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Lignin 24 Ultrafiltration and Light-Scattering Evidence for Association of Kraft Lignins in Aqueous Solutions

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ABSTRACT: Ultrafiltration and light-scattering evidence is presented pointing to the growth of large, stable associated complexes from smaller lignin moieties as the alkalinity of an aqueous kraft lignin (KL) solution is decreased. Ultrafiltrates showed a decrease in the number of small molecules available to permeate the membrane as the solution alkalinity was decreased from pH 13.8 to 8.5. Light-scattering measurements indicated a large increase in the weight-average molecular weight (i.e., from about 3500 to 200 000) when the alkalinity was reduced. The association was found to be reversible and rapid. A model of the association is proposed in which the controlling step is presumed to be the protonation of phenolic hydroxyl groups. Association seems to explain the difficulties experienced in fractionation of KL on a molecular weight basis by use of incremental precipitation by acidification of alkaline solutions.

Introduction

Lignins are phenylpropane type polymers that make up about one-fourth of the mass of all woody plant tissue. Structural features of native soft-wood lignins have been proposed by Adler.[1] Characteristics of lignins have been described by Sarkanen and Ludwig.[2]

Several investigators have reported that kraft lignins (KL), which are extracted from wood by action of aqueous sodium hydroxide–sodium sulfide solutions at elevated temperatures and are schematically pictured in Figure 1 according to Marton,[3] may associate in aqueous solution to form complexes. Changes in diffusion coefficients with changes in concentration or alkalinity have been observed by Benko.[4] Increases in specific viscosity with decreases in alkalinity have been found by Yaropolov and Tishchenko[5] and also by Lindstrom,[6] who proposed that association occurs as a result of hydrogen bonding between carboxylic acid and phenolic hydroxyl groups. Shifts in molecular weight distributions (MWD), as estimated by size exclusion chromatography (SEC), have been seen in this laboratory by Sarkanen et al.,[7] who suggested that the complexes may arise as a result of HOMO–LUMO bonding of the π orbitals of benzene rings.

With this background, the now-reported research was undertaken[8] to assemble more information about the phenomenon of association of kraft lignins in aqueous solutions.

Experimental Section

Solutions. The KL studied was Indulin AT, a purified southern pine lignin solid obtained from the Westvaco Co. This KL was dissolved in sufficient aqueous sodium hydroxide to yield a solution (160 g L^{-1}, pH 9.2) which was then filtered through Whatman number 1 paper. The filtrate was divided into five aliquots, and each was adjusted to a different alkalinity by the addition of carbonate-free, saturated sodium hydroxide solution or by the removal of sodium by ion exchange. Solutions at pH 8.5, 9.2, 11.0, 12.0, and 13.6 were identified as KL85, KL92, KL11, KL12, and KL14. These were aged under nitrogen for about 1 month at room temperature and, before use, were passed through a fine-sintered glass filter. No precipitate was observed on the filter surface. The ionic strength of each solution was approximately 0.2 M.

Ultrafiltration Procedures. Experiments were conducted in a stirred ultrafiltration cell (Model 202, Amicon Co.) modified so that the stir bar was situated about 2.5 cm above the membrane surface. Polysulfone membranes from DDS, Ltd. (Denmark), and from the Amicon Co. were used. Three sets of experiments were performed to determine the effects of alkalinity on the concentration of solutes in the permeates. A fourth experiment was conducted to explore the effects of association on the molecular weight distribution.

For set UF-1, individual 160 g L^{-1} KL solutions were ultrafiltered separately at three different randomly chosen transmembrane pressures (134, 268, and 536 kPa) through a DDS GR8P membrane with stirring at 145 rpm. The initial 10 mL of permeate was discarded, and a 2-mL permeate sample was then collected. Lignin concentration was determined in each permeate. Between runs at different alkalinities, the membrane was washed by using an acid–base–detergent procedure described by Woerner.[8]

In UF-2, the KL92 solution (160 g L^{-1}, pH 9.2) was placed in an ultrafiltration cell and titrated with a saturated sodium hydroxide solution to yield several alkalinity levels and finally pH 13. Solutions were allowed to stand for 2 h between alkaline additions. Ultrafiltrations (GR8P membrane) were conducted at each alkalinity level with the transmembrane pressure and the stirring rates held constant at 134 kPa and 145 rpm, respectively. The initial ionic strength was approximately 0.2 M.

