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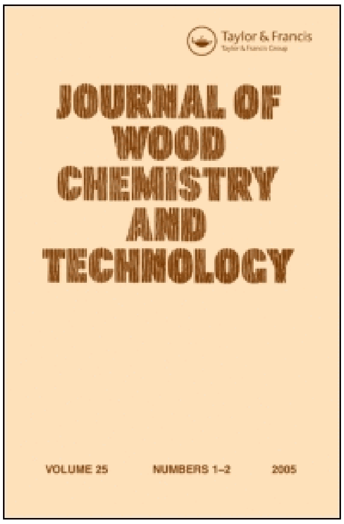

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SOME PROPERTIES OF PAUCIDISPERSE GYMNOSPERM LIGNIN SULFONATES OF DIFFERENT MOLECULAR WEIGHTS

Richard F. Buchholz and John A. Neal
Georgia Pacific Corporation, Chemicals Division
1754 Thorne Road
Tacoma, WA 98421

and

Joseph L. McCarthy
Department of Chemical Engineering
University of Washington
Seattle, WA 98195

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Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

Five purified paucidisperse gymnosperm lignin sulfonate samples (M_w @ 2,400 to 140,000), prepared by fractionation using ultrafiltration and dialysis, have been characterized in part. The relationship was established between the molecular weights of the fractions and those of the dissolved lignin sulfonates representing nearly all of the total lignin originally present in the woody tissue. The chemical composition, ultraviolet and infrared absorption spectra, intrinsic viscosity, diffusion coefficient, specific volume, hydraulic radius and streaming current properties of the several samples have been determined or estimated as a function of molecular weight.

INTRODUCTION

Among the natural polymers, lignin is found in an abundance which is exceeded only by cellulose. The formation, structure and properties of this phenolic propane type polymer have been extensively investigated, as has been reported by Sarkanen and Ludwig[1]. Sakakibara[2] summarized available information concerning its chemistry, functional groups and proposed structural models. Much attention has been devoted to the kraft lignins and lignin sulfonates (LS) which arise as by-products in the manufacture of cellulosic

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pulps[3]. Schematic structures for soluble gymnosperm lignin sulfonate molecules have been proposed by Glennie[4] and others. The structural units - sometimes called "C_9 units" - of native gymnosperm lignins are, at least mainly, guaiacyl propanes. In lignin sulfonates, some catechol propane units are also present.

Since little is known in an orderly way about how certain basic properties of purified paucidisperse lignin sulfonates vary as a function of molecular weight, the present investigation was undertaken.

EXPERIMENTAL

Preparation of Purified Lignin Sulfonates

Fermented calcium-based spent sulfite liquor (SSL) from the Georgia-Pacific Corporation "acid sulfite" pulp mill at Bellingham, WA, arising mainly from Western hemlock (*Tsuga heterophylla*) along with small amounts of true fir (*Abies grandis*) and Sitka spruce (*Picea sitkensis*) woods, was the source of the lignin sulfonates studied. Delignification was conducted using an initial acidity of pH 2 (determined cold) and initial levels of 9.25 and 1.2 percent total and combined sulfur dioxide, respectively.

To remove residual sugars and associated lignins, 1000 g of aqueous SSL containing about 500 grams of non-volatile solids were mixed with 3 L of ethanol. With stirring, the mixture was warmed to 65°C, then cooled to room temperature whereafter the LS-containing solution was separated by filtration. After removal of the ethanol by vacuum evaporation, the aqueous solution, at about pH 7, provided purified lignin sulfonates, PLS.

Preparation of Fractions of Purified Lignin Sulfonates

Fractionation (Figure 1) of PLS was accomplished by exhaustive ultrafiltration (UF) and dialysis. Dialysis tubing was used to separate the low molecular weight preparations because no suitable UF membranes were available. To prepare paucidisperse LS samples A, B, C, D and E of differing molecular weights, five membrane types were used: "GR" and "FS" (Pasilac-DDS, Minneapolis, MN), "C" and "Spectrapor" (Spectrum Medical Industries, Los Angeles, CA) and "XM" (Amicon Corp., Lexington).

Molecular Weight Distribution of the Purified LS Preparation

High pressure size exclusion chromatography (SEC) was conducted on PLS using Zorbax PSM Type S (duPont) columns 60-S and 1000-S in series using the method of Briggs and Zybak[5]. The solvent was a 35% aqueous solution of acetonitrile containing 0.1 N sodium sulfate flowing at 1 mL/min. LS concentra-

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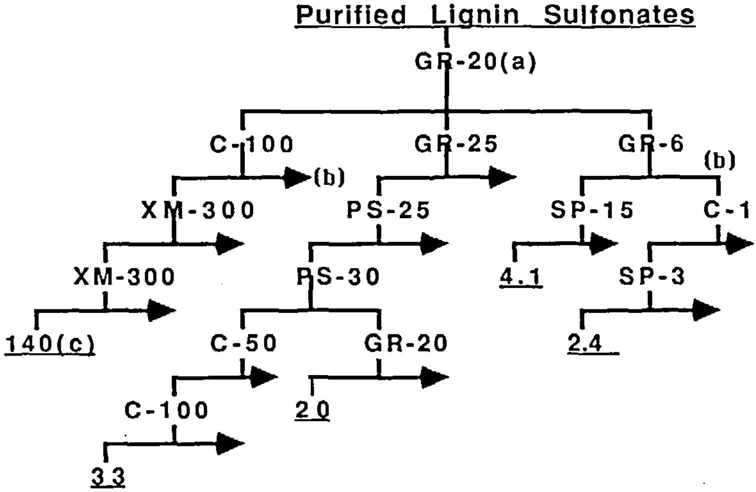

FIGURE 1. Scheme for Fractionation of PLS by Ultrafiltration.
(a) Designates the ultrafiltration membrane where letters show the supplier (see Expt Section) and the numbers indicate the nominal level of "cut off" as mol. wt. in thousands.
(b) Left- and right-hand streams indicate retentate and permeate, respectively. Arrow shows rejected streams.
(c) Designates resulting LS fractions A, B, C, D and E with expt. mol. wts. of 2.4, 4.1, 20, 33 and 140 thousand, respectively.

