varies as $\bar{M}_D^{0.42\pm0.04}$, compared with the theoretical variation of $M^{1/2}$.

Scaling law theory, with its descriptive subchain ("blob") model, is enjoying some popularity, but it does not appear to be helpful in interpreting the results of this work in the dilute regime: indeed, there is little support for it. The model supposes that at any temperature there is a characteristic length of polymer chain (blob) over which Gaussian statistics hold. The length is infinite at the Θ point and decreases away from it as a function of τ $(=|T - \Theta|/\Theta)$. One consequence of this simple model, as predicted by Daoud and Jannink,[6] is the existence of a finite Θ region for finite chains. Thus, as shown explicitly by Akcasu and Han,[14] $\mathrm{d}\alpha_\mathrm{h}/\mathrm{d}T$ should be zero at the Θ point, but this is not found to be the case. It appears that perturbation expansions for α_h, such as first derived by Stockmayer and Albrecht,[15] offer a more convincing explanation.

Acknowledgment. We thank J. Cambridge for his assistance in carrying out this work. We are also grateful to Unilever Research for financial assistance and to the Science Research Council for a studentship to M.J.P.

References and Notes

(1) Pritchard, M. J.; Caroline, D. *Macromolecules* **1980**, *13*, 957.
(2) Sanchez, I. C. *Macromolecules* **1979**, *12*, 980.
(3) McCracken, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973**, *6*, 859.
(4) Clark, A. T.; Lal, M. *Br. Polym. J.* **1977**, *9*, 92.
(5) Nierlich, M.; Cotton, J. P.; Farnoux, B. *J. Chem. Phys.* **1978**, *69*, 1379.
(6) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.
(7) Bauer, D. R.; Ullman, R. *Macromolecules* **1980**, *13*, 392.
(8) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(9) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 1122.
(10) Jones, G.; Caroline, D. *Chem. Phys.* **1979**, *37*, 187.
(11) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.
(12) Landolt-Bornstein, 6 Auflage, Band II/5a, p 157.
(13) Gulari, E.; Gulari, E.; Tsunashima, Y.; Chu, B. *Polymer* **1979**, *20*, 347.
(14) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(15) Stockmayer, W. H.; Albrecht, A. C. *J. Polym. Sci.* **1958**, *32*, 215.

Lignin. 18. Associative Effects among Organosolv Lignin Components[†]

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Revised Manuscript Received November 6, 1980

ABSTRACT: Organosolv lignins isolated under relatively mild conditions from angiosperms are composed of quite low molecular weight entities. The weight-average and number-average molecular weights of the preparations generally lie within the ranges $\bar{M}_\mathrm{w} \sim 2000$–$5000$ and $\bar{M}_\mathrm{n} \sim 800$–$1200$. Varying degrees of association between the constituent species are characteristic of these samples both in solution and in the solid state. Profiles described by eluting Organosolv lignins from dextran gels with 0.10 M aqueous NaOH represent effective molecular weight distributions which approach those of the discrete components. Under aqueous conditions of pH 13–14, dissociation of Organosolv lignin species occurs in dilute solutions ($\sim$0.5 g L^{-1}), while a marked tendency to associate prevails at higher concentrations ($\sim$100 g L^{-1}). The extent to which an individual component may participate in association depends appreciably upon the relative proportions of the other species present. Within the bounds of this constraint, the association–dissociation process is reversible and involves at least two kinetically distinguishable steps. Certain counterions and zwitterions reduce the degree of association between Organosolv lignin components. The mechanism may involve the blocking of proton uptake from solution which presumably accompanies the formation of higher molecular weight associated complexes. The relationship between $\bar{M}_\mathrm{w}$ and $\bar{M}_\mathrm{n}$ for Organosolv lignin samples during association implies that the process is dominated by preferential interactions between lower and higher molecular weight components.

Introduction

Among the naturally occurring polymers, lignins are second only to cellulose in abundance. They are constituted from (p-hydroxyphenyl)propane units by eight different linkages, of which about 50% are β-0-4 ether structures.[1]

It has been suggested that the widespread disparities between reported molecular weight distributions of byproduct lignins (other than the sulfonates) may be due in part to varying degrees of association in different solvents.[2] However, until quite recently,[3] only two exploratory studies seeking to establish that such phenomena may exist had been published.[4,5] On the other hand, association between lignin components can be further complicated by aggregation between the resulting complexes.[6–8]

Marked associative interactions among lignin components are conveniently documented by the striking variations between gel permeation chromatographic profiles observed with different eluants. The effective distributions found when nonaqueous solvents (or nonaqueous solvent–water mixtures in the absence of added salts) are employed exhibit a well-defined multimodal pattern of species extending to very high molecular weights, while those obtained with alkaline aqueous eluants generally consist of a broad envelope of components with distinguishable features apparent only in the lower molecular

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[†] This work was supported by National Science Foundation (RANN) Grant NSF-7708979 and (to D.C.T.) National Institutes of Health Grant GM 13401.

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0024-9297/81/2214-0426$01.25/0

weight region.[9,10] Recent work at our laboratories has clearly demonstrated that such disparities are due to the formation, in nonaqueous solvents without additional electrolyte, of associated complexes with molecular weights as much as 3 orders of magnitude larger than those of the individual components.[3]

The present work has been directed toward determining reliable molecular weight distributions of the discrete angiosperm Organosolv lignin species formed during exposure to the hydrolytic conditions encountered in aqueous ethanol at elevated temperatures with low concentrations of trivalent aluminum ion present. The problem is not trivial: such lignin samples not only exhibit different degrees of association between their constituent components, but the associative tendency is so pronounced that it is operative even under quite strongly alkaline aqueous conditions.

Experimental Section

Organosolv Lignins. The Organosolv lignins were obtained from Professor K. V. Sarkanen and co-workers, College of Forest Resources, University of Washington. They were prepared by subjecting wood chips (or straw) to the hydrolytic conditions encountered in organic solvent–water mixtures (generally called "liquors") at elevated temperatures (135–165 °C) with small quantities of trivalent aluminum ion (usually between 8×10^{-3} and 2×10^{-2} M) present as either the chloride or the sulfate. These pulping conditions were maintained for periods ranging between 1 and 6 h. The most commonly used 50% aqueous ethanol and 75% aqueous dioxane liquors were effective in providing sufficient solubility for the partially degraded lignin components formed during pulping at the 10:1 to 70:1 (v/w) liquor:substrate ratios employed. After the pulping reaction is stopped, removal of the organic cosolvent (by evaporation under reduced pressure) results in the precipitation of the partially degraded Organosolv lignin components from solution into a form that may be conveniently filtered. Precipitation was found to approach completeness except under conditions in which the pulping reaction had been conducted for more extended periods ($\sim$6 h) at lower temperatures ($\sim$135 °C), whereupon a substantial fraction (as much as 35%) could remain water soluble at the prevailing concentrations. In such instances complete evaporation to dryness followed by leaching with acetone provided for ready isolation of the water-soluble Organosolv lignin components.

Kraft Lignin. The gymnosperm kraft lignin (used as an auxiliary calibrant in these studies) was isolated from kraft black liquor donated by the Weyerhaeuser Co. from the mill at Longview, Wash. Diluted kraft black liquor (500 mL containing 120 g L^{-1} dissolved solids after filtration through a VW&R crepe white paper to remove residual fibrous materials) was acidified with 1.0 M aqueous H_2SO_4 (0.5 mL min^{-1}) to pH 2.5. The resulting solution (containing suspended solids) was centrifuged, and the precipitate was washed twice by resuspending in aqueous solution at pH 2.5 and centrifuging. The sample thus obtained was redissolved in the minimum volume of aqueous solution at pH 8.5 and freeze-dried.