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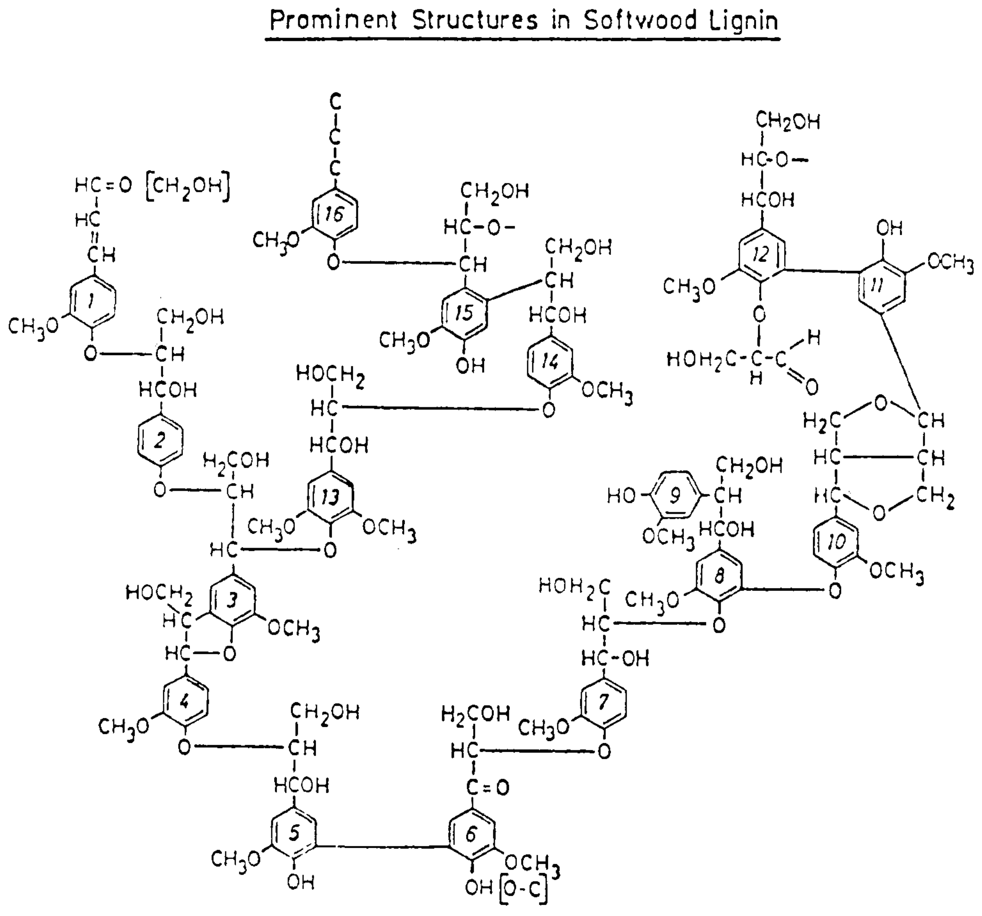

Figure 1. Schematic structure of kraft lignins as proposed by Marton.[3]

In UF-3, the KL solute concentration was reduced to about 14 g L^{-1} to minimize concentration polarization and ionic strength effects; the stir bar rate was increased to 345 rpm, and the pressure was kept constant at 67 kPa. Individual solutions were ultrafiltered (GR8P membrane) at pH 8.5, 10.1, 11.4, and 12.6, at a constant ionic strength of 0.1 M created by adjustment with NaCl.

In UF-4, the pH 8.5 and 12.6 solutions for UF-3 were ultrafiltered by using four different membranes, GR8P, GR6P, G5P, and XM300, which have cutoff levels corresponding to nominal molecular weights of 10 000, 25 000, 65 000, and 300 000, respectively.

