color from almost black (No. I) to light gray (No. III) to almost unchanged (No. VII). The Klason lignin contents and pulp yields were at a minimum with No. III and are listed in Table V.

Preparation of Ethanol Spruce Lignin in a Mixed Solvent.—Two hundred grams of air-dried Norway spruce meal (40–80 mesh, ethanol–benzene extracted, 27.6% Klason lignin) was refluxed with 0.2 *N* hydrogen chloride in 1,930 ml. of chloroform absolute ethanol (8:2 by volume) under carbon dioxide. After 43 hours, the wood residue was separated, washed with chloroform-ethanol and treated with fresh reaction solution for two more periods of about 43 hours. The reflux temperature was about 60°. The solutions and washings from each ethanolysis were washed with 5% bicarbonate and with water and were dried over magnesium sulfate. The three liquors were individually concentrated to about 100 ml. under reduced pressure (20–25°) and precipitated into ligroin. The ligroin-soluble oils (largely from the first ethanolysis) were combined and weighed 11.0 g. The ligroin-insoluble ethanol lignins, I, II and III, were washed with ligroin and isolated separately as light colored powders. A lignin balance is given in Table VI.

A sample of these lignin fractions was combined and distilled with 12% hydrochloric acid after the "Tappi" standard pentosan determination.[31] The distillate from one gram of lignin absorbed 0.2 milliequivalent of bromine, the equivalent of 1.3% pentosan, without correction.

The ethanol lignin samples were analyzed for chlorine and contained less than 0.5%.

Lignin Partitioning.—Thirty grams of sodium hydroxide was dissolved in 1000 ml. of 48% ethanol. This solution on equilibration with 430 ml. of chloroform gave 750 ml. of a chloroform layer and about 670 ml. of an aqueous phase.

Approximately 1-g. lignin samples were partitioned between 25 ml. of each of these two phases and the phases transferred and equilibrated in a countercurrent fashion as previously[23] according to Craig's technique.[32] Four separatory funnels were used and in each case the bulk of the lignin appeared in the first "A" (alkali-soluble) and in the fourth "N" (chloroform-soluble) fractions. After partitioning, the liquid layers were acidified with sulfuric acid, the layers separated and the water extracted with 1 ml. of chloroform. The chloroform layers were dried, concentrated *in vacuo* to less than 5 ml. and precipitated into a small centrifuge cup filled with petroleum ether. The precipitates after washing were recovered in the percentages listed in Table VII.

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[30] L. Brickman, J. J. Pyle, J. L. McCarthy and H. Hibbert, THIS JOURNAL, **61**, 868 (1939).

[31] L. E. Wise, "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, p. 622.

[32] L. C. Craig, C. Golumbic, H. Mighton and E. Titus, *J. Biol. Chem.*, **161**, 321 (1945).

TABLE VII

SEPARATION OF ALKALI-SOLUBLE AND NEUTRAL LIGNIN FRACTIONS

Lignin sample	Wt. in g.	Recovered in funnel, % A	B	M	N	Total recovered
Lignin I unfract.	1.0	49	8	..	31	88
Lignin II unfract.	1.0	56	5	5	20	86
Lignin III unfract.	1.0	73	6	4	11	94
Lignin I_1 high mol. wt.	0.9	51	6	5	19	81
Lignin I_3 med. mol. wt.	1.27	36	4	6	32	78
Lignin I_6 low mol. wt.	1.2	28	3	5	22	58
Lignin II high mol. wt.	0.85	81	2	4	10	97
Lignin II low mol. wt.	1.05	38	8	6	29	81
Lignin III low mol. wt.	1.0	61	4	5	12	82

Viscosity Determinations.—One-gram samples of ethanol lignins I, II and III (Table VI) were dissolved in 25 ml. of dioxane, filtered through glass and their viscosities determined at 20° in an Ostwald viscosimeter. Five duplicate readings were obtained and 20 ml. of the solutions diluted again to 25 ml. In this fashion readings at five dilutions were obtained. The time of efflux for pure dioxane was 129.3 seconds. The values of N_{sp}/C are listed in Table VIII.

The lines of best fit are

lignin I, $N_{sp}/c = 0.0477 + 0.002146C$; correlation coefficient = 0.949

lignin II, $N_{sp}/c = 0.0502 + 0.004649C$; correlation coefficient = 0.958

lignin III, $N_{sp}/c = 0.06259 + 0.003815C$; correlation coefficient = 0.954

Solving for k' in the equation

$$\frac{N_{sp}}{c} = [n] + k'[n]^2C$$

lig I, $k' = 0.943$
lignin II, $k' = 1.845$
lignin III, $k' = 0.974$

TABLE VIII

VALUES OF N_{sp}/C FOR UNFRACTIONATED ETHANOL LIGNINS[a]

Sample	4%	3.2%	2.56%	2.05%	1.64%
Lignin I	0.0548	0.0516	0.0518	0.0498	0.0495
Lignin II	.0692	.0642	.0616	.0618	.0567
Lignin III	.0783	.0740	.0718	.0722	.0680

[a] Concentration expressed in g./100 ml. solution. See reference 29 for details.

Fractional Precipitation of Lignin.—Three- or four-gram samples of lignin I, II and III were separately dissolved in acetone–ethanol (9:1) (or less advantageously in dioxane) to make 10% solutions. Each solution was stirred in a 250-ml. centrifuge cup and ligroin was added dropwise. On precipitation of a suitable fraction the mixture was stirred for about ten minutes, centrifuged, and the supernatant transferred to a new centrifuge cup. The lignin fraction was redissolved in a minimum amount of acetone–ethanol and precipitated into a small centrifuge cup of ligroin, centrifuged, washed with fresh ligroin and air-dried. Six fractions were obtained and recombined to give two or three main fractions, the first precipitating in each case being called "high mol. wt." in Table VII. Only in the case of lignin I are the three fractions essentially the equivalent of the unfractionated material. In the case of lignin II the high molecular weight fractions were not all recombined and the result of partitioning the fractionated material is not completely comparable with the unfractionated material.

Calculation of Solubility Parameter.—The solubility parameters of several glycol derivatives were calculated from data obtained from the Carbide and Carbon Chemicals Company and listed in Table IX. The following formula was used

$$\sqrt{\frac{(\Delta H - RT)\ \text{s.g.}}{\text{M.W.}}} = \delta\text{-value}$$

where

ΔH = heat of vaporization in cal./mole
T = b.p., °K.
s.g. = specific gravity
M.W. = molecular weight

TABLE IX

DATA FOR THE CALCULATION OF SOLUBILITY PARAMETER

Compound	Heat of evaporation B.t.u./lb.	Sp.g. 20°/20°	Mol. wt.	B.p., °C.	δ Value in (cal./cc.)$^{1/2}$
Ethylene chlorohydrin	221	1.2045	80.5	128.8	11.6
Ethylene glycol	344	1.1155	62	197.2	14.2
Diethylene glycol	150	1.1184	106	244.5	9.1
Cellosolve	234	0.9311	90.1	135.1	10.6
Methyl Cellosolve	239	.9663	76.1	124.3	10.8
Butyl Cellosolve	171	.9019	118.2	170.6	8.9
	Cal./mole at 55°	50°/4°			
Glycerol	21,060[a]	1.242	92	...	16.5

[a] From D. F. Stedman, *Trans. Faraday Soc.*, 24, 296 (1928).

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