Gel Permeation Chromatography (GPC). Fractionation of lignins according to molecular size was carried out by means of GPC. Sephadex G75 (Pharmacia, Piscataway, N.J.) was chosen for the purpose because it was found to offer an acceptable degree of separation between the lower molecular weight components while extending resolution to sufficiently high molecular weights for adequate characterization of angiosperm Organosolv byproduct lignins. Aqueous sodium hydroxide eluant solutions were prepared so as to be carbonate free, thereby both allowing pH conditions to be reproducibly maintained and maximizing the extent of resolution between the lower molecular weight species. Gel samples were allowed to swell at room temperature for 3 days in eluant before packing in order to ensure long operational life for each column.

A 70 × 2.5 cm (cylindrical) column was found to be adequate for routine analysis under the conditions employed in the present work. Band spreading for components of molecular weight $\sim$500 was generally no more than 8% of the relative column retention volume, V_R. A single-beam LKB 8300 A Uvicord II photometer (LKB-Produckter AB, Stockholm), set to operate at 280 nm as a detector at the column outlet, maintained base line stability within acceptable tolerance limits.

Within any family of consecutive chromatographic fractionations, in which small sample volumes (less than 1 mL) were introduced, the salient features of the respective elution profiles (namely, "peaks", "shoulders", and "valleys") were found to exhibit associated V_R values reproducible to within 5%. Owing to variations between void and imbibed volumes of solvent in the column, however, more substantial differences were ordinarily observed among the corresponding mean values between results obtained from different column packings. In order to facilitate reliable molecular weight calibration of the fractionated components (vide infra), therefore, the V_R values of each elution profile were appropriately scaled to those characteristic of standard profiles for which accurate comparison with data from direct molecular weight determinations was available. Thus the raw chromatographic data (transmittance vs. time) was digitized and transformed, using a flexible Fortran IV program, to plots of absorbance vs. V_R. The area under each curve was normalized assuming a linear variation in flow rate between initiation and completion of each run.

Ultracentrifuge Studies. Narrow fractions of low polydispersity were isolated from the profiles of selected lignin samples (adopted as standards for calibration purposes) eluted with 0.10 M carbonate-free aqueous NaOH. After being made up to 0.10 M NaCl at pH 9.5 so as to contain less than 3.0×10^{-2} g L^{-1} lignin components, these fractions were characterized with respect to their weight-average molecular weights, $\bar{M}_w$, using ultracentrifuge sedimentation equilibrium monitored by the photoelectric scanner in a Beckman Spinco Model E analytical instrument.

Data from the scanner were collected by a PDP-12 computer and in each case involved averaging between 3 and 10 scans. The electronic components of the apparatus have been described elsewhere by Teller.[11] Nine samples were sedimented simultaneously in three Yphantis[12] six-channel centerpieces. AnF or Ti–AnF rotors were employed.

The holders for the sapphire window were milled to a width sufficient to observe the entire channel. The window gaskets occlude the base of the most centrifugal channel, however. The problem was circumvented by the introduction of 7.5 μL of FC-43 (perfluorobutylamine) into this channel in order to raise the sample (0.122 mL) so that data could be obtained to the end of the solution column. Otherwise 5 μL of FC-43 was sufficient to permit data collection to the cell base in the solution sectors (0.125-mL sample volume) of the inner two channels. The volume of solvent in the reference channels was 0.130 mL.

Base line scans were made at 546 or 620 nm. After subtraction of the unsmoothed but interpolated base line data, the equilibrium data were smoothed with orthogonal polynomials followed by the least-squares derivative polynomial to obtain $M_{w,r}$. $M_{z,r}$ data were calculated by the methods outlined earlier by Teller.[11] The weight-average and z-average molecular weights of the sample were calculated from $M_{w,r}$ and $M_{z,r}$, using the equations of Lansing and Kraemer.[13] Although the z-average molecular weights were characterized by very large errors, the weight-average molecular weights appeared to be reliable.

Each of the sample fractions was scanned at two wavelengths (chosen between 280 and 365 nm) and at two rotor speeds (between 17 000 and 36 000 rpm). The weight-average molecular weights from the four scans for a given sample were found to be consistent. However, at the time of these studies, the condition of the scanner electronics did not permit rotor speeds above 36 000 rpm multiplexed in the same runs at low speed. Consequently $\bar{M}_w$ values for components with molecular weight below 500 could not be obtained.

Computation of $\bar{M}_w$ values for the fractions have assumed a partial specific volume of 0.653 cm^3 g^{-1} for the components as being independent of their molecular weight.[14] Integration of the sedimentation curve for each fraction confirmed that in every run, from which data were included in computing the respective $\bar{M}_w$, the total detectable mass of components was effectively conserved.

Apparent Average Molecular Weights. The apparent weight-average and number-average molecular weights, $\bar{M}_w$ and $\bar{M}_n$, respectively, were directly calculated from elution profiles,

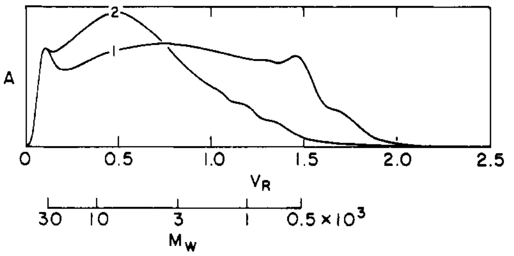

Figure 1. Elution profiles of calibrant standard lignin samples (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm): (1) red alder Organosolv lignin (Table V); (2) gymnosperm kraft lignin.

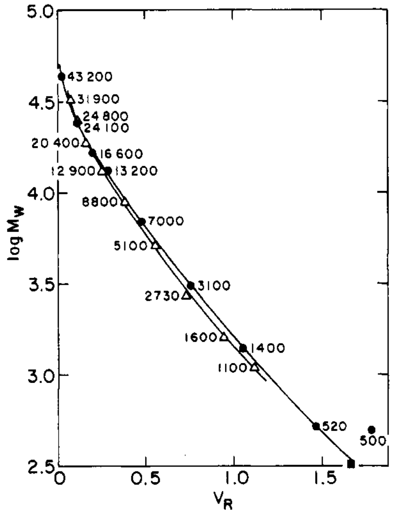

Figure 2. Calibration curve for 70 × 2.5 cm analytical column (Sephadex G75/0.10 M aqueous NaOH). Semilogarithmic plots of weight-average molecular weight vs. retention volume for (▲) red alder Organosolv lignin (Table V), (●) gymnosperm kraft lignin, and (■) guaiacylglycerol β-(2-methoxyphenyl) ether.

assuming a constant absorptivity at 280 nm for all species in a particular Organosolv lignin preparation. Although this assumption is only approximately true for component molecular weights below 1000, the relative changes in $\bar{M}_w$ and $\bar{M}_n$ are quantitatively reliable: the areas of the profiles for a given sample were, within experimental error, unaffected by solution history.