Light-Scattering Procedures. Experimentation was conducted with the helpful guidance of Professor J. M. Schurr (Department of Chemistry, University of Washington) and by using his apparatus, which has been described by Wilcoxon.[10] A wavelength of 632.8 nm was employed to minimize absorption. Scattered-light intensity data were collected only during quiescent periods to minimize the effects of dust. The effects of anisotropy were not evaluated. A narrow-bandwidth filter was used to eliminate the influence of fluorescence.

Prior to taking observations, we washed each light-scattering cell with a copious amount of solvent that had been filtered through a 0.22-μm Millipore filter to remove dust. The solutions studied were similarly filtered. The sample cell was judged to be substantially dust-free when no bright flashes of light were observed at a small angle.

Aqueous sodium hydroxide solutions, at pH 8.5 and 13.8, were prepared for use as solvents by adding appropriate amounts of a carbonate-free 1.0 N NaOH solution to 1 L of deionized water. About 26 h prior to experimentation, two KL samples were prepared by diluting 0.15 mL of KL85 to 25 mL with pH 8.5 solvent or with 25 mL of the pH 13.8 solvent. The KL concentration in each solution was 0.96 g L^{-1}. The ionic strengths of the pH 8.5 and 13.8 samples were about 1.5×10^{-5} and 0.63 M, respectively. In all experiments, the light path was 1 cm.

In LS-2 and LS-3, the intensity of the light scattered by the pH 13.8 and 8.5 solutions, respectively, was measured as a function of angle of observation. At the end of LS-3, about 0.5 mL of 0.63 N NaOH solution was added to the pH 8.5 solution. The scattering was then observed and is reported as LS-3A.

In LS-4 and LS-5, 0.05-mL droplets of 0.1 NaCl or 0.1 NaOH, respectively, were added to 1.7 mL of the pH 8.5 solution. Scattering was measured at 90° only. Prior to observation of the intensity of scattered light, samples were allowed to stand for 2–5 min to allow for mixing and equilibration. In LS-5, alkalinities were estimated by titrating a 5.1-mL aliquot of the dilute pH 8.5 solution with 0.15-mL droplets of 0.1 N NaOH solution.

Lignin Determination. Concentration of KL in all samples was determined by measurement of absorption of ultraviolet radiation at 280 nm, assuming the validity of Beer's law and that the absorptivity of KL was 18 L g^{-1} cm^{-1} and independent of molecular weight.

Molecular weight distributions were estimated by use of the SEC procedures developed by Sarkanen et al.[7] which were amended to include computer acquisition of the levels of eluant concentration and the eluant weight as functions of time. The eluant was 0.1 N NaOH prepared from deionized water and saturated CO_2-free NaOH.

Results and Discussion

Ultrafiltration can be used to monitor the effects of changes in a solution of the numbers of small molecules present that are available to permeate the membrane. The pores in the membranes are of oligomeric dimensions, and the passage of molecules probably occurs by hindered diffusion. Thus the concentration of solutes in the permeate is affected only by the pore size distribution and by the membrane surface concentration of molecules that retard mass transfer. During ultrafiltration, molecules or entities that cannot pass through the pores of the membrane and are thereby "rejected" tend to accumulate at the surface of the membrane. This phenomena is known as "concentration polarization". In extreme cases of concentration polarization, the rejected molecules may form

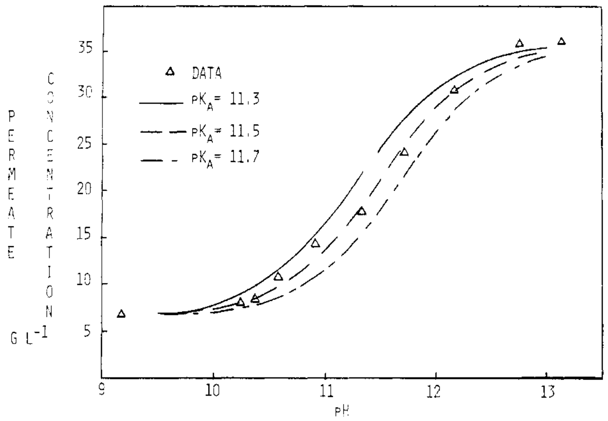

Figure 2. Effect of alkalinity of initial solution upon the concentration of kraft lignin in permeate solutions (experiment UF-2).

a "gel layer" that can provide an additional resistance to the passage of solvent and solute molecules through the membrane. Some degree of gel layer formation is associated with most industrial operations. In all presently reported experiments, concentration polarization occurred to some extent. Gel layer formation took place in experiments UF-1 and UF-2.