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tions in column eluants were measured in terms of absorption of 232.2 nm radiation. A typical elution pattern is shown in Figure 2.

As described below in this paper, calibration of the SEC columns was established using the M_w data determined, by ultracentrifuge procedures, for the paucidisperse lignin sulfonate fractions. Counted at peak modes, their retention times and molecular weights, M_w, were: A, 9.24 minutes, 2,400; B, 9.04, 4,100; C, 8.76, 20,000; D, 8.53, 33,000; E, 8.24, 137,000. By linear regression, the relationship is:

$$\mathrm{Log}_{10}\, M_w = 19.6 - (1.76)(t) \quad R^2 = 0.98 \qquad (1)$$

where t = retention time in minutes.

Since the column was known to "tail", the above question was not useful at long retention times. Thus, the following relation was assumed to prevail

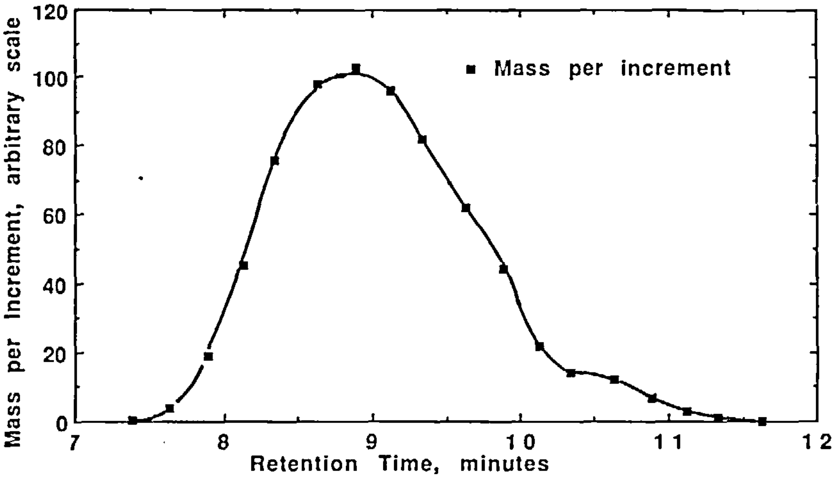

FIGURE 2. SEC Elution Pattern for Purified Lignin Sulfonates.

TABLE 1

Estimated Distribution in Mol. Wts. of PLS

Increment	Time (min)	M_w (g/mol)(.001)	Rel. Freq. (arbitrary)	Cum. Mass (wt %)
1	7.38	8,200	0.5	100
2	7.63	1,500	4	99.9
3	7.88	540	19	99.4
4	8.13	200	45	96.6
5	8.33	71	76	90.1
6	8.63	26	98	79
7	8.88	9.4	103	65
8	9.13	3.4	96	50
9	9.38	2.1	82	36
10	9.63	1.7	62	24
11	9.88	1.3	44	15
12	10.13	1.1	22	8.7
13	10.38	0.9	14	5.5
14	10.63	0.7	12	3.5
15	10.88	0.6	7	1.8
16	11.13	0.4	3	0.7
17	11.38	0.4	1	0.3
18	11.62	0.3	.05	0.2

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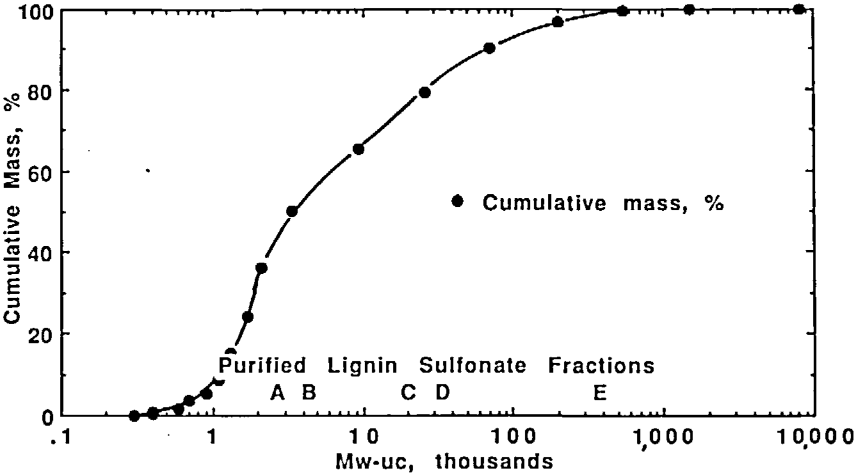

FIGURE 3. Cumulative Mw Distribution of Purified Lignin Sulfonates.

between 2,400, the molecular weight of the smallest LS fraction, and 250, the approximate monomer weight, at an assumed base line level of 11.0 minutes:

$$\mathrm{Log}_{10}\ M_w = 6.98 - (0.39)(t) \tag{2}$$

From the elution pattern, cumulative molecular weight distribution data were generated by combining the molecular weights reflected by retention times on the abscissa together with the integrals of the absorbance with respect to a number of different retention times as shown in Table 1. A plot of the cumulative percent of mass versus the logarithm of M_w is shown in Figure 3.

Molecular Weight of LS Fractions

To evaluate weight average molecular weights, M_w (Table 2), a short column sedimentation equilibrium technique[6] was employed with a Beckman Model E ultracentrifuge (UC) using 0.01 M aqueous sodium chloride solutions at 25°C. For Samples B and D, the refractive index increments, dn/dc, were determined to be 0.183 and 0.188 (mean = 0.186) by utilizing a determined to be 0.183 and 0.188 (mean = 0.186) by utilizing a Brice-Phoenix refractometer. For the same samples, the partial specific volumes, v, were found to be 0.616 and 0.623 (mean = 0.62 cm^3/g) by use of a Model DM1 Parr Digital Densitometer with the solvent and solutions of known concentrations.

TABLE 2

Molecular Weight and Polydispersity of LS Fractions[a]

	M_w(UC)	M_n(SEC)	M_n(FIA)	DP_w(UC)	DP_n(SEC)	DP_n(FIA)
A[b]	2.4	2.1 (1.1)	1.6 (1.1)	9.1	8.0	6.1
B	4.1	3.3 (1.2)	2.8 (1.5)	16	13	11
C	20	8.9 (2.2)	7.0 (2.9)	84	38	30
D	33	17 (1.9)	13 (1.9)	140	72	55
E	140	47 (3.0)	40 (3.5)	600	200	170

[a] Molecular weights shown in thousands. For calculation of DP, structural units weights for LS A, B, C, D, and E were taken to be the following: 264,250, 237, 236 and 232, respectively.