Results and Discussion

Calibration of GPC Elution Profiles. Figure 1 depicts the profiles, upon elution from Sephadex G75 with 0.10 M aqueous carbonate-free NaOH, of two distinctly different lignin samples, namely red alder Organosolv lignin and a gymnosperm kraft lignin. Narrow fractions of low polydispersity selected from each were analyzed with respect to their component weight-average molecular weights, $\bar{M}_w$, by means of ultracentrifuge sedimentation equilibrium studies. The resulting calibration curves are shown in Figure 2 as plots of log $\bar{M}_w$ vs. V_R, the relative column retention volume. They are quite evidently, within experimental error, not only parallel but actually coincident even though the effective molecular weight distributions of the respective lignin samples differ markedly in form. It is thus unlikely that spurious effects such as ion inclusion and ion exclusion[10] or "adsorption" of the lignin components onto the gel matrix[15-18] can have an appreciable impact in the analytical system at hand. Indeed, the experimentally determined value of V_R for guaiacylglycerol β-(2-methoxyphenyl) ether places this dimeric lignin model compound, as shown in Figure 2, directly on the calibration curve.

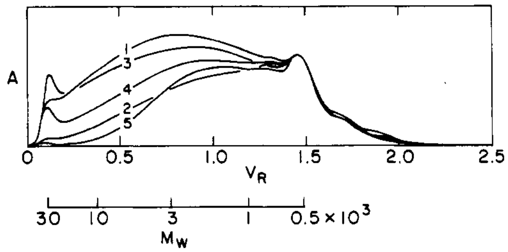

Figure 3. Molecular weight distributions of representative Organosolv lignin samples (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm): (1) red alder; (2) western cottonwood; (3) wheat straw; (4) trembling aspen; (5) bagasse. (Pulping conditions listed in Table I.)

The lignin fractions selected for ultracentrifuge sedimentation equilibrium studies were made up to 0.10 M NaCl at a pH of 9.5. Thus, as far as the samples subjected directly to $\bar{M}_w$ analysis were concerned, the solution conditions involved the same ionic strength as, but pH over 3 units lower than, the respective parameters prevailing during elution from Sephadex G75 with 0.10 M aqueous NaOH. However, careful diffusivity measurements have revealed a significant increase in molecular weight with pH decreasing between 11.5 and 7 for a spruce kraft lignin sample in aqueous solution.[4] Nevertheless, the calibration curves deduced from the present work not only span a range of $\bar{M}_w$ values reasonably to be expected upon fractionation from Sephadex G75 but also are virtually superimposable for the two samples adopted as standards.

It is reasonable to assume, therefore, that associative effects between components in the paucidisperse fractions scanned with the ultracentrifuge have not occurred to a significant extent upon acidification from 0.10 M aqueous carbonate-free hydroxide to pH 9.5 under the solution conditions (concentration less than 3×10^{-2} g L^{-1}, ionic strength 0.10 M) employed here—at least not during the time (50 h) elapsed between fraction preparation and the attainment of equilibrium in the centrifugal field prior to data collection for $\bar{M}_w$ analysis. Of course, it would be prudent, however, for the calibrations placed upon the presently reported results to be taken as provisional *upper* limits to the true molecular weights.

Molecular Weight Distributions of Organosolv Lignins. The molecular weight distributions of a representative selection of angiosperm (including grass) Organosolv lignins are illustrated in Figure 3. They have been depicted as calibrated elution profiles (0.10 M aqueous carbonate-free NaOH as eluant from Sephadex G75) with the relative populations of components at different molecular weights represented by their absorbance at 280 nm.

Despite diverse origins, the same well-defined features (although differing somewhat in relative proportions) are found for these Organosolv lignins in the region below $\bar{M}_w = 1000$, namely, the presence of tetramer, trimer, dimer, and, to varying extents, monomer. On the other hand, larger variations are evident in the higher molecular weight region approaching $\bar{M}_w = 40\,000$; these are determined not merely by the source of origin of the sample but more particularly by the pulping conditions. As shown in Table I, the apparent weight-average and number-average molecular weights of these preparations are quite low ($\bar{M}_w \sim$ 2000–4000; $\bar{M}_n \sim$ 800–1200).

The most prominent single group of components are trimeric, a finding deduced directly from the ultracentrifuge sedimentation equilibrium studies and confirmed by coelution of guaiacylglycerol β-(2-methoxyphenyl) ether with an Organosolv lignin sample (Figure 4). (We are indebted to Mr. L. Hoo, College of Forest Resources, University of Washington, for kindly donating a sample

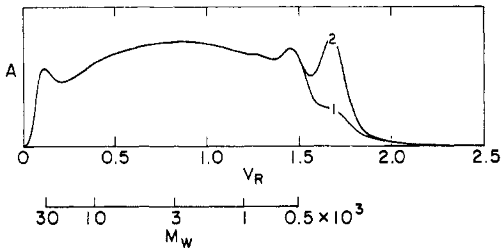

Figure 4. Accuracy of calibration in low molecular weight region. Coelution of (1) calibrant standard red alder Organosolv lignin with (2) guaiacylglycerol β-(2-methoxyphenyl) ether (present to extent of 10% w/w). (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm.)

Table I
Apparent $\overline{M}_w$ and $\overline{M}_n$ of Representative Organosolv Lignin Samples[a]

source	pulping conditions[b]	$\overline{M}_w$	$\overline{M}_n$
red alder	8:1 (v/w) liquor:substrate, 2×10^{-2} M $AlCl_3$, 1 h, 150 °C	4120	1130
western cottonwood	10:1 (v/w) liquor:substrate, 8×10^{-3} M $AlCl_3$, 3 h, 135 °C	2370	860
wheat straw	20:1 (v/w) liquor:substrate, 1.5×10^{-2} M $Al_2(SO_4)_3$, 1 h, 150 °C	4460	1150
trembling aspen	40:1 (v/w) liquor:substrate, 8×10^{-3} M $AlCl_3$, 1 h, 150 °C	3540	1020
bagasse	10:1 (v/w) liquor:substrate, 4×10^{-2} M $Al_2(SO_4)_3$, 1 h, 150 °C	1800	824

[a] Without incubation prior to fractionation. [b] 50% aqueous ethanol employed as liquor.

of this dimeric lignin model compound.) This contrasts with reports that, upon acidolysis (refluxing with 0.2 M HCl in 90% aqueous dioxane) for 4 h, milled wood lignin (the fraction soluble in 90% aqueous dioxane after milling) from angiosperms yields monomers and dimers as the most abundant species.[19]

Dissociative Effects in Alkaline Aqueous Solution. The Organosolv lignin samples studied during the present work are characterized by varying degrees of association. As exemplified in Figure 5, incubation at 0.4 g L^{-1} in 0.10 M aqueous NaOH has been found to result in different extents of dissociation for all samples investigated. Noteworthy in each case is the significant increase in the proportion of trimeric species. The time taken for the process to reach completion was dependent upon the identity of the sample and as such ranged between 500 and 1500 h under these conditions. The accompanying changes in the apparent weight-average and number-average molecular weights of the lignin preparations are listed in Table II.