An initial experimentation, aqueous sodium hydroxide solutions ranging in alkalinity from pH 8.5 to 14 were ultrafiltered through GR8-P membranes. The flux rate remained substantially constant. This result indicated that the distribution in pore size in the membranes was not significantly influenced by changes in the alkalinity.

UF-3 was conducted under conditions designed substantially to eliminate the effects of concentration polarization during the ultrafiltration of KL. Dilute solutions at a number of alkalinity levels and at constant ionic strength (0.1 M) were ultrafiltered by using rapid stirring of the cell and a constant transmembrane pressure. The flux rates were found to be nearly the same (within 1 or 2%) as the flux rates observed with the aqueous solutions not containing KL, thus indicating that concentration polarization was not a significant factor.

However, it was found that the concentration of KL solutes in the permeates increased markedly with increase in alkalinity of the solutions being ultrafiltered. The observed permeate solute concentrations were 0.35, 0.58, 0.97, and 1.06 g L^{-1} for initial solution concentrations of 13.1, 13.1, 14.9, and 14.9 g L^{-1} at pH levels of 8.55, 10.13, 11.4, and 12.43, respectively.

Thus the proportion of small molecules that were available in the initial solution and could pass through the membrane seemed to increase as the alkalinity level was increased. Since the total KL concentration in the initial solution was approximately constant at the several alkalinity levels studied, it appears that the increased concentration of small molecules may be attributed appropriately to the disassembly of complexes that existed at lower degrees of alkalinity in the initial solution.

UF-1 and UF-2, which were conducted at several transmembrane pressures with high levels of KL concentration and thus significant concentration polarization, exhibited similar decreases in the permeate solute concentration as the alkalinity was lowered (Figures 2 and 3).

In UF-2, a KL92 solution was titrated with a NaOH solution, and the permeate concentration was found to increase as the alkalinity increased, as shown in Figure 2. At pH 9.2 the solute concentration in the permeate was 6 g L^{-1}. It rose slowly as alkalinity was increased to pH 10.5 and then rapidly in the alkalinity range of pH 10.5 to 12.7 and finally leveled off at 37 g L^{-1} at pH >13.1. This relationship is sigmoidal and suggests an acid–base titration curve.

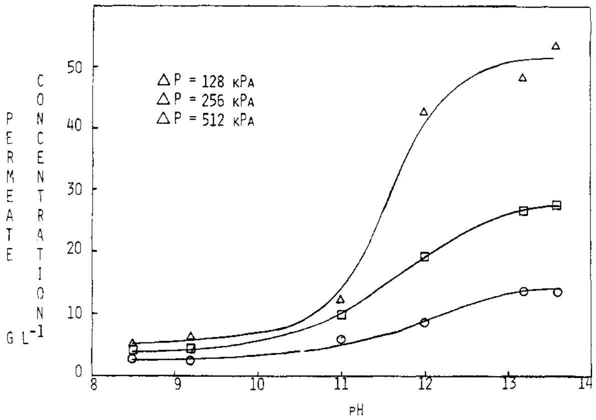

Figure 3. Effect of alkalinity of initial solution and of transmembrane pressure upon the concentration of kraft lignins in permeate solutions (experiment UF-1).

In UF-1, the individual KL solutions were ultrafiltered at three different transmembrane pressures (134, 256, 512 kPa). At each condition, the permeate solute concentrations changed approximately as observed in UF-2. The manifested differences seem to be due to the sieving effect of the gel layer that forms on the upstream surface of a membrane, as discussed elsewhere in some detail.[8]

The differences observed between the permeate solute concentrations in UF-2 and those in UF-1 at 134 kPa may have arisen from a secondary time-dependent dissociative process or by the degradation of KL under conditions of high alkalinity.

