Table III. Polymers Evaluated

Sample No.	$CH_2{=}CHCO_2R$ R-	Acrylic Acid, %
101	$—CH(C_2H_5)C_3F_7$	...
102	$—CH(C_2H_5)C_3F_7$	0.015
103	$—CH(CH_3)C_3F_7$	...
104	$—CH(CH_3)C_3F_7$	0.015
1F4	$—CH_2CF_2CF_2CF_3$	0.015

Table IV. Evaluation of Vulcanizates

	101		1F4	
	Original	Aged[a]	Original	Aged[a]
Tensile strength, lb./sq. inch	950	1000	1050	900
Elongation, %	120	90	170	100
Modulus, 100%, lb./sq. inch	730	...	...	...
Permanent set[b], %	10	10	10	3
Shore A hardness	77	85	72	75
Volume swell, %	...	2.5	...	1.5
TR_{10}, °C.	0		+5	

[a] Aged 100 hours at 350°F. in MIL-L7808 diester type fluid.
[b] Two minutes after break.

iodide, and dimethylethanolamine-calcium oxide were unsuccessful. These results are in agreement with an earlier attempt to cure poly-(1-methyl-1-hydroperfluorobutyl acrylate) (*4*).

A vulcanizate using the standard recipe was ultimately obtained on only one experimental sample, 101, by preheating the raw polymer 12 hours at 250°F. Properties of this vulcanizate and a 1F4 vulcanizate are given in Table IV.

Although no physical properties were measured, data on the partially cured 102, 103, and 104 samples indicated very low volume swell in diester fluids.

No further work was done on obtaining optimum polymerization or curing techniques, as the physical properties of the experimental vulcanizate were similar to those of the commercial 1F4 and only marginal improvement in thermal stability might be expected.

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Polyelectrolytic Properties of Ligninsulfonic Acids

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Lignin sulfonates from spent sulfite liquor were separated into eight fractions of osmotic molecular weights ranging from 3500 to 58,000 by ultrafiltration and fractional dialysis. The methoxyl, sulfur, and phenolic hydroxyl contents, neutralization equivalent weights, reducing powers, and ultraviolet absorption spectra of the fractions were determined.

The concentration dependence of the reduced viscosities, specific conductivities, and dyestuff-absorbing powers of the individual fractions in aqueous solutions indicates that they behave as flexible polyelectrolytes. There is evidence that lignin sulfonates of molecular weight less than 5000 associate in solution in a manner analogous to micelle formation in colloidal electrolytes. The dependence of intrinsic viscosities and of diffusion coefficients on molecular weight indicates that sodium lignin sulfonates in solution form flexible coils which are impermeable to water in the presence of sufficient amounts of sodium chloride and permeable to water in absence of added electrolytes.

One of the aims of this work was to find the fundamental properties of lignin sulfonates from the sulfite pulping of wood, which make possible their use as dispersants and binders. The broader aim was to investigate their solution behavior and get information on their molecular shape and molecular weight distribution.

The present research can logically be divided into three parts: (1) preparation of fractions of different molecular weights and determination of their analytical properties, (2) determination of molecular weights and diffusion coefficients, and (3) investigation of viscosities, conductivities, and dyestuff-adsorbing powers of solutions prepared from the fractions.

Figure 1 shows the process of fractionation. The starting material was spray-dried spent sulfite liquor drawn from cooks of a mixture of approximately equal amounts of balsam and spruce. This material was dissolved in water, ion-exchanged to remove the inorganic materials, and exhaustively dialyzed through denitrated nitrocellulose membranes of low porosity. Four fractions of low molecular weight were prepared from dialyzates corresponding to different dialysis times by precipitating the barium salts with alcohol (*1*). The dialyzed liquor was separated into four fractions by ultrafiltration (*1, 2*) through cellophane and parchment membranes. All fractions were converted into sodium salts and dried at 60°C. under vacuum.