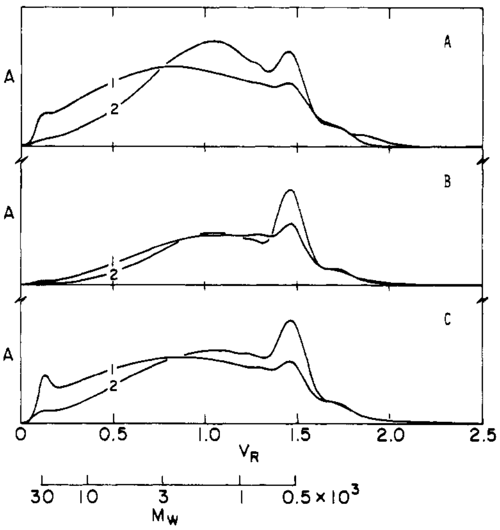

Figure 5. Dissociation of Organosolv lignins at 0.40 g L^{-1} in 0.10 M aqueous NaOH (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm): (A) red alder, after (1) 0.5 h and (2) 2010 h; (B) cottonwood water-insoluble fraction, after (1) 0.5 h and (2) 650 h; (C) wheat straw, after (1) 0.5 h and (2) 1990 h. (Pulping conditions listed in Table II.)

Precise evaluation of these observations is complicated by the fact that Organosolv lignin samples from certain sources can be expected to contain small but appreciable numbers of unhydrolyzed ester linkages to organic acids: *p*-hydroxybenzoic acid in the case of cottonwood[20] and *p*-hydroxycinnamic acid in bagasse.[21] The saponification of these esters during prolonged incubation in alkaline aqueous solution will presumably result in an anomalous contribution from these acids to the elution profiles. Thus *p*-hydroxybenzoic acid is routinely observed in the trimer region.

It is important to emphasize that the areas of the Organosolv lignin elution profiles (described by the absorbance at 280 nm) for a given sample have been found to be, within experimental error, independent of prior incubation conditions. It is not certain how closely the equilibrium molecular weight distribution in 0.10 M aqueous NaOH at a 0.4 g L^{-1} sample concentration (the lowest practicable during the present work) approaches that of the discrete components. To the extent that this approximation is adequate, however, the apparent molecular weight distributions resulting from direct elution of Organosolv lignins from dextran gels with 0.10 M aqueous NaOH appear to be well within an order of magnitude of those for the fully dissociated species.

Dissociation of Organosolv lignin components upon incubation at high dilution in alkaline aqueous solution has been confirmed by direct observation with ultracentrifuge sedimentation equilibrium techniques. Narrow fractions selected from the profiles of red alder Organosolv lignin

Table II
Effect of Dissociation on Apparent $\overline{M}_w$ and $\overline{M}_n$ of Representative Organosolv Lignin Samples Incubated at 0.40 g L^{-1} in 0.10 M Aqueous NaOH[a]

source	pulping conditions[b]	time, h	$\overline{M}_w$	$\overline{M}_n$
red alder	8:1 (v/w) liquor:substrate, 2×10^{-2}	0.5	4120	1130
	M $AlCl_3$, 1 h, 150 °C	2010	2760	1030
western cottonwood (65% (w/w)	10:1 (v/w) liquor:substrate, 8×10^{-3}	0.5	2380	928
water-insoluble fraction)	M $AlCl_3$, 6 h, 135 °C	650	1740	797
wheat straw	20:1 (v/w) liquor:substrate, 1.5×10^{-2}	0.5	4460	1150
	M $Al_2(SO_4)_3$, 1 h, 150 °C	1990	2810	922

[a] Dissociation under these conditions was complete within time given. [b] 50% aqueous ethanol employed as liquor.

Table III
Effect of Dissociation on $\overline{M}_w$ of Paucidisperse Red Alder Organosolv Lignin Fractions during Incubation for 2200 h in 0.10 M Aqueous NaOH[a]

concn during incubation, g L^{-1}	$\overline{M}_w$ after 40 h	$\overline{M}_w$[b] after 2200 h
0.04	23200	5380
0.07	18200	4550
0.10	14400	4010
0.20	7260	3010
0.27	3300	2160
0.20	1590	1390

[a] Selected from profile generated by eluting with 0.10 M aqueous NaOH from Sephadex G75. Pulping conditions for lignin sample: 50% aqueous ethanol, 10:1 (v/w) liquor:substrate, 2 × 10^{-2} M $Al_2(SO_4)_3$, 1 h, 165 °C.
[b] Monitored directly by ultracentrifuge sedimentation equilibrium; solutions made up to 0.10 M NaCl at pH 9.5 so as to contain 4 × 10^{-2} g L^{-1} lignin components.

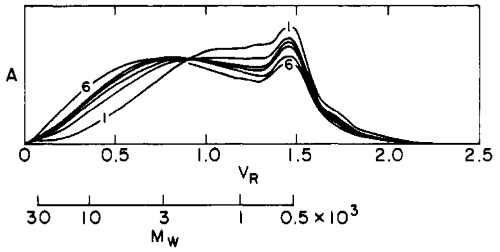

Figure 6. Association of cottonwood Organosolv lignin at 100 g L^{-1} in 1.0 M aqueous NaOH (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm: after (1) 0.5, (2) 21, (3) 42, (4) 72, (5) 144, and (6) 190 h. (Pulping conditions listed in Table IV.)

samples eluted from Sephadex G75 with 0.10 M aqueous NaOH were analyzed at component concentrations of 4 × 10^{-2} g L^{-1} after incubation for 40 and 2200 h, respectively. The weight-average molecular weights of fractions with $\overline{M}_w$ values initially above 1500 were observed to decrease upon extended incubation by progressively larger factors approaching 5 in the $\overline{M}_w$ = 40 000 region (Table III).

Associative Effects in Alkaline Aqueous Solution. Incubation at 30–180 g L^{-1} in 1.0 M aqueous NaOH has been found to permit association to occur between components of all Organosolv lignin samples investigated. This is remarkable in view of the fact that the individual species are almost certainly polyanionic under such conditions. The effect is illustrated in Figure 6 for a preparation isolated from cottonwood during mild but protracted pulping. (In this case, an unusually high 35% (w/w) proportion of the lignin components was fully water soluble at the concentrations prevailing after removal of ethanol under reduced pressure from the liquor.) The apparent weight-average and number-average molecular weights for the sample as a whole increase by factors of 1.9 and 1.4, respectively, during the process (Table IV).

Both the extent and pattern of the associative process appear to depend upon the identity of the components present. For example, the degree of association observed for the water-insoluble cottonwood Organosolv lignin fraction under similar conditions was much smaller (Figure 7, curves 1 and 2); furthermore, the trimeric species seemed to exhibit a proportionately smaller tendency to become incorporated in associated complexes. The effect was confirmed at a 1.5-fold higher concentration of the fraction: the same pattern was maintained although the extent of association was found to be much larger (Table IV).

Reversibility of Associative–Dissociative Effects. It is worth emphasizing that the behavior of Organosolv lignin components at varying concentrations in alkaline aqueous solution (pH 13–14) is appropriately interpreted in terms of intermolecular association and dissociation and is not due to covalent chemical changes such as oxidative coupling of phenols[22,23] or reactions of the retroaldol type.[24]

Table IV
Effect of Association on Apparent $\overline{M}_w$ and $\overline{M}_n$ of Organosolv Lignin Samples in 1.0 M Aqueous NaOH[a]

fraction	concn, g L^{-1}	time, h	$\overline{M}_w$	$\overline{M}_n$
total sample	100	0.5	2050	837
		21	2700	942
		42	3010	1000
		72	3170	1040
		144	3280	1050
		190	3860	1150
water-insoluble	100	0.5	2380	928
fraction (65%		50	3020	984
(w/w))	150	51	4230	1220

[a] From western cottonwood pulped under the following conditions: 50% aqueous ethanol, 10:1 (v/w) liquor:substrate, 8 × 10^{-3} M $AlCl_3$, 6 h, 135 °C.