Model for Association. The permeate solute concentration–alkalinity curves obtained in UF-1, -2, and -3 are similar in form to those associated with the titration of a weak acid (pK_a > 10) with a strong base. This pK_a level suggests that ionization of phenolic groups, as alkalinity is increased, brings about disruption of complexes consisting of associated lignin molecules. Since no flocculation was observed in these experiments, it appears that association of kraft lignin precedes flocculation and may exert an important influence on the difficulties associated with separation of kraft lignins by fractional precipitation.

A simple algorithm has been developed to rationalize the above and other results on a preliminary basis. It is assumed (1) that KL molecules associate to yield complexes by an unknown mechanism that is related to the protonation of phenolic groups, (2) that the phenolic hydroxyl groups of KL can be characterized approximately by a single pK_a value, (3) that the mass fraction of lignin molecules, which are not associated at a particular alkalinity level and thus are available to pass through the ultrafilter membrane (χ_{TS}), will be equal to the mass fraction of KL carrying ionized phenolic hydroxyl groupings (χ_p) plus the mass fraction of the lignins that are soluble in neutral aqueous solution (W_{LS}), i.e.

$$\chi_{TS} = W_{LS} + (1 - W_{LS})\chi_p \qquad (1)$$

and (4) that all protonated phenolic hydroxyl groups participate in the association process. The symbols used in this paper are defined in the Nomenclature section.

For our KL sample, W_{LS} was determined experimentally to be 0.16 in aqueous solution. A known oven-dried mass of KL was added to the pH 7.0, I = 0.2 M solution at a total concentration of 160 g L^{-1}. The solution, after equilibriation at room temperature, was filtered through Whatman number 1 filter paper. The oven-dried mass of KL retained on the filter paper was divided by the total

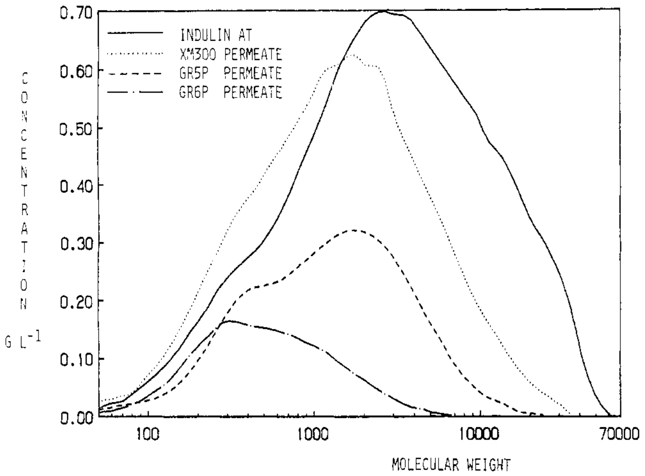

Figure 4. Estimated molecular weight distribution of kraft lignins in initial solution at pH 12.6 and in permeate solutions (experiment UF-3).

initial mass of KL to obtain $1 - W_{LS} = 0.84$.

On the basis of weak acid–base chemistry,[10] the mole fraction of ionized phenolic groups can be formulated approximately as

$$\chi_p = \frac{1}{1 + K_w/(K_a[\mathrm{OH}])} \tag{2}$$

where K_w and K_a are the dissociation constants of water and of phenolic groups, and [OH] is the concentration of hydroxyl ions.

The model has been tested by conducting ultrafiltration experiments which yield results reflecting the effects of the rejection coefficient:

$$R \equiv 1 - C_p/C_0 \tag{3}$$

where R includes the influence of both membrane porosity and of concentration polarization. C_p and C_0 are the concentrations of KL in the permeate and in the initial solutions, respectively.

For present purposes, more useful is an "effective" rejection coefficient

$$R' = 1 - C_p/(C_0\chi_{TS}) \tag{4}$$

where $C_0\chi_{TS}$ represents the concentration of dissolved lignins that are *not* associated into high molecular weight complexes and thus may be available to pass through an ultrafiltration membrane into the permeate.