[b] Calculated values of polydispersity ($M_{w(UC)}/M_n$) are given within the parentheses.

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Polydispersity indices, M_w/M_n, were estimated (Table 2) by SEC[5] using a set of Zorbax PSM-Type S (silanized; duPont) columns in series together with a solvent consisting of a 4:1 (v/v) water-acetonitrile solution containing 5% sodium dioctylsulfosuccinate. Determination of column parameters was accomplished using paucidisperse polystyrene sulfonate fractions, PSS, (Pressure Chemicals, Pittsburgh, PA) of known degree of dispersity. The M_n values for our paucidisperse LS fractions were calculated from the ultracentrifuge M_w evaluations and the just-described polydispersity degrees.

In addition, M_n levels (Table 2) were evaluated by use of diffusion coefficients estimated by the flow injection analysis (FIA) method described by Boyle et al.[7] in an aqueous 1.0 N NaCl solution. Here, the widths at half height, $w_{1/2}$, of the several PSS standards were determined. These were plotted against the M_n values for the PSS. Then $w_{1/2}$ of the LS fractions were determined and their M_n values were interpolated from the calibration curve.

Chemical Composition

Contents of carbon, hydrogen, oxygen, sulfur, methoxyl and calcium were analytically determined (Tables 3 and 4), with two or more replications, in the Galbraith Laboratories, Knoxville, Tenn. The sums of the determined percentages of C, H, O, S and Ca were evaluated for each fraction (Table 3) and also the average molecular weight of the structural unit, or SU (Table 4).

TABLE 3

Elemental Analyses of Ca LS Fractions[a]

Sample	A	B	C	D	E
C	44.31 (0.10)	46.71 (0.10)	50.37 (0.13)	50.93 (0.07)	51.29 (0.21)
H	4.50 (0.17)	4.74 (0.13)	5.01 (0.16)	4.95 (0.06)	5.13 (0.01)
S	9.39 (0.17)	8.15 (0.01)	7.04 (0.09)	7.17 (0.04)	6.47 (0.02)
O	36.95 (0.02)	34.87 (0.02)	34.87 (0.02)	34.56 (0.06)	33.86 (0.01)
Ca	5.17 (0.13)	4.55 (0.12)	3.70 (0.06)	3.73 (0.09)	3.54 (0.08)
Sum	100.3	99.02	100.0	101.3	100.3
OCH_3	9.84 (0.14)	10.47 (0.08)	11.45 (0.06)	11.62 (0.08)	11.71 (0.09)
PhOH	2.73 (0.00)	2.38 (0.01)	2.29 (0.01)	2.13 (0.05)	2.16 (0.01)

[a]Analyses are reported in weight percentages. Determinations were made at least in duplicate. The tabulation gives the mean values which are followed, in parenthesis, by the standard deviations. "Sum" is the total of the percentages found for C, H, S, O and Ca. "PhOH" signifies phenolic hydroxyl. Assuming that all sulfur was present as sulfonate, equivalents in terms of weight percent calcium are 5.85, 5.08, 4.39, 4.47, and 4.04 for Samples A, B, C, D, and E, respectively, i.e. the ratios of observed to calculated are 0.88, 0.90, 0.84, 0.83, and 0.89, respectively.

TABLE 4

Atoms and Groups/C_9 Unit in LS Fractions[a]

Sample	A	B	C	D	E
C	9	9	9	9	9
H	9.4	9.4	9.1	8.8	9.1
O	3.0	2.9	2.9	2.9	2.8
OCH_3	0.85	0.85	0.87	0.87	0.87
PhOH	0.39	0.32	0.29	0.27	0.27
SO_3	0.70	0.58	0.44	0.43	0.41
S, other	0.08	0.06	0.08	0.09	0.06
Wt/SU	264	250	27	236	232
PhOH/mol	2.4	3.6	8.6	15	47
SO_3/mol	5.6	7.7	17	31	83

[a]Mean values of the analytical results were converted to atoms and moles per nine carbon atoms, i.e. reflecting structural units with each presumed to consist of an aromatic ring with a propyl side chain. Sulfonate sulfur was assumed to be that proportion of the total sulfur which was equivalent to the determined values of calcium. "Wt/SU" is molecular weight per structural unit. "PhOH"/mol" and "SO_3/mol" are estimated numbers of phenolic hydroxyl and sulfonate groups per LS molecule, respectively.

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TABLE 5

Ultraviolet Abs. Spectra of LS Fractions[a]

Sample	A	B	C	D	E
Conc, g/L	.968	.977	1.036	1.110	1.061
$A_{232.5}$	.261	.290	.330	.369	.359
a', L/g cm	33.52	37.09	39.77	41.49	42.23
a, L/mol cm	80,447	152,071	795,436	1,369,263	5,785,811
A_{280}	.281	.305	.351	.391	.372
a', L/g cm	14.51	15.61	16.93	17.60	17.52
a, L/mol cm	34,822	64,006	138,612	580,949	2,400,791

[a] Mean values from duplicate trials are shown for absorbance, A. The absorptivity values reported are arithmetic means where a' = weight units and a = molar units.

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Phenolic Hydroxyl

Determinations were made using a modification of the bathochromic shift method of Goldschmid[8]. Results are reported in weight percent (Table 3) and as number of groups per SU (Table 4).

Ultraviolet and Infrared Absorption Spectra

Measurements of ultraviolet absorption spectra (Table 5) were made in unbuffered aqueous solutions at about pH 4.5 using quartz cells with a light path of 1.0 cm.

Infrared absorption spectra were determined using a Perkin-Elmer Model 1750 Fourier Transform spectrophotometer. KBr pellets were prepared which were of equal thickness and contained equal concentrations of lignin sulfonates which had been vacuum oven dried at 93°C for 14 hours.

Viscosity

In preliminary work, viscosities were measured, at several solute concentrations, of solutions of two paucidisperse PSS. Determinations were conducted using a Cannon-Ubbelholde type viscosimeter at 25°C with a 0.1 M Na_2SO_4 aqueous solution containing 35% acetonitrile. Solvent viscosity = 0.994 centipoise at 25°C.