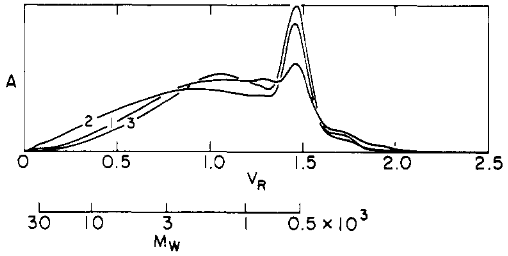

Figure 7. Reversibility of associative–dissociative effects exemplified for water-insoluble fraction of cottonwood Organosolv lignin (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm): after (1) 0.5 and (2) 50 h at 100 g L^{-1} in 1.0 M aqueous NaOH, followed by (3) 2100 h at 0.40 g L^{-1} in 0.10 M aqueous NaOH. (Pulping conditions listed in Table IV.)

The pattern revealed by the results as a whole renders appreciable contributions from the making and breaking of covalent bonds quite unlikely. Concentrated solutions on standing yield larger proportions of high molecular weight species. Although no consistent attempt was made to quantify the phenomenon during these essentially preliminary investigations, the final invariant molecular weight distribution was found in each case to be dependent upon the concentration of Organosolv lignin components in solution. On the other hand, incubation of dilute solutions produces a marked reduction in the proportions of higher molecular weight species, again through a process characterized by final invariant distribution of components. Indeed, as exemplified in Figure 7, the association–dissociation process is essentially reversible. Upon complete association at 100 g L^{-1} in 1.0 M aqueous NaOH, dilution of a water-insoluble cottonwood Organosolv lignin fraction to 0.40 g L^{-1} in 0.10 M aqueous NaOH allowed subsequent dissociation to occur: the molecular weight distribution after prolonged incubation was identical with that for the initial sample fully dissociated under the same conditions without prior association (cf. Figure 5B).

During the present work, dissociation was effected by incubation of dilute aqueous solutions 0.10 M in NaOH. However, the solubility behavior of Organosolv lignin samples required 1.0 M NaOH solutions to permit concentrations sufficient for substantial association in purely aqueous media. Under these circumstances, the rate of association was at least an order of magnitude larger than that of dissociation. This is no doubt partly due to the prevailing differences in ionic strength, but it also may be a preliminary indication that the overall process involves

Table V
Counterion and Zwitterion Effects on Apparent $\overline{M}_w$ and $\overline{M}_n$ of Representative Organosolv Lignin Samples

source	liquor:substrate ratio (v/w)[a]	incubation conditions prior to fractionation[b]	$\overline{M}_w$	$\overline{M}_n$
red alder[c]	10:1	0.5 h, 15 g L^{-1}, 0.10 M aq NaOH	5360	1230
		0.5 h, 15 g L^{-1}, 0.10 M aq LiOH	4110	1010
red alder[d]	8:1	1.0 h, 12 g L^{-1}, 0.10 M aq NaOH	4120	1130
		2.0 h, 12 g L^{-1}, 0.10 M aq NaOH containing 0.10 M betaine	3230	1070
		2010 h, 0.40 g L^{-1}, 0.10 M aq NaOH[f]	2760	1030
red alder[d]	20:1	1.0 h, 12 g L^{-1}, 0.10 M aq NaOH	2840	906
		2.0 h, 12 g L^{-1}, 0.10 M aq NaOH containing 0.10 M betaine	2190	878
		1970 h, 0.40 g L^{-1}, 0.10 M aq NaOH[f]	2080	841
wheat straw[e]	20:1	1.0 h, 13 g L^{-1}, 0.10 M aq NaOH	4460	1150
		1.0 h, 13 g L^{-1}, 0.10 M aq NaOH containing 0.10 M betaine	3410	1030
		1990 h, 0.40 g L^{-1}, 0.10 M aq NaOH[f]	2810	922
wheat straw[e]	65:1	1.0 h, 13 g L^{-1}, 0.10 M aq NaOH	3330	914
		1.0 h, 13 g L^{-1}, 0.10 M aq NaOH containing 0.10 M betaine	3010	880
		1990 h, 0.40 g L^{-1}, 0.10 M aq NaOH[f]	2330	816

[a] During pulping. [b] Same solution as eluant during GPC. [c] Pulping conditions: 75% aqueous dioxane, 6 × 10^{-3} M $AlCl_3$, 2 h, 140 °C. [d] Pulping conditions: 50% aqueous ethanol, 2 × 10^{-2} M $AlCl_3$, 1 h, 150 °C. [e] Pulping conditions: 50% aqueous ethanol, 1.5 × 10^{-2} M $Al_2(SO_4)_3$, 1 h, 150 °C. [f] Dissociation under these conditions was complete within time given.

more than one kinetically distinguishable step (vide infra): the dissociation of polymer aggregates is usually much more rapid than association.[25,26]

Molecular Weight Distributions of Discrete Organosolv Lignin Components. Although consistent for byproduct lignins of quite diverse origins, the effective molecular weight distributions deduced by elution with 0.10 M aqueous NaOH from Sephadex G75 do not necessarily approximate those of the discrete species. Indeed it cannot be assumed that extended preincubation periods at the lowest practicable concentrations (0.4 g L^{-1} as far as the present experimental limitations were concerned) have permitted complete dissociation between Organosolv lignin components to occur.

A convenient solution to the problem could be derived from the polyanionic character of Organosolv lignin components in alkaline aqueous solution. Thus it is unlikely that the extensive degree of association would be possible under these conditions were the process not accompanied by proton abstraction from solution: the negative charge density on the resulting complexes would otherwise be prohibitively large. It may reasonably be expected, therefore, that any means of effectively blocking proton uptake will significantly reduce the extent of association in alkaline solution. Either counterions or zwitterions could act in such a manner.

(i) Counterion Effects. Recent work has demonstrated that the presence of LiCl in the eluant DMF facilitates dissociation of kraft lignin (indulin) components during gel permeation chromatographic fractionation from octyl-Sepharose CL-4B.[3] Indeed, the calculated weight-average molecular weights of the same kraft lignin fractions deduced from the octyl-Sepharose CL-4B/0.10 M LiCl–DMF system and from Sephadex G75/0.10 M–aqueous NaOH were found to be quite similar.[3] It was not clear, however, to what extent site binding by the lithium ion contributes to the effect. In order to clarify the matter, the elution of Organosolv lignin samples from Sephadex G75 with 0.10 M aqueous LiOH was investigated. As shown in Figure 8, the elution profile for the standard red alder Organosolv lignin sample is attenuated almost by a factor of 2 in the higher molecular weight region approaching $\overline{M}_w$ = 40 000 compared to when 0.10 M aqueous NaOH is used as eluant.

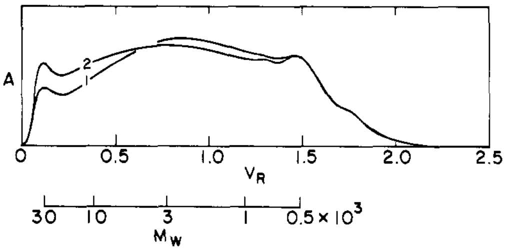

Figure 8. Counterion effects on the molecular weight distribution of red alder Organosolv lignin (Table V). Elution from Sephadex G75 with (1) 0.10 M aqueous LiOH and (2) 0.10 M aqueous NaOH (monitored at 280 nm).