Table I gives analytical data of the fractions. There is strong indication that fractions 1 to 4 are pure lignin sulfonates. All acidic groups on these fractions are sulfonic; they have high methoxyl contents and high ultraviolet extinctions. The reducing power of these fractions is low, in the range of 3.5% equivalent glucose, and is probably

Table I. Analytical Data of Sodium Lignin Sulfonate Fractions

Fraction No.	% of Total Original Solids	% of Total of Fractions	% Methoxyl	% S	% Phenolic[a] Hydroxyl	Reducing Power, % Eq. Glucose	Neutralization Eq. Wt.	Acid Groups / Sulfur	S / MeO	Mol. Wt.	Diffusion, Coeff. Sq. Cm./Day
1	7.3	11.87	10.45	5.22	0.945	3.56	599	1.03	0.53	58,000	0.0314
2	18.7	30.41	10.40	5.58	0.739	3.36	570	1.01	0.56	19,200	0.0849
3	2.8	4.55	10.41	5.40	0.780	3.35	585	1.01	0.55	15,500	0.113
4	10.2	16.58	9.82	5.98	0.870	3.79	535	1.00	0.64	8,450	0.134
5	4.8	7.80	8.80	6.37	0.770	7.18	450	1.11	0.81	4,770	0.178
6	9.5	15.45	7.24	6.25	0.696	9.20	375	1.36	0.89	4,350	0.194
7	3.4	5.53	4.06	5.55	0.672	9.42	289	2.00	1.46	3,700	0.219
8	4.8	7.80	2.25	5.02	0.530	8.47	227	2.81	2.38	3,650	0.221
Total	61.5	100									

[a] Calculated from differential ultraviolet extinction coefficient.

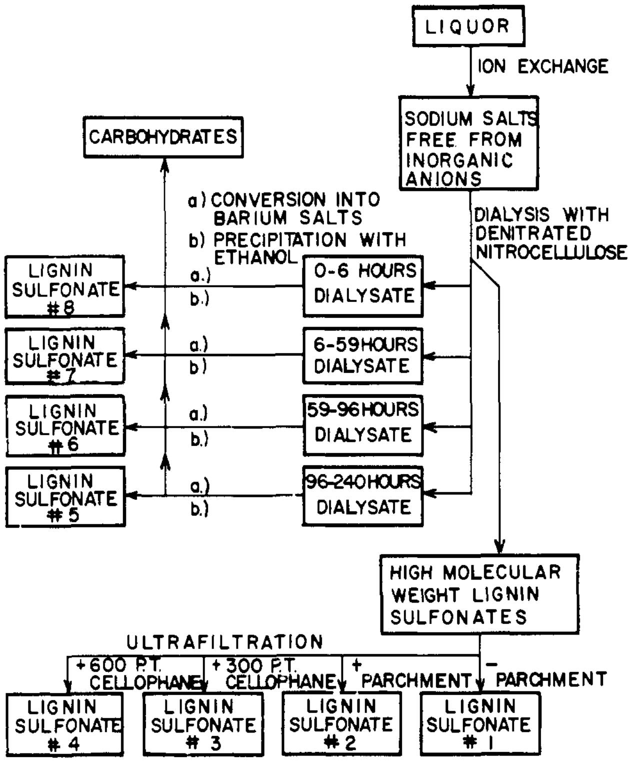

Figure 1. Flowsheet for fractionation of lignin sulfonates

inherent. This inherence is also indicated by the change in the reducing power of the solids in the dialyzed liquor and dialyzates during the dialysis. At the end both values became practically identical.

There is no conclusive evidence whether fractions 5 to 8 are pure lignin sulfonates or not. They contain acidic groups other than sulfonic and have lower methoxyl contents and high reducing powers.

The chemical similarity of the fractions is indicated by their ultraviolet light-absorbing properties (Table II). For all fractions, except the last, the ultraviolet absorbance per methoxyl-bearing unit is the same. The ratios of the extinctions at the maxima and minima of the spectra are also identical in neutral and alkaline solution. The extinctions, however, decrease with molecular weight. The spectra exhibit a bathochromatic shift when determined in alkaline solution. The phenolic hydroxyls, the cause of this behavior, seem to decrease with molecular weight and range from 0.5 to 1%, as calculated from the differential extinctions according to Goldschmid (*4*).

The molecular weights of fractions 1 to 6 were determined osmometrically in 0.5*N* sodium chloride solutions with cellophane and denitrated nitrocellulose membranes. When necessary, the results were corrected for membrane leakage (*3*). The diffusion coefficients were measured by the porous plate method (*3*). The molecular weights of the two lowest fractions were determined from the correlation between diffusion coefficients and molecular weights.

The integral molecular weight distribution of the lignin sulfonates, which represent 61% of the solids in the waste sulfite liquor, is shown in Figure 2. The lowest fraction has a molecular weight of 3600, the highest 58,000, and 35% of the material has a molecular weight in the range 10,000 to 25,000. The distribution curve indicates the presence of materials with molecular weights as high as 100,000. Similar distribution curves were obtained by Moakanin, Felicetta, Hatter, and McCarthy (*5*).