Intrinsic viscosities were derived from plots of specific viscosity versus concentration. The weight average molecular weights for the PSS sam-

TABLE 6

Specific Viscosity of Solutions of LS[a]

Sample	A	B	C	D	E[b]
1	41.1/53.2	54.4/45.6	98.3/64.6	98.8/45.1	171/31.5
2	41.6/35.4	48.3/22.8	84.8/32.3	82.6/22.6	153/21.0
3	8.1/26.2	42.7/11.4	80.3/32.3	73.9/15.0	141/15.84
4	37.5/21.3	44.1/11.4	76.5/25.8	72.7/11.3	136/12.6
5	38.9/17.7	46.1/9.12	79.2/21.5	67.8/9.03	131/10.5

[a] The reported numbers, e.g. 145/44.5 for Trial 1 of Sample A, show the specific viscosity in the numerator and the solute concentration (grams/L) in the denominator.

[b] With Sample E, additional trials yielded specific viscosity/concentration results as follows: 127/9.01, 126/7.89 and 125/7.01.

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ples were specific by the supplier to be 16,000 and 354,000; for both, Mw/Mn < 1.1. For the pair of parameters of the Mark-Houwink equation[9]:

$$[\eta] = (K)(M)^a \qquad (3)$$

the supplier reported $K = (4.0)(10)^{-5}$ and $a = 0.815$ in aqueous 0.1 Na_2SO_4 solution; in our solvent, we found $(3.24)(10)^{-5}$ and $a = 0.802$, respectively, where $[\eta] = dL/g$.

These procedures were also employed with the LS samples (Table 6).

Diffusion Coefficient; Gel and Flow Injection Methods

Diffusion coefficient evaluations (Table 7) were conducted using a gel method described by Felicetta *et al.*[10] where the solvent was an aqueous 1 M NaCl solution buffered at pH 5.5 with 0.1 M sodium phosphate. Determinations were also made using a flow injection procedure reported by Boyle *et al.*[7] with calibration utilizing either the protein, bovine chymopepsin A, or potassium ferricyanide.

Estimation of Hydrodynamic Radii

Using three sets of the above described parameters, calculations were made to estimate the hydrodynamic radii of the LS molecules in the five subject samples (Table 8).

TABLE 7

D Values and Calculated Mol. Wts. of LS Fractions

Method	A	B	C	D	E
		Diffusion Coefficients x $(10)^{+7}$ @ cm^{+2}/sec			
FIA[a]	25.6	18.4	11.3	9.60	4.46
FIA[b]	24.9	17.6	10.8	9.21	4.26
Gel	20.9	16.6	9.66	7.71	5.18[c]
		Mol. wts., thousands, wt ave. Calculated by use of Eq. 7			
FIA[a]	1.8	4.2	11	19	110
FIA[b]	2.0	4.8	13	31	130
Gel[c]	3.3	5.8	18	38	70[c]
		Mol. wts., thousands, wt ave. Expts by ultracentrifuge			
$M_{w(UC)}$	2.4	4.1	20	33	140

[a] Calibrated by use of bovine chymotrypsinogen A, a spherical monodisperse protein of molecular weight known to be 25,656.4 g/mol.

[b] Calibrated by use of potassium ferricyanide.

[c] Probably in error because some LS molecules were larger than available pores of gel network.

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Streaming Current

Measurements were made using a Waters and Associates Streaming Current Detector which is based on the functioning of a reciprocating piston system. The procedure recommended by W. F. Gerdes[11] in a booklet published by Waters was used. A series of aqueous sodium chloride (reagent grade) solutions was prepared in which the lignin sulfonate concentration always was $(7.2)(10)^{-6}$ M. Solutions were put through the flow-through cell until a steady milliamperemeter reading was obtained. Results of measurements are shown in Table 9.

RESULTS AND DISCUSSION

To separate purified lignin sulfonates, PLS, from the mixture of substances present in fermented (*Saccharomyces cerevisiae*) aqueous spent sulfite liquor solution, the residual sugars (mostly xylose) and some lignins were removed by an ethanol extraction procedure.

TABLE 8

Estimates of Hydraulic Radius[a] of Dissolved

			LS		
Sample	A	B	C	D	E
			Experimental Parameters		
M_{W-UC}, thousands	2.4	4.1	20	33	140
D_{FIA}, $cm^2/sec \times (10)^{-7}$	24.5	17.6	10.8	9.21	4.26
$[\eta]$, $dL/g\ (10)^{+3}$	36.6	41.2	65.6	63.0	111
			Calculation Method and Results; $r \times (10)^7$ cm		
D_{FIA}[b]	0.82	1.1	1.9	2.5	4.7
v/M_W[c]	0.84	1.0	1.7	2.0	3.2
$[\eta]/M_W$[d]	1.1	1.4	2.8	3.2	6.2

[a] Assuming LS molecules are spheres. Calculation procedures are shown in Results and Discussion section. Under M_{W-UC} conditions, $v = 0.62\ cm^3/g$.

[b] Solvent was 1.0 N NaCl in aqueous solution.

[c] Solvent was 0.01 M aqueous NaCl.

[d] Solvent for $[\eta]$ was 0.1 N NaCl aqueous solution containing 35% acetonitrile.

TABLE 9

Streaming Current of Dissolved LS Fractions

Solvent (NaCl, m)	A	B	C (milliamperes)	D	E
0	-68	-64	-59	-56	-50
10^{-3}	-65	-64	-60	-55	-48
10^{-2}	-50	-50	-47	-43	-40
10^{-1}	-18	-18	-18	-17	-13
10^{0}	0	-.3	+0	+.2	+0.1

[a] Lignin sulfonate conc. = 7.2×10^{-6} M in aqueous NaCl solutions.

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Paucidisperse lignin sulfonate fractions, LS, of different molecular weights were prepared from PLS by use of a series of ultrafiltrations (Figure 1). Each was carried out exhaustively and gave rise to a pair of products, a retentate and a permeate, which were appropriately combined or rejected.

Five purified and paucidisperse samples of different average molecular weights, i.e.·A, B, C, D, and E, were prepared and these have now been characterized in part.