It is evident that Li^+ binds more strongly to the Organosolv lignin species than Na^+ and that the degree of association is reduced in the process (Table V). Complexation between the counterion and Organosolv lignin components thus appears to be favored by a small crystallographic radius of cation; it presumably is not a result of solvent-separated ion pair formation. A similar sequence has been observed with alkali salts of poly(carboxylic acids)[27-31] and also with polyphosphates.[32] On the other hand, site binding to polymers carrying strongly acidic groups, namely, poly(sulfonic acids), is favored by a small size of hydrated cation and is thus probably caused by formation of ion pairs.[33,34]

The greater radius of the hydrated lithium cation compared with that of the sodium ion suggests that the former would bind more tightly with functional groups of lignin. Some clarification is desirable for the conditions under which the larger hydrated counterion may kinetically effect a greater separation between the polyion chains. Suppose that the polyion and counterions were entirely solvent separated. This would imply that the free energy difference (and the equilibrium constant) between the associated and dissociated species would be independent of the counterion. If the counterion were to interfere sterically with association, the rate of the associative process would, of course, be reduced by some numerical factor. It is, on the other hand, difficult to conceive in molecular terms of a mechanism by which the rate of dissociation would be lowered by the same factor. Only when specific binding between counterion and polyion prevails, therefore, would

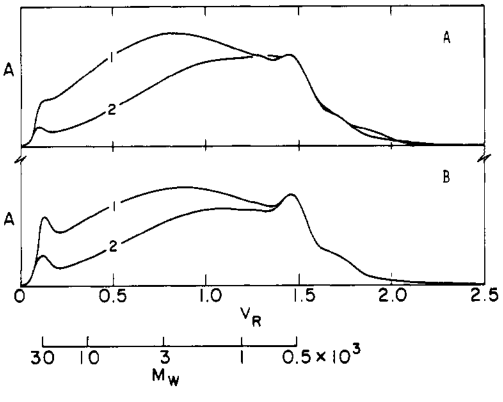

Figure 9. Effect of varying liquor:substrate ratio (under pulping conditions otherwise held constant) on the molecular weight distributions of Organosolv lignins (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm): (A) red alder lignins formed with ratios of (1) 8:1 (v/w) and (2) 20:1 (v/w); (B) wheat straw lignins formed with ratios of (1) 20:1 (v/w) and (2) 65:1 (v/w). (Pulping conditions listed in Table V.)

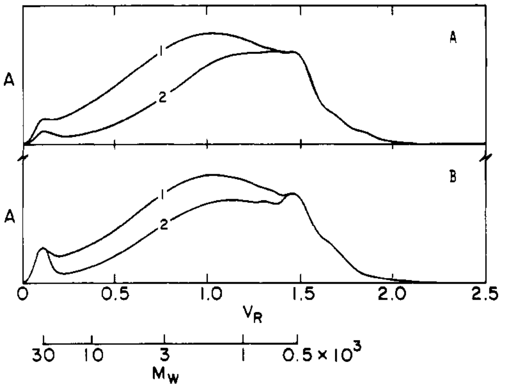

Figure 10. Effect of betaine on the molecular weight distributions of Organosolv lignins (Sephadex G75/0.10 M aqueous NaOH containing 0.10 M betaine, monitored at 280 nm): (A) red alder lignins formed with liquor:substrate ratios of (1) 8:1 (v/w) and (2) 20:1 (v/w); (B) wheat straw lignins formed with liquor:substrate ratios of (1) 20:1 (v/w) and (2) 65:1 (v/w). (Pulping conditions listed in Table V.)

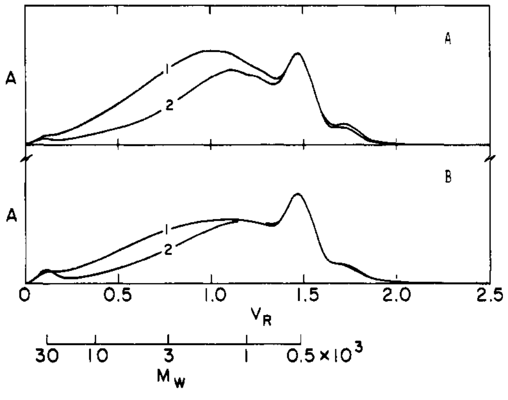

Figure 11. Complete dissociation at 0.40 g L^{-1} in 0.10 M aqueous NaOH of Organosolv lignins formed with varying liquor:substrate ratios (under pulping conditions otherwise held constant) (Sephadex G75/0.10 M aqueous NaOH, monitored at 280 nm): (A) (1) red alder (8:1) after 2010 h, (2) red alder (20:1) after 1970 h; (B) (1) wheat straw (20:1) after 1990 h, (2) wheat straw (65:1) after 1990 h. (Pulping conditions listed in Table V.)

such steric effects be possible. How much these may contribute in the present case is a subject of continuing studies. However, since zwitterions (vide infra) markedly increase the degree of dissociation between polyanionic Organosolv lignin components, it provisionally appears likely that the counterion effects are primarily dictated by the extent to which proton abstraction from solution is affected.

(ii) Zwitterion Effects. It would seem reasonable to suppose that zwitterions held in the ionic atmospheres of Organosolv lignin species under alkaline aqueous conditions could also reduce the extent of proton uptake and thereby increase the degree of dissociation between the components. The effect would be anticipated to be particularly significant for cases where the negative pole of the zwitterion possesses a pK_b higher than those of the polyanion phenolate groups.

The possibility of such a result was investigated for Organosolv lignin samples formed from red alder and wheat straw, respectively, under pulping conditions employing different liquor:substrate ratios but otherwise held constant. It is clear in both cases that the proportion of higher molecular weight species approaching $\bar{M}_w = 40000$ substantially decreases with increasing liquor:substrate ratio (Figure 9). Elution of the same lignin samples from Sephadex G75 with 0.10 M aqueous containing betaine (at an arbitrarily chosen concentration of 0.10 M) reveals two related effects (Figure 10): not only has there been a marked reduction in the proportion of higher molecular weight species but also the different effective molecular weight distributions arising from the use of the two liquor:substrate ratios pulping have tended to converge in each case (cf. Figures 9 and 10). These findings suggest that the zwitterion does act so as to reduce the degree of association between lignin components in aqueous alkaline solution (Table IV). (A careful check confirmed that the absorptivity at 280 nm of Organosolv lignin samples was not affected by the presence of betaine in 0.10 M aqueous NaOH solutions.)

Complete dissociation to discrete lignin components has not, however, occurred in 0.10 M aqueous NaOH containing 0.10 M betaine. Extended incubation of the Organosolv lignin samples at 0.4 g L^{-1} in 0.10 M aqueous NaOH alone caused further attenuation in the proportion of higher molecular weight species; even closer convergence between the profiles of samples formed under pulping conditions employing different liquor:substrate ratios is also evident (Figure 11). The residual differences between the molecular weight distributions of the discrete components derived from the same substrate may be caused during pulping by (a) shielding from hydrolytic attack of species incorporated in associated complexes and (b) condensation reactions through which higher molecular weight entities can be generated through interunit carbon-to-carbon bond formation.[35] Variations in the concentration of Organosolv lignin species in the pulping liquor primarily affect the degree of association between components, however.