Viscosity, conductivity, and dyestuff adsorption measurements show that lignin sulfonates behave like typical flexible polyelectrolytes.

The dependence of the charge of the molecules of the polyelectrolyte on its concentration can be shown by conductivity measurements. As more counter ions become associated with each polymer molecule with increasing concentration, less and less current can be carried by each molecule. The specific conductivity decreases with increase of the square root of the concentration, but not linearly, as predicted by the Onsager equation for simple electrolytes. The corresponding plot is curved and is steep at low concentrations.

The dependence of the reduced specific conductivities upon the concentration of sodium lignin sulfonates is shown in Figure 3. The shapes of curves *A* and *B* for the two fractions of highest molecular weight are typical for polyelectrolytes.

Curves *C*, *D*, and *E* are, however, different. These curves, obtained for the three fractions of lowest molecular weight, show apparent discontinuities. This may indicate association or micelle formation as generally observed for colloidal electrolytes but not for polyelectrolytes.

Colloidal and polyelectrolytes are similar, in that their molecules contain hydrophilic and hydrophobic parts. The same mechanisms by which the big and flexible polyelectrolyte molecules curl up as their net charge decreases, cause association of the small and rigid colloidal electrolyte molecules. It is possible that the lignin sulfonate fractions of low molecular weight are intermediates between colloidal and polyelectrolytes.

To clarify this matter further, the dyestuff-adsorbing powers of the fractions were investigated. It is customary to determine the critical concentration at which the micelles of colloidal electrolytes are formed by means of suitable color indicators, as certain dyestuffs are differently colored in polar and nonpolar media. When adsorbed from water on the nonpolar micelles or polyelectrolyte aggregates, these dyestuffs change color.

Table II. Characteristic Data on Ultraviolet Absorbance Spectra

Fraction No.	pH 6						pH 12			Differential Spectrum	
	ϵ 280, cm.$^{-1}$ g.$^{-1}$ liter	Absorbance at 280μ per methoxyl-bearing-unit	λ_{max}, mμ	λ_{min}, mμ	$\frac{\epsilon_{max}}{\epsilon_{min}}$	$\frac{\epsilon_{245}}{\epsilon 260 m\mu}$	λ_{max} mμ	λ_{min}, mμ	$\frac{\epsilon_{max}}{\epsilon_{min}}$	λ_{max}, mμ	$\Delta\epsilon_{max}$, cm.$^{-1}$ g.$^{-1}$ liter
1	13.9	4200	282	263	1.32	2.28	282	266	1.13	300	2.28
2	13.3	4090	283	263	1.39	2.28	281	267	1.13	298	1.78
3	13.5	4150	282	262	1.38	2.23	281	267	1.12	301	1.88
4	12.4	4020	282	262	1.29	2.20	281	268	1.07	298	2.10
5	11.1	4100	283	263	1.39	2.15	281	268	1.09	299	1.86
6	8.8	3900	283	262	1.38	2.05	282	270	1.10	300	1.68
7	5.8	4200	277	261	1.34	1.89	281	270	1.16	299	1.62
8	4.2	6360	277	258	1.30	1.59	282	273	1.09	297	1.28