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Molecular Weights of Purified Lignin Sulfonates and Fractions

The PLS preparation, which represented about ninety-five percent of the total lignin originally present in the wood, provided the elution pattern graphed in Figure 2. The curve is roughly Gaussian at retention times earlier than the mode; thereafter it is skewed and suggests two "shoulders".

Average molecular weights were estimated to be $M_w = 56,000$ and $M_n = 3,000$ when the complete elution pattern (Figure 2) was considered. However, when the first and last one percent of material represented on the elution pattern was disregarded; $M_w = 32,000$ and $M_n = 3,000$. The estimated cumulative distribution of molecular weights is given in Table 1 and graphed in Figure 3.

For each of the five LS fractions, molecular weights were estimated (Table 2) by use of three methods, i.e., ultracentrifuge sedimentation equilibrium, UC, size exclusion chromatography, SEC, and diffusion coefficients via a flow injection analysis procedure, FIA, which was calibrated by use of paucidisperse PSS fractions. The corresponding degrees of polymerization, DP, have also been estimated (Table 2).

The UC method is a "thermodynamic method" and preferred because it does not require calibration - it yields weight averages, M_{w-UC}. The latter two methods require calibration against substances of known molecular weight and give number averages, M_n. The values of M_n now found by each method for a particular sample are in moderate agreement.

Two sets of polydispersity ratios, M_w/M_n, have been evaluated (Table 2) by using the M_{w-UC} with each of the two types of M_n results. The two ratios are approximately in agreement and their levels indicate that the preparations were indeed paucidisperse.

The PLS preparation shows M_w values ranging from less than one thousand up to nearly 10,000,000 or DP = 40,000, a distribution seemingly in general accord with current concepts of the formation and reactions of lignin sulfonates as polymers Felicetta et al.[12], Nokihara et al.[13], Goring[14], Dolk et al.[15], Pla et al.[16]. The five LS fractions now studied are found (Fig. 3) to be generally representative of the total range of molecular weights of the dissolved LS. Thus, these samples provide the desired opportunity to evaluate certain properties of LS widely different in molecular weight.

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Results, quite similar to those now reported with respect to distribution in molecular weight of lignin sulfonates, were obtained recently by Krut'ko, Vorob'eva and Mozheiko[17] who subjected an industrial lignin sulfonate preparation to an ethanol-water fractional precipitation technique to secure ten fractions. For these, neither the source wood species nor the polydispersity levels were reported. Mean molecular weights were estimated by gel permeation chromatography, using Sephadex G-75 and an aqueous 1 N NaCl solution along with a column calibration equation, and also by use of viscometry along with the Mark-Houwink equation and the Yean, Rezanovich and Goring[18] parameters of $K_\eta = 0.0016$ and $a = 0.32$. In accord with present results, they reported that the average molecular weight of the fractions studied ranged from about two thousand up to more than 100,000. Their differential distribution curve was found to be bimodal.

The molecular weight distribution and certain other properties of gymnosperm lignin sulfonate preparations have been studied recently also by Kotz *et al.*[19]. The shape of their differential distribution curve proved to be unimodal and very similar to ours.

Chemical Composition

The carbon, hydrogen, oxygen, sulfur, methoxyl, and calcium contents of the purified LS samples were determined analytically (Table 3). The results of the elemental analyses sum to nearly one hundred percent for all five cases.

To permit useful comparisons, these data have been calculated in terms of atom and group ratios (Table 4) relative to a basis of nine carbon atoms, i. e. a guaiacyl-propane type *structural unit* (SU). Molecular weights per SU are shown in Table 4, and based on these and the estimated molecular weights/SU (Table 3), values of weight and number average degrees of polymerization, DP, have also been calculated for the five fractions. The hydrogen, oxygen, and methoxyl ratios found experimentally for each of the five LS (Table 4) are in approximate agreement with one another demonstrating consistency in the composition of the polymer fractions.

The proportion of methoxyl groups per structural unit, i. e. OCH_3/SU, for the five LS samples presently investigated, is nearly constant at about 0.85 (Fig. 4). This is very similar to the level of about 0.82 recently reported by Kotz *et al.*[19], but both are lower than previously published lignin sulfonate values of about 0.94 (Peniston *et al.*[20]; Markham *et al.*[21]). The departure from the ratio of 1.0 is believed to reflect the presence in lignin sulfonates, in addition to guaiacyl and possibly hydroxyphenylpropane types, of about one catecholpropane type per each ten SU. These latter groupings are

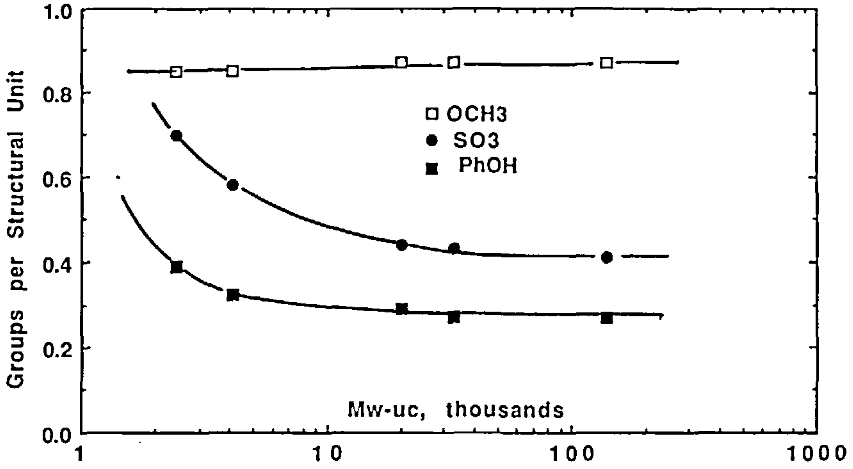

FIGURE 4. OCH_3, SO_3 and PhOH Groups per Structural Unit.

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believed to be formed by demethylation reactions which proceed during delignification (Glennie[4]).

Phenolic hydroxyl groups per SU ranged downward from 0.39 to 0.27 as LS molecular weight increased (Fig. 4). These values are similar to those obtained by Glasser *et al.*[10] using proton NMR measurements carried out on fractionated lignin sulfonates as acetyl methyl esters, who found phenolic hydroxyl contents ranging downward from 0.61 to 0.25 as the molecular weight of fractions increased from about 400 up to 7000. The departure may arise, at least in part, because of use of different analytical procedures as recently discussed by Sakakibara[2].