It is important to emphasize that the effects of counterions and zwitterions documented here are indeed due to dissociation between Organosolv lignin components and are not caused by polyanion contraction of the kind observed, for example, with polysulfonates.[34,36] Under given elution conditions, the attenuation of the higher molecular weight region in the profiles is more marked when the proportion of larger species is greater (Figures 9 and 10). These higher molecular weight species have been shown to be comprised primarily of associated complexes, and as such their conformations would be expected to be relatively little affected by counterions or zwitterions held in the surrounding ionic atmosphere. Indirect confirmation is forthcoming from the behavior of kraft lignins, the components of which in all probability possess a somewhat higher density of charged groups than those of Organosolv lignins. A viscosimetric study of a kraft lignin fraction,[8] consisting of high molecular weight associated complexes,[3] revealed that the intrinsic viscosity of the preparation in aqueous solution is independent of pH between pH 8.5 and pH ~13; furthermore, no significant increase in reduced viscosity with decreasing concentration of the sample could be detected. Indeed, among lignin derivatives, only the lignin sulfonates, which on the average contain one sulfonate group for every two monomer units in the polymer, have been found to exhibit effects of polyion expansion.[37,38]

Mechanism and Mode of Association. The effect of the zwitterion upon the molecular weight distributions of the Organosolv lignins has revealed that dissociation of the associated complexes involves at least two kinetically distinguishable steps. Preincubation of the samples in aqueous NaOH containing betaine followed by elution from Sephadex G75 with 0.10 M aqueous NaOH alone resulted in elution profiles identical with those obtained with prior incubation was carried out under the same conditions but without the zwitterion. Thus the removal of betaine (through diffusion) permits a rate of reassociation at least 2 orders of magnitude faster in aqueous alkaline solution than that observed had the zwitterion not been introduced to the system. These findings may be rationalized in terms of two coupled processes: a rapid equilibrium between associated complexes and dissociated components (which is perturbed by the zwitterion in the direction of dissociation) and a slow change, possibly conformational in nature, during which the dissociated species undergo conversion to forms for which reassociation is not directly accessible.

$$\begin{matrix}\text{associated}\\ \text{complex}\end{matrix} \xrightleftharpoons{\text{rapid}} \begin{matrix}\text{dissociated}\\ \text{components}\end{matrix} \xrightleftharpoons{\text{slow}} \begin{matrix}\text{discrete}\\ \text{components}\end{matrix}$$

The variation of the weight-average molecular weight, $\bar{M}_w$, with number-average molecular weight, $\bar{M}_n$, for a lignin sample during the course of association can provide insight into the mode of the process. As shown in the Appendix, the relationship between the two parameters is given by

$$\partial \bar{M}_w/\partial \bar{M}_n = 2\langle m_i m_j\rangle(1/\bar{M}_n^2)$$

where $\langle m_i m_j\rangle$ at any particular point is the appropriate ensemble average product of the molecular weights of associating components. The problem, then, is reduced to one of deriving expressions for $\langle m_i m_j\rangle$ from reasonable hypothetical models. In most instances this is quite complicated, but useful information may be gained by testing the relationship for two simple cases.

(i) The form of $\langle m_i m_j\rangle$ would be identically equal to $\bar{M}_n^2$ for the whole sample if the probability of association between any two components were independent of their molecular weights. A plot of $\bar{M}_w$ vs. $\bar{M}_n$ would thus generate a straight line with a slope of 2. This is explored in Figure 12 for a cottonwood Organosolv lignin sample (Table IV). The data points do indeed approximate to a straight line, but with a slope of 5.9 rather than 2.0. Although the underlying assumption is hereby invalidated, the result is revealing: it indicates that the range of variation in $\bar{M}_w$ and $\bar{M}_n$, while relatively small, is sufficient for discrimination between certain limiting expressions for $\langle m_i m_j\rangle$.

(ii) A plot of $\bar{M}_w$ vs. $1/\bar{M}_n$, on the other hand, will form a curve, the slope of which at any point would be given by $-2\langle m_i m_j\rangle$. This is illustrated in Figure 12 for the same cottonwood Organosolv lignin sample (Table IV). The magnitude of $\langle m_i m_j\rangle$ deduced from any point on the curve is greater than the respective value of $\bar{M}_n^2$. This suggests that, *for the relative populations of species present*, association between lower and higher molecular weight components is preferred: species with molecular weights below 2100 are depleted as those with larger molecular weights proportionately increase (Figure 6). The upper limit to the number-average molecular weight of these lower molecular weight components is, clearly, $\bar{M}_n$ for the sample as a whole. The lower limit to the effective average molecular weight for the complementary higher molecular weight species (namely, $\langle m_i m_j\rangle/\bar{M}_{n,\text{sample}}$) was thus estimated from Figure 12 to be 2800 ± 200 in this range of the associative process.

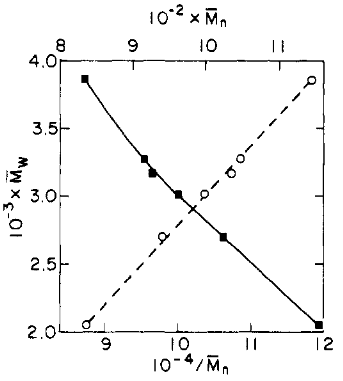

Figure 12. Relationship between $\bar{M}_w$ and $\bar{M}_n$ during association between cottonwood Organosolv lignin components present at 100 g L^{-1} in 1.0 M aqueous NaOH (Table IV): (○) variation of $\bar{M}_w$ with $\bar{M}_n$; (■) variation of $\bar{M}_w$ with $1/\bar{M}_n$.

Experimental corroboration has been provided by the finding that no appreciable tendency to associate seems to be evident among lower molecular weight components when present alone in aqueous alkaline solution. This was revealed by the behavior of the water-soluble fraction (comprising 35% (w/w)) of the cottonwood Organosolv lignin sample which consisted almost entirely of species with molecular weights below 3000: no significant associative effect was observed for these components at the highest concentrations attainable in 1.0 M aqueous NaOH.

In marked contrast to the patterns obtained with alkaline aqueous eluants, gel permeation chromatography using nonaqueous solvents or aqueous mixtures in the absence of additional electrolyte generates bi- and multimodal distributions of species with molecular weights ranging to values which are larger by over 3 orders of magnitude.[9] Recent work in our laboratories has demonstrated that such disparities result from the association of lignin components to well-defined high molecular weight complexes.[3]

These effects should not be confused with aggregative interactions between associated complexes leading ultimately to gelation or precipitation. For example, observed changes in viscosity with pH below 8.5 of aqueous kraft lignin solutions have been interpreted as being governed by variations in intermacromolecular sol particle hydrogen bonding with degree of dissociation of the carboxylic acid groups present.[6-8]

Generally, exhaustive methylation and acetylation of lignin samples have not appreciably affected the proportions of high molecular weight species observed by means of gel permeation chromatography with nonaqueous eluants.[39] This seems to have been the main factor responsible for there having been so little recognition of the pronounced associative interactions operative between lignin components. Certainly it affirms that hydrogen bonding does not appear to play a direct role in such effects. Presumably intermolecular orbital interactions, dominated by those of the HOMO-LUMO type, govern the underlying mechanisms of these processes.

Appendix. Relationship between $\bar{M}_w$ and $\bar{M}_n$ during Association

The effect upon the weight-average molecular weight, $\bar{M}_w$, and number-average molecular weight, $\bar{M}_n$, due to the association between two component *molecules* with average molecular weights $\langle m_i \rangle$ and $\langle m_j \rangle$, respectively, at a given point during the process may be deduced in the following manner. (Note that the forms of the expressions for $\langle m_i \rangle$ and $\langle m_j \rangle$, which are appropriately averaged over all components present, will depend upon the nature of the governing molecular interactions.)