We assume for UF-2 that dissociation of the phenolic hydroxyl group is complete at pH 13, whence $\chi_p = 1$ (eq 2), $\chi_{TS} = 1$ (eq 1), and $R = R'$. For the conditions of UF-2 and at pH 13, $R = 0.78$. We also assume that R is a unique property of the membrane and of the prevailing concentration polarization and is independent of solution alkalinity.

It is known from the conditions of UF-2 that $C_0 = 160$ g L^{-1}. Therefore eq 1–4 can be used to calculate values for C_p for selected values of alkalinity (see Appendix A for an example calculation). Three different values of the pK_a were assumed, and Figure 3 shows that the predicted form and calculated values fit the UF-2 experimental results moderately well; p$K_a = 11.5$ gives the best fit.

Thus it appears that it is the degree of association of the dissolved KL molecules (as reflected in R') that controls the results of ultrafiltration. The variations of the experimental results from the model probably arise mainly because the pK_a of the lignin moieties is not constant but depends on molecular weight, structure, and perhaps other factors as well.

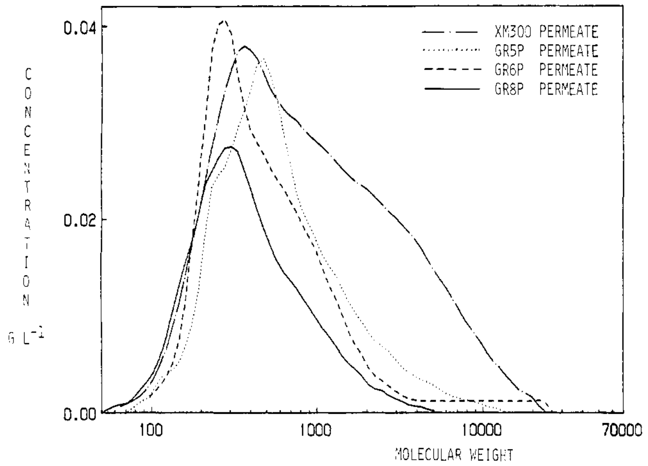

Figure 5. Estimated molecular weight distribution of kraft lignins in initial solution at pH 8.5 and in permeate solutions (experiment UF-3; note that the ordinate scale is expanded 15 times relative to Figure 4).

Effect of Association on the MWD of Permeate Solutions. Experiments UF-3 and -4 were conducted with dilute solutions and high-speed stirring conditions, which were employed to eliminate or minimize the effects of concentration polarization. Ultrafiltrations were conducted with initial solutions at pH 12.6 and 8.5 by using membranes with several different pore sizes. Molecular weight distributions of the KL in the permeates were evaluated to secure information concerning the KL molecules in the initial solution.

At pH 12.6, where the degree of association is believed to be small, the permeate MWD pattern (Figure 4) indicates that the KL arising from the most porous membrane (XM-300; nominal MW cutoff = 300 000) includes most of the KL molecules present in the initial solution except those in the higher molecular weight range. With membranes that have lower cutoff levels, progressively smaller proportions of the KL in the original solutions were transmitted.

At pH 8.5, the concentration of KL found in the permeates (Figure 5) is much less than observed in the pH 12.6 permeates. Since the porosity of the membranes is substantially unaffected by changes in solution alkalinity, it appears that the observed effects may be attributed appropriately to changes in the extent of association of KL molecules to yield high molecular weight entities. Since only a small proportion of total KL mass passed through the membrane with the largest pore size (nominal MW cutoff = 300 000), the effective molecular weight of the complexes appears to be higher than 300 000.