The other acidic groups in the samples studied were assumed to consist of sulfonate residues combined as calcium salts. The ratios of equivalents of the analytically-determined calcium to sulfur are: 0.88, 0.90, 0.84, 0.83, and 0.89. Thus non-sulfonate sulfur appears to exist only in small amounts and probably is present as sulfides or thioethers (Glennie[4]).

The sulfonate ratios show a definite trend with respect to molecular weight (Fig. 4). A ratio of about 0.4 per structural unit is found in the highest molecular weight LS and this increases to about 0.7 in the smaller molecules.

The similarity between the increase in sulfonate and phenolic hydroxyl content per SU with a decrease in molecular weight suggests that both may be

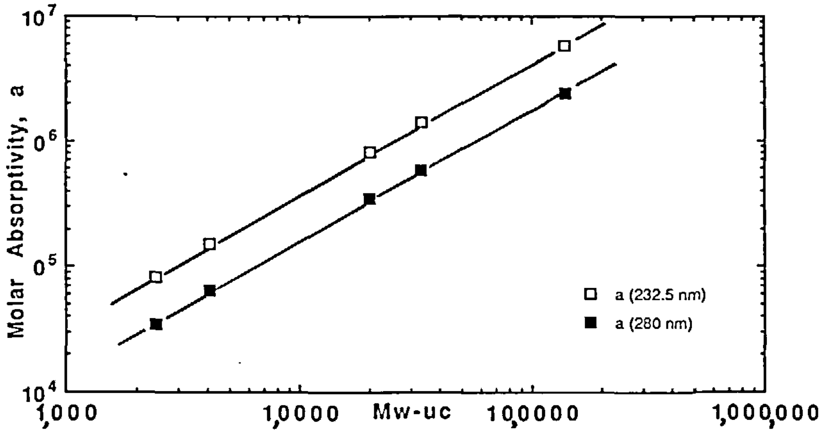

FIGURE 5. UV Mol. Absorption versus Molecular Weight.

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formed by related processes such as by the cleavage reaction proposed by Gellerstedt and Gierer[23].

Ultraviolet and Infrared Absorption Spectra

Aqueous solutions of the five LS samples were found to manifest the expected ultraviolet absorption spectra (Glennie[4]; Goldschmid[24]) and were very similar to one another. Absorptivity values were calculated for radiation of 232.5 and 280 nm (Table 5). On a mass basis, the values at both wave lengths were found to be larger for the samples of higher molecular weight and these same samples also contained smaller proportions of sulfur or sulfonate groups. When the absorptivity values at 280 nm were recalculated to a sulfonate-free basis (under the assumption that hydroxyl groups in the native lignins had been replaced by the sulfonate residues), the absorptivities proved to be almost the same although perhaps manifesting a small trend upward with increasing molecular weight, i. e. 19.2, 19.8, 20.7, 21.6, and 21.0 L/g cm for A through E, respectively. The mean, i. e. 20.5, is similar to values previously reported for lignin sulfonates (Glennie[4]) and significantly smaller than values reported for kraft lignins, e. g. about 25 L/g cm by J. Marton[25].

When the molar ultraviolet absorptivity values at both wavelengths are plotted against M_w, linear relationships are found (Figure 5) and these are described by equations of the form:

$$a = b\ M_w \qquad (4)$$

where b = 42.2 and 17.5 for radiation of 232.5 and 280 nm, respectively, and where a = L/mol cm. Thus, the change in absorptivity with molecular weight is nearly independent of wavelength in the present case.

Felicetta et al.[26] found that the absorbance ratios at 280 nm/260 nm decreased linearly as the logarithm of the molecular weight was increased from several hundred to about 100,000.

The infrared spectra found for the five lignin sulfonate samples proved to be similar to one another and to spectra reported in the literature (Hergert[27]). No clear trend with molecular weight was noted although weak shifts with sample number appeared at wave numbers of 1200 and perhaps 650. The absorption at around 1200 wave numbers probably arises mainly as a result of presence of sulfonate groups.

Comparison of Composition and Spectral Data with Literature

In general, after accounting for the different degrees of sulfonation, the chemical composition and also the ultraviolet and infrared absorption spectra of the now-studied fractions are found to be of nearly the same as expected for participants in a polymeric series. Also, our results are also in approximate agreement with the analytical data reported in the literature (Glennie[4]) and especially with results reported (Peniston et al.[20]; Markham et al.[21]) for lignin sulfonate samples provided from the same source several years ago.

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Reduced and Intrinsic Viscosities

After preliminary experimentation with paucidisperse polystyrene sulfonates (see Experimental section), viscosity measurements were carried out (Table 6) using the five lignin sulfonate fractions in an aqueous 0.1 M Na_2SO_4 solution containing 35% acrylonitrile. Plots of reduced viscosity versus concentration were linear (Figure 6) and are fitted by the equation:

$$\eta_{red} = [\eta] + bc \qquad (5)$$

where, for LS samples A, B, C, D, and E; parameter values for $[\eta]$ are 0.0364, 0.0412, 0.0656, 0.063, 0.1112; for b, 000096, 0.000281, 0.000484, 0.000801, 0.001917; and, for R^2, 0.56, 0.84, 0.94, 0.99, and 0.98, respectively, and where η_{red} = dL/g.

For the Mark-Houwink Equation[9] 3, as applied to M_w and to M_n-sec, the parameters were calculated to be: K_η = 0.028 and 0.028; a = 0.26 and 0.34; and R^2 = 0.97 and 0.95, respectively, and where $[\eta]$ = dL/g.