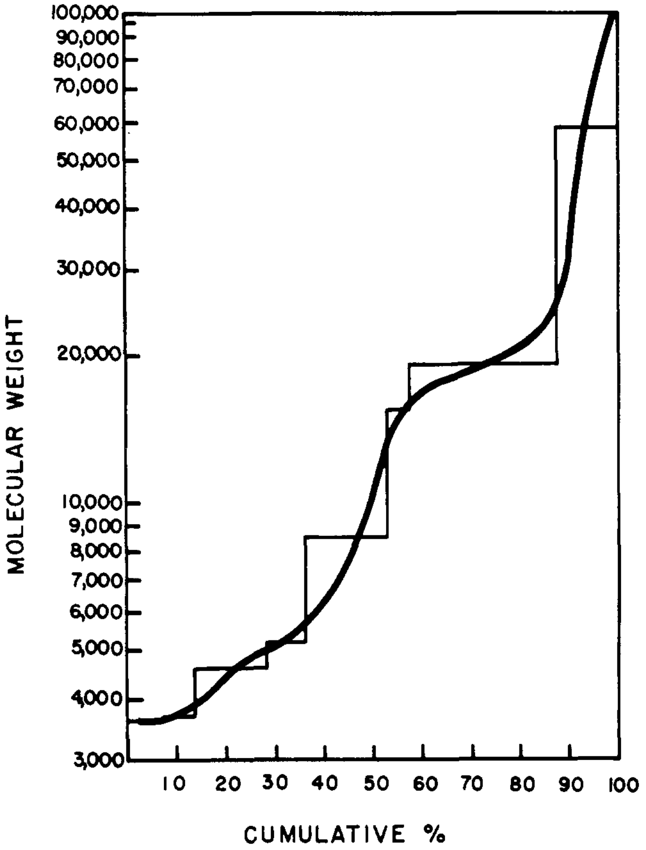

Figure 2. Integral molecular weight distribution of lignin sulfonates

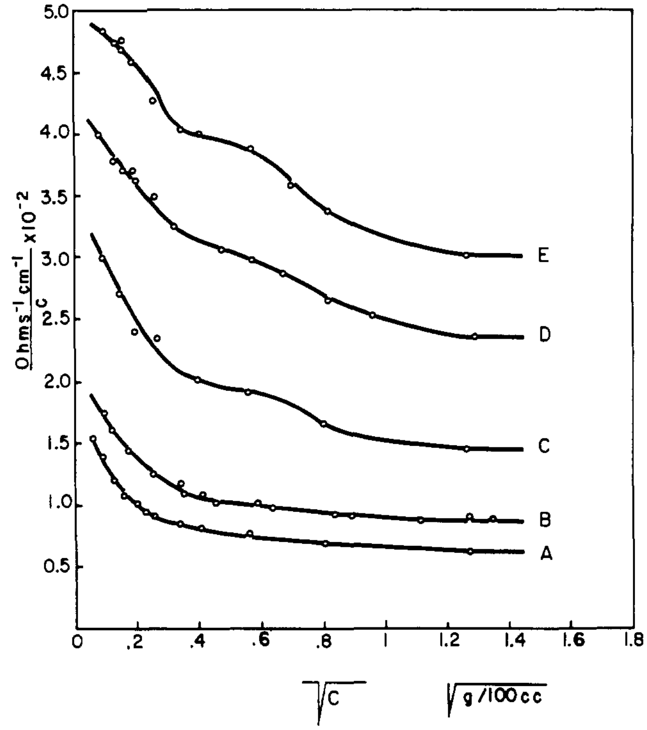

Figure 3. Relation of reduced specific conductivities of sodium lignin sulfonate to concentration

Molecular weights
A. 58,000
B. 19,200
C. 4350
D. 3700
E. 3650

Pinacyanole was found suitable as a color indicator to measure aggregation of lignin sulfonates. It was established that the absorbances at 630 mμ of solutions containing lignin sulfonates and pinacyanole are proportional to the formation of aggregate-dyestuff complexes. Measurements were carried out on solutions containing a fixed amount (1.2 mg. per 100 cc.) of pinacyanole and different concentrations of lignin sulfonates (Figure 4). All fractions but the one of lowest molecular weight yield continuous curves, and the curves for the three fractions of highest molecular weight are identical. They are represented by *A*.

Curves *B*, *C*, and *D* indicate that the ability of the fractions of lower molecular weight to adsorb dye is smaller than that of the fractions of high molecular weight. The aggregates of fractions of low molecular weight are probably smaller than those of high molecular weight and, if they contain associated lignin sulfonate molecules, the number of the molecules per aggregate is probably small. The discontinuity in curve *D* may indicate that at least the fraction of lowest molecular weight associates in solution.

Figure 5 (left) shows the reduced viscosity-concentration curves of the five fractions of highest molecular weight in distilled water. The shape of these curves is typical of