The effective rejection coefficient (eq 4) should be a function only of solute radius and pore radius distributions. On this basis, the MWD of solutes not participating in large associated complexes in the initial solutions at pH 8.5 was estimated by use of eq 5:

$$R'(i) = 1 - \frac{C_p(i)\ (\mathrm{pH}\ 8.5)}{\chi_{TS}C_0\ (\mathrm{pH}\ 8.5)} = 1 - \frac{C_p(i)\ (\mathrm{pH}\ 12.6)}{\chi_{TS}C_0(i)\ (\mathrm{pH}\ 12.6)} \tag{5}$$

The $R'(i)$ distribution for the XM300 membrane was calculated from eq 5 by assuming that no association occurred. The distribution of molecules in the pH 8.5 solution free to permeate the membrane ($\chi_{TS}C_0$) was then calculated from the right-hand side of eq 5. The data used in these calculations were obtained from Figures 4 and 5 as reported in Table I. The values of χ_{TS} and C_0 at p H 8.5 appear in Figure 5 as a solid line. The difference between the distributions at pH 12.6 and 8.5 is taken to

Table I[a]
Estimated Degree of Association of Indulin AT Lignins at pH 8.5

mol wt increment	KL concn, mg L^{-1} pH 8.5[b]	KL concn, mg L^{-1} pH 12.6[c]	mass fraction associated = $f(i)$
200–400	35	290	0.87
400–600	36	380	0.90
600–800	31	440	0.93
800–1000	29	490	0.94
1200–1400	26	610	0.95
1800–2000	23	610	0.96
2800–3000	21	540	0.96
4400–5000	16	400	0.96
10000–12000	6	180	0.97
20000–22000	1	50	0.98

[a] Calculations were made for the XM300 membrane results over the entire range of MWD by using the increments as indicated above and also as follows: 200, 400, 600, 800, 1000, and 2000 for molecular weights up to 3200, 4400, 5600, 6400, 10 000 and 22 000, respectively [b] From data in Figure 4. [c] From data in Figure 5.

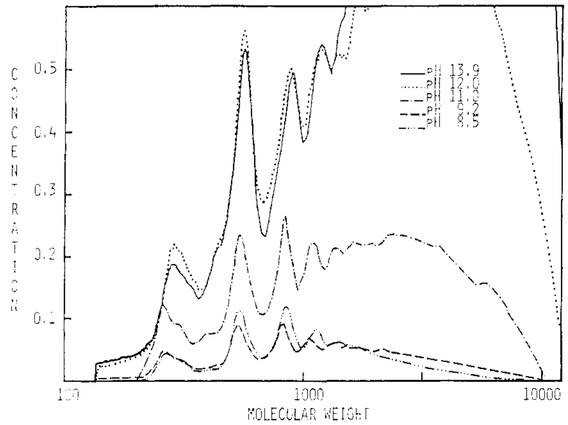

Figure 6. Estimated molecular weight distributions calculated from the results of experiment UF-1 at transmembrane pressure = 134 kPa.

be the distribution of molecules in the associated complex. The fraction of the mass of the associated complex in each molecular weight is reported in Table I as $f(i)$. Example calculations are shown in Appendix B.

As the alkalinity is decreased from pH 13.2, the larger oligomers seem to associate in greater proportions than is the case with the smaller molecules. However, at any alkalinity level, all oligomers appear to participate in the formation of complexes. This proposition is supported by the data in Figure 6 relative to the permeate solutions obtained from the UF-1 experiments at 134 kPa. Between pH 13.9 and 12.0, association occurs primarily between molecules with molecular weights greater than 1000 as indicated by the decrease in concentration of permeate solutes in this molecular weight range. As the alkalinity is decreased, molecules of all molecular weights participate, to varying degrees, in the association.

Light Scattering. Light-scattering experiments were conducted to obtain evidence of KL association by use of a procedure other than ultrafiltration. Ultrafiltration is sensitive to the concentration of small molecules, whereas light scattering is strongly influenced by the presence of large particles. Four light-scattering experiments were conducted to try to observe the formation of large particles as association occurs. In the first two (LS-2 and LS-3), the apparent molecular weight of solutes was measured at high and low alkalinities. In the third (LS-4), the effect of ionic strength at low alkalinity was explored, and in the fourth experiment (LS-5), the effects of change of alkalinity in a light-scattering cell were observed.

Table II
Count Rate from Light Scattering of Kraft Lignin Preparations

exptl	pH	angle, deg	count rate[a] obsd	count rate[a] corr
LS-2	13.8	90	13 000	13 000
		60	15 000	13 000
		30	34 000	17 000
LS-3	8.5	90	800 000	800 000
		60	950 000	828 000
		30	1 880 000	940 000
LS-3A	13.2	90	13 000	13 000

[a] Corrected rate = (observed rate)(sin θ).