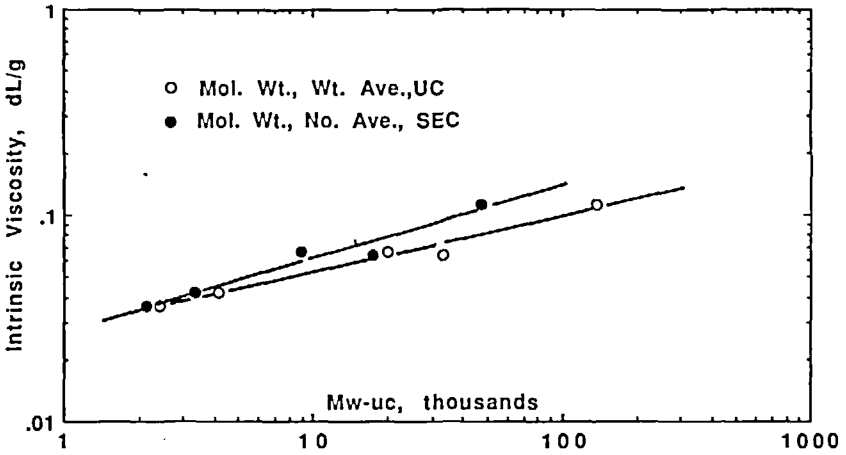

FIGURE 6. Intrinsic Viscosity versus Molecular Weight.

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Yean, Rezanowich and Goring[18], for fractionated lignin sulfonates in aqueous 0.10 N NaCl solution, evaluated the Mark-Houwink parameters as K_η = 0.0016 and a = 0.32 for M_w. The differences between the two pair of values are probably attributable to the effects of use of two different solvents.

Thus, Rezanowich and Goring[28] showed that reducing the ionic strength of NaCl solutions from 1.0 down to 0.0004 brought about an increase in the intrinsic viscosity of a certain lignin sulfonate preparation from about 0.1 to nearly 0.5 dL/g.

As pointed out by Yean et al.[18], the values of the exponents found in both studies suggests that the behavior of dissolved LS molecules lies between that of hard Einstein spheres for which a = zero and that of non-free draining coils in a poor or theta solvent where a = 0.5.

Diffusion Coefficients and Molecular Weights

Diffusion coefficients were measured by a gel and also a FIA procedure and the latter was calibrated by use of two different substances (Table 7). The methods gave similar results. Generally, somewhat higher values were obtained with the FIA procedures, perhaps because these involve fluid flow which, according to a 1985 report[29], may alter shape of the molecule and thereby the diffusion coefficient to a degree which depends on the velocity gradient and/or shear field.

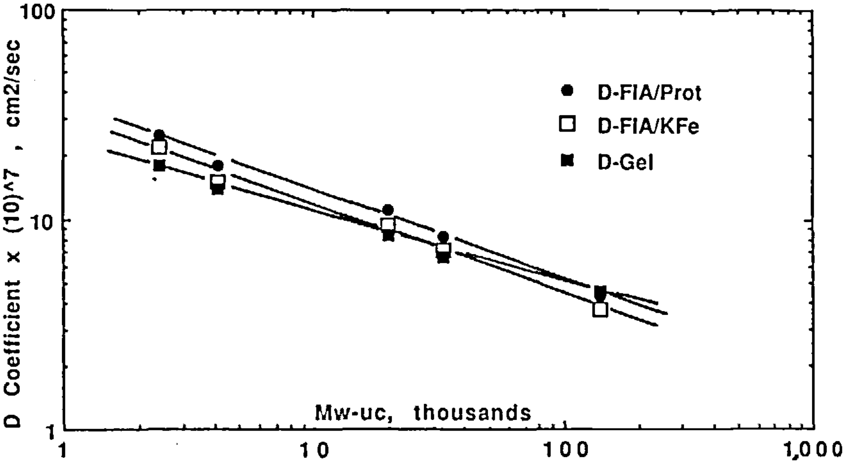

FIGURE 7. Diffusion Coefficient versus Molecular Weight.

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The two sets of FIA results are somewhat different depending on the calibration procedure and the one based on potassium ferricyanide agrees more closely with the results obtained from the gel method. The gel procedure gives orderly results except for the highest molecular weight sample which shows a significantly larger value of the coefficient than does the FIA result - this outcome is probably due to selective retardation of diffusion of the higher molecular weight entities into the gel network.

Plots of the log D vs the logarithm of the molecular weight are shown in Figure 7. These are fitted by the equation:

$$D - K_D M_w^{-b} \qquad (6)$$

and the K_D $(10)^{+5}$ and b parameters, respectively, are: with FIA-chymotryp, 5.9 and 0.40, with FIA-$_{KFe}$, 3,8 and 0.41; and with the gel method, 3.0 and 0.36 where values for R^2 are 0.98, 0.98 and 1.0, and D = cm^2/sec.

To permit comparison among the three diffusion coefficients and with Mw-UC, molecular weights were calculated using diffusion coefficients along with intrinsic viscosity values in the empirical Mandelkern-Flory[30] equation which was derived for flexible synthetic polymer molecules forming non-free draining coils in a theta solvent:

$$M_w = ((kT/n_o)^3 (N))/((38600)([n])(D)3) \qquad (7)$$

The results are shown in Table 7. Although substantial unexplained departures are evident in some cases, the several calculated M_w values are moderately close to those found by ultracentrifuge sedimentation equilibrium.

Hydrodynamic Radius

Assuming that lignin sulfonate molecules are approximately spherical in shape, estimates of the hydrodynamic radius (Table 8) were made by calculations based on three different sets of properties:

Intrinsic viscosity and molecular weight: The Einstein equation relating intrinsic viscosity (solvent: 0.1 N NaCl in 35% acetonitrile) with specific volume is combined with the expression for molar volume in terms of specific volume, weight average molecular weight and Avagadro's number to give:

$$r = [((M_w)([n]/(4/3)(0.025)(\pi)(N)]^{1/3} \tag{8}$$

Diffusion coefficient and solvent viscosity: The Einstein equation relating the diffusion coefficient (solvent: 1.0 N NaCl) with temperature and friction factor is combined with the Stokes formulation of friction factor and hydrodynamic radius to yield:

$$r = (kT)/(6\ \pi\ n_o\ D_{FIA}) \tag{9}$$

Partial specific volume and molecular weight: The weight average molecular weight is combined with the specific volume ($v = 0.62\ cm^3/g$) to provide:

$$r = [(M_w)(v)/(4/3\ \pi)(N)]^{1/3} \tag{10}$$

Plots of the logarithm of the three resultant estimates of the radii vs. the logarithm of the molecular weight are substantially linear (Fig. 8) and are described by equations of the form:

$$r = (a)(M_w)^{(b)} \tag{11}$$

where values are: $a\ (10)^{+9} = 3.3$, 4.2, and 6.5 while $b = 0.41$, 0.42 and 0.33, with $R^2 = 0.99$, 1.00 and 1.00 for Eq. 8, 9, and 10, respectively, when $r = cm$.