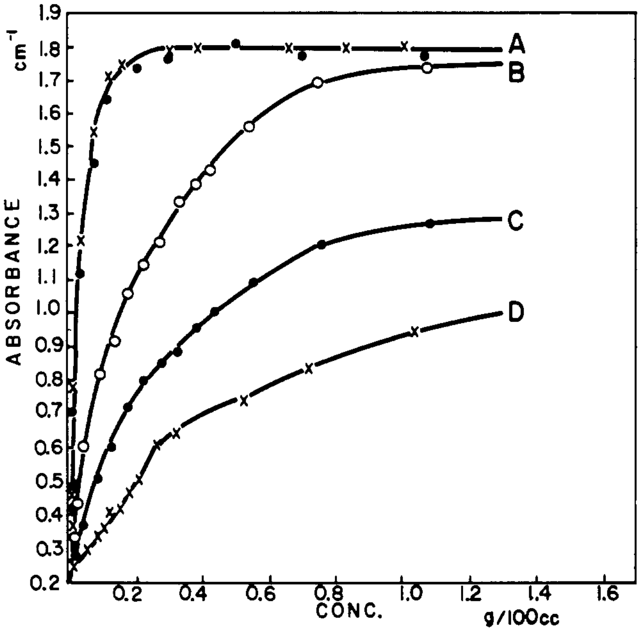

Figure 4. Relation of absorbance to formation of aggregate-dyestuff complexes

Molecular weights
A. 58,000 and 15,500
B. 4350
C. 3700
D. 3650

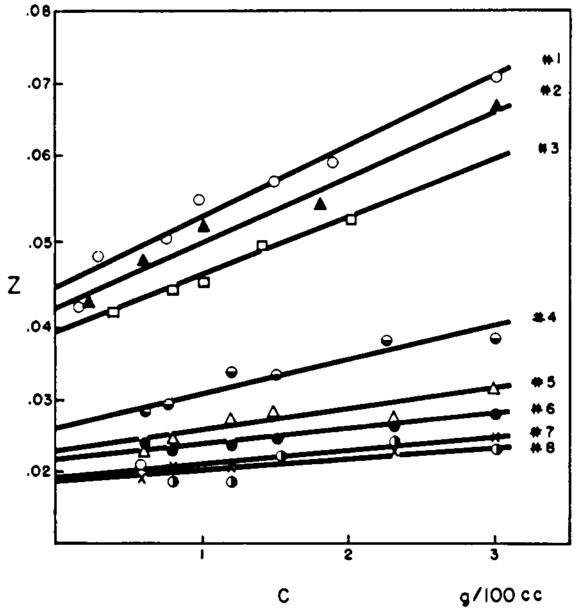

Figure 6. Effect of concentration on reduced viscosity in 2*N* sodium chloride solution. Molecular weights listed in Table I

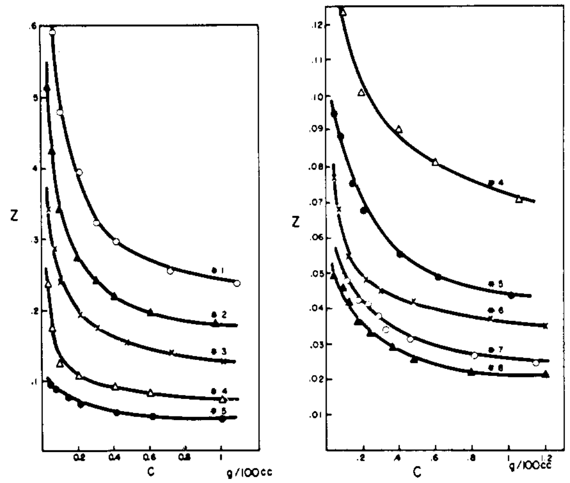

Figure 5. Reduced viscosities, *z*, at various concentrations of sodium lignin sulfonates in water Molecular weights given in Table I

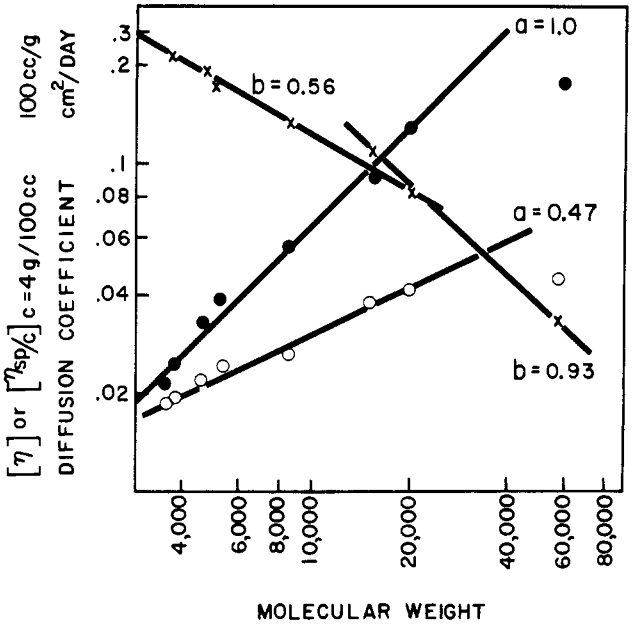

Figure 7. Relation of diffusion coefficients and viscosity data to molecular weight