For the sample as a whole, $\delta(\sum_k c_k) = 0$ and $\delta(\sum_k n_k) = -N_A^{-1}$, where c_k is the weight in grams and n_k is the number of moles for the kth component. (N_A is Avogadro's number.) Furthermore

$$\delta(\sum_k c_k m_k) = N_A^{-1}[(\langle m_i \rangle + \langle m_j \rangle)^2 - \langle m_i \rangle^2 - \langle m_j \rangle^2] = 2N_A^{-1}\langle m_i \rangle \langle m_j \rangle = 2N_A^{-1}\langle m_i m_j \rangle$$

since, for a particular average component molecule, $\langle c_k \rangle = N_A^{-1}\langle m_k \rangle$. Thus

$$\delta(\bar{M}_w) = \delta\left(\frac{\sum_k c_k m_k}{\sum_k c_k}\right) = \frac{(\sum_k c_k)\delta(\sum_k c_k m_k) - (\sum_k c_k m_k)\delta(\sum_k c_k)}{(\sum_k c_k)^2} = \frac{2N_A^{-1}\langle m_i m_j \rangle}{\sum_k c_k}$$

and

$$\delta(\bar{M}_n) = \delta\left(\frac{\sum_k c_k}{\sum_k n_k}\right) = \frac{(\sum_k n_k)\delta(\sum_k c_k) - (\sum_k c_k)\delta(\sum_k n_k)}{(\sum_k n_k)^2} = \frac{N_A^{-1}(\sum_k c_k)}{(\sum_k n_k)^2}$$

The increments $\delta(\bar{M}_w)$ and $\delta(\bar{M}_n)$ are in effect limitingly small, and so the ratio of the two may be written

$$\partial \bar{M}_w / \partial \bar{M}_n = 2\langle m_i m_j \rangle (1/\bar{M}_n)^2$$

References and Notes

(1) Adler, E. *Wood Sci. Technol.* **1977**, *11*, 169.
(2) Obiaga, T. J.; Wayman, M. *J. Appl. Polym. Sci.* **1974**, *18*, 1943.
(3) Connors, W. J.; Sarkanen, S.; McCarthy, J. L. *Holzforschung* **1980**, *34*, 80.
(4) Benko, J. *Tappi* **1964**, *47*, 508.
(5) Brown, W. *J. Appl. Polym. Sci.* **1967**, *11*, 2381.
(6) Yaropolov, N. S.; Tishchenko, D. V. *Zh. Prikl. Khim.* **1970**, *43*, 1120.
(7) Yaropolov, N. S.; Tishchenko, D. V. *Zh. Prikl. Khim.* **1970**, *43*, 1351.
(8) Lindström, T. *Colloid Polym. Sci.* **1979**, *257*, 277.
(9) Hüttermann, A. *Holzforschung* **1978**, *32*, 108.
(10) Forss, K. G.; Stenlund, B. G.; Sågfors, P.-E. *Appl. Polym. Symp.* **1976**, *28*, 1185.
(11) Teller, D. C. *Methods Enzymol.* **1973**, *27*, 346–441.
(12) Yphantis, D. A. *Biochemistry* **1964**, *3*, 297.
(13) Lansing, W. D.; Kraemer, E. O. *J. Am. Chem. Soc.* **1935**, *57*, 1369.
(14) McNaughton, J. G.; Yean, W. Q.; Goring, D. A. I. *Tappi* **1967**, *50*, 548.
(15) Gelotte, B. *J. Chromatogr.* **1960**, *3*, 330.
(16) Porath, J. *Svensk. Kem. Tidskr.* **1962**, *74*, 6.
(17) Porath, J. *Svensk. Kem. Tidskr.* **1962**, *74*, 306.
(18) Flodin, P. Dissertation, Uppsala, 1962.
(19) Lundquist, K.; Lundgren, R. *Acta Chem. Scand.* **1972**, *26*, 2005.
(20) Smith, D. C. C. *J. Chem. Soc.* **1955**, 2347.
(21) Smith, D. C. C. *Nature (London)* **1955**, *176*, 267.
(22) Kratzl, K.; Gratzl, J.; Claus, P. *Adv. Chem. Ser.* **1966**, *No. 59*, 157.
(23) Kratzl, K.; Schafer, W.; Claus, P.; Gratzl, J.; Schilling, P. *Monatsh. Chem.* **1967**, *98*, 891.
(24) Wallis, A. F. A. In "Lignins"; Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley: New York, 1971; pp 345–72.
(25) Doty, P.; Wagner, H.; Singer, S. J. *J. Phys. Colloid Chem.* **1947**, *51*, 32.
(26) Strauss, U. P.; Gershfeld, N. L.; Crook, E. H. *J. Phys. Chem.* **1956**, *60*, 577.
(27) Gregor, H. P.; Frederick, M. *J. Polym. Sci.* **1957**, *23*, 451.
(28) Quadrifoglio, F.; Crescenzi, V.; Delben, F. *Macromolecules* **1973**, *6*, 301.
(29) Rinaudo, M.; Pierre, C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *269*, 1280.
(30) Rinaudo, M.; Milas, M. *J. Chim. Phys.* **1969**, *66*, 1489.
(31) Zana, R.; Tondre, C.; Rinaudo, M.; Milas, M. *J. Chim. Phys.* **1971**, *68*, 1258.
(32) Strauss, U. P.; Ross, P. D. *J. Am. Chem. Soc.* **1959**, *81*, 5295.
(33) Eisenberg, H.; Mohan, G. R. *J. Phys. Chem.* **1959**, *63*, 671.
(34) Chu, P.; Marinsky, J. A. *J. Phys. Chem.* **1967**, *71*, 4352.
(35) Harkin, J. M. *Adv. Chem. Ser.* **1966**, *No. 59*, 65.
(36) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(37) Gardon, J. L.; Mason, S. G. *Can. J. Chem.* **1955**, *33*, 1491.
(38) Rezanowich, A.; Goring, D. A. I. *J. Colloid Sci.* **1960**, *15*, 452.
(39) Ekman, K. H.; Lindberg, J. J. *Pap. Puu* **1966**, *48*, 241.

Rubber Elasticity Theory. A Network of Entangled Chains

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Received May 12, 1980

ABSTRACT: Following Edwards, the effect of entanglements on the chains of a concentrated polymeric system is described by means of "tubes" endowed with a harmonic potential. The elastic free energy of the entangled network is then calculated by assuming that the tube constraints deform affinely. The resulting expressions predict various nonclassical effects. Some of them qualitatively coincide with the predictions of the modern theories of rubber elasticity by Ronca and Allegra and by Flory which are based on the restrictions of junction fluctuations due to entanglements. However, the value of the shear modulus predicted here is significantly different and it is related to the plateau modulus of the un-cross-linked polymer.

Introduction

Recent network theories which account for the effect of entanglements can be grouped in two categories. Those advanced by Ronca and Allegra[1] and Flory[2-5] emphasize the role of entanglements in restricting the fluctuations of the junctions. They are successful in qualitatively explaining the various departures of the behavior of real networks from that predicted by classical theories of phantom networks. In particular, the well-known Mooney effect is accounted for and even the maximum in the