The observed differences, again, probably result mainly from the use of different solvents and experimental error.

Kro'ko *et al.*[17] also estimated the hydrodynamic radii of their LS fractions in an aqueous 0.1 N NaCl solution and reported, for example, r = 0.89,

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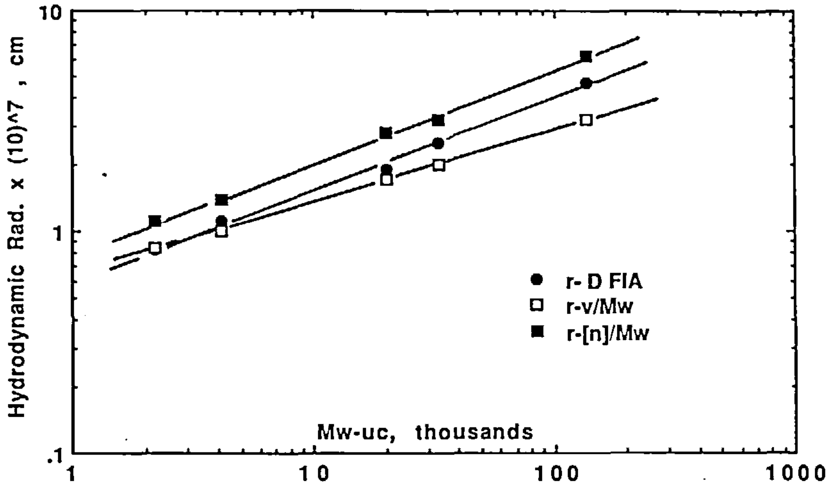

FIGURE 8. Hydrodynamic Radius versus Molecular Weight.

1.7, 2.5, 3.3, and 4.9 $(10)^{-7}$ cm for their values of M_w = 2,300, 9,500, 23,000, 47,000 and 110,000. These results are mainly in excellent agreement with our values (Table 8).

Ionic strength strongly influences hydrodynamic radius of lignin sulfonates as indicated by the size exclusion chromatography experiments of Gupta and McCarthy[31] who showed that the effective hydrodynamic radius of lignin sulfonates was approximately doubled as the electrolyte environment of an aqueous solution was decreased from 1.0 M NaCl to approach zero in water.

Streaming Current

Determinations were made employing an apparatus which functioned using a reciprocating piston in such a manner that, according to the derivation of W. F. Gerdes[11] the measured streaming current, I, is approximately linearly related to the product of the zeta potential of the walls of the experimental cylinder, Z, and the dielectric constant of the liquid, D:

$$I = (K)(D)(Z) \tag{12}$$

The electrical conductivity and viscosity of the liquid do not enter into the derivation.

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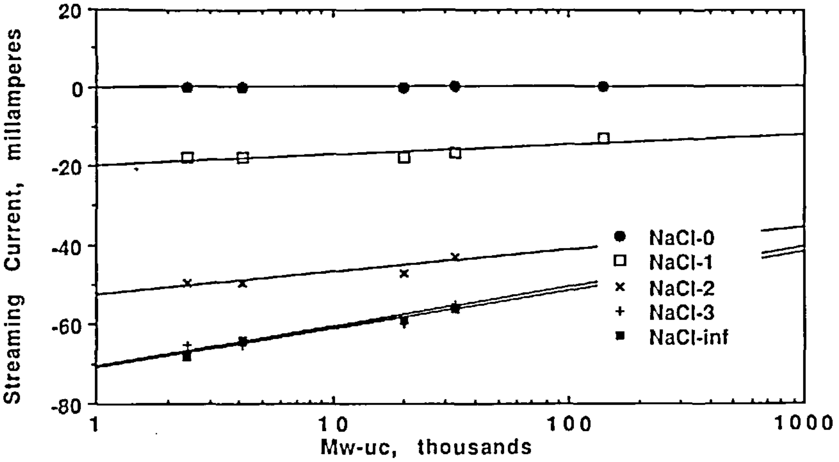

FIGURE 9. Streaming Current versus Molecular Weight.

Thus, for present experimentation, always with water as the solvent where D = 78 (approximately), it appears that the zeta potential should be nearly linearly related to the values of the streaming current.

Values of the streaming current were determined for each of the five lignin sulfonates and at five different levels of ionic strength (Table 9).

Figure 9 shows that plots of the streaming current versus the weight average molecular weight on a logarithm scale at constant values of ionic strength provide substantially linear relationships of the form:

$$I = a + b \log_{10}(M_w) \qquad (13)$$

where values of the parameters are: a = -100, -98, -71, -27, and -0.69 and b = 9.8, 9.6, 6.0, 2.5, and 0.16 for aqueous solutions, approximately, N NaCl = 0, $(10)^{-3}$, $(10)^{-2}$, $(10)^{-1}$, $(10)^{0}$ and where R^2 = 0.99, 0.95, 0.94, 0.68, and 0.40 with I in millivolts and M_w in thousands.

At constant ionic strength, the streaming current decreased as the Mw of the LS was increased. For all lignin sulfonates, the current was highest in pure water, decreased as ionic strength was increased and fell to substantially zero in aqueous 1 M NaCl solution. The powerful effects of differences of ionic strength are evident.

CONCLUSIONS

The approximate uniformity of chemical composition and of absorptivity of ultraviolet radiation of purified paucidisperse fractions of a lignin sulfonate preparation, reflective of nearly all of the lignin in gymnosperm wood, is confirmed over a wide range of molecular weight provided that differences in degree of sulfonation are taken into account. The presence in solution of lignin sulfonate molecules of molecular weight of ten million (DP = 40,000) is indicated.

The logarithms of the intrinsic viscosity, diffusion coefficient and hydrodynamic radius, and also the numerical values of the streaming current, vary substantially linearly with the logarithm of the weight average of the lignin sulfonate fractions studied. Numerical values of the parameters for the fitting equations have been established.

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