○ Intrinsic viscosity in 2*N* NaCl determined from straight-line plots in Figure 6
X Diffusion coefficients in 0.5*N* NaCl
● Reduced viscosities of 4% sodium lignin sulfonate in pure water

polyelectrolytes. In Figure 5 (right) the same curves for the five lowest fractions are shown with a tenfold increase in reduced viscosity scale. These curves are also continuous, and do not show discontinuities as do the conductivity and dyestuff-adsorption curves. Figure 6 shows that the reduced viscosities change linearly with concentration when measured in $2N$ sodium chloride solution.

The concentration dependence of the conductivities, dyestuff-absorbing powers, and reduced viscosities proves that the lignin sulfonates are flexible polyelectrolytes. The change of the viscosity data and diffusion coefficients with molecular weight offers additional evidence of the flexible nature of the lignin sulfonate molecules and indicates that they are coiled when uncharged in solution.

The relations between intrinsic viscosities $[\eta]$, diffusion coefficients, D', and molecular weights, M, of homologous polymers are given by the following equations:

$$[\eta] = KM^{a}$$
$$D' = K'M^{-b}$$

For the two important models of polymer chemistry, the free-draining and the solvent-impermeable random molecular coils, constants a and b have been calculated. Both a and b are equal to unity for the free-draining and to 0.5 for the solvent-impermeable coil.

The results indicate that in the presence of sodium chloride the lignin sulfonates form compact water-impermeable coils. In Figure 7 the logarithms of the diffusion coefficients and of viscosity data are plotted against the logarithm of the molecular weights. If the fraction of highest molecular weight is disregarded, these data suggest a power exponent, a, equal to 0.47, and a power exponent, b, equal to 0.56. McCarthy and others (*5*) have found practically the same values independently.

The data on the fraction of highest molecular weight do not fit the straight-line plots. This may be due to its higher degree of polydispersity and/or higher degree of branching. It is probably fortuitous that a straight line with the slope of -0.93 can be drawn through the diffusion data corresponding to the three highest fractions.

The concentration dependence of the reduced viscosity of a polyelectrolyte in the absence of simple electrolytes can be described by Schaefgen's extention of the Fuoss-Strauss formula (*6*):

$$Z = \frac{\eta_{sp}}{c} = \frac{A}{1 + B\sqrt{c} + B'c} + D$$

where $(A + D)$ is the intrinsic viscosity corresponding to the fully charged (extended) molecular state; D is the reduced viscosity at high concentrations and is a measure of the intrinsic viscosity corresponding to the discharged and coiled molecular state; and B and B' are hydrodynamic and molecular interaction constants. From the data only D could be evaluated, as the reduced viscosities above 2% concentration were constant. A, B, and B' could not be determined, as the measurements could not be extended into a sufficiently low concentration range to allow accurate extrapolation, because of the low accuracy of η_{sp} at low concentrations.

The full circles in Figure 7 represent the D values, measured as the reduced viscosities of 4% solutions in distilled water. Disregarding the fraction of highest molecular weight the experimental points fit a straight line with a slope equal to unity. The power exponent, a, is unity for free-draining random coils. In the absence of electrolytes the discharged lignin sulfonates are apparently in this form. It is not surprising that a difference exists between coils in the presence and absence of simple electrolytes. Sodium chloride has an effect similar to salting-out action; besides reducing the net charge on the lignin sulfonate molecules, it also reduces the interaction forces between the lignin sulfonate molecule and water. Thus, in the presence of sodium chloride the coiled lignin sulfonate molecule is not free-draining but water-impermeable; for this more compact form the interaction between solute and solvent is greatly reduced.

CONCLUSIONS

The molecular weights of the lignin sulfonates in spent sulfite liquor range from 3600 to perhaps 100,000. The molecular weight of about 35% of the material is in the range of 10,000 to 25,000. Fractions of different molecular weights show some variation in analytical properties.

The lignin sulfonates are flexible polyelectrolytes. At high concentrations in water and in the presence of a suitable electrolyte such as sodium chloride, the molecules become coiled. The structure of the coiled sodium lignin sulfonate molecules is loosened by removing the salt. There are indications that the fractions of low molecular weight associate in solution and that the molecules of the fraction of highest molecular weight are more branched than those of the other fractions.

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