Scattering by vertically polarized light is related to weight average molecular weight by the following relationships (Hiemenz[12]):

$$\frac{KC}{R_\theta} = \frac{1}{P(\theta)}\left[\frac{1}{M_w} + 2BC\right] \qquad (6)$$

$$R_\theta = (I_s/I_0)d^2 \qquad (7)$$

$$K = \frac{2\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \qquad (8)$$

$$P(\theta) = \frac{1}{1 + \left(\frac{16\pi^2 R^2 g}{3\lambda^2}\right)\left(\sin^2\frac{\theta}{2}\right)} \qquad (9)$$

These relationships provide the capability of comparing the relative size of the KL molecules and/or complexes in solutions at pH 8.5 (LS-3) versus pH 13.8 (LS-2).

The concentration of KL in the solutions was low, i.e., about 1 g L^{-1}, and thus the second virial coefficient term in eq 6 should exert only a small influence. Since the two sets of data were taken at the same angles of observation and distance from the cell, the Rayleigh ratio, eq 7, should be dependent only on values of K and of the form factor, $P(\theta)$. Assuming that the index of refraction and its concentration dependence are nearly the same for the pH 8.5 and 13.8 solutions, the constant K in eq 8 should be approximately the same at both alkalinities.

Equation 9 gives the form factor as a function of angle of observation. For the solutes in the pH 13.8 solution, Table II shows that the corrected intensities are small and nearly angle-independent, which indicates a value of about 1 for the form factor and is consistent with the weight-average molecular weight of about 3500 (M_w/M_n = 2.2) reported by Marton and Marton.[13] At pH 8.5, the intensities seem to increase with a decrease in scattering angle, suggesting that the form factor may be of some influence in this environment. With these considerations in mind, eq 6 indicates that the ratio of the intensities of the scattered light should be roughly equal to the ratio of the apparent weight-average molecular weights.

Thus the data in Table II seem to show that under the particular conditions studied the apparent weight-average molecular weight of the dissolved KL complexes was about 60 times greater in the LS-3 versus the LS-2 solutions, i.e., about 210 000 versus 3500. Since the only significant difference between the two solutions was alkalinity, it appears that high molecular weight entities are formed from KL oligomers as the solution alkalinity is decreased.

In LS-3A, aqueous sodium hydroxide solution was added to the LS-3 solution to bring its alkalinity to about pH 13.25, a value that was calculated by use of a mass balance because the volume of the light-scattering cell was too small to permit direct measurement of alkalinity. As the

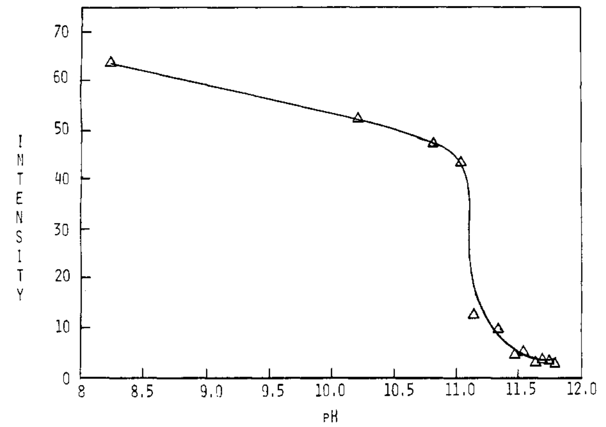

Figure 7. Light scattering by kraft lignins at several levels of alkalinity.

more dense NaOH solution sank and mixed with the pH 8.5 solution, the change in the intensity of the scattered light was readily apparent. Where tongues of high alkalinity reached into the beam, the intensity visibly decreased. After mixing, the final count rate observed in LS-3A was essentially the same as that found in LS-2. Thus, the association process is reversible and rapid.

In LS-4, a 1.0 N aqueous sodium chloride solution was added dropwise to a dilute pH 8.5 solution until a final ionic strength of 0.245 M was attained. The count rate of scattered light decreased from 100 000 to 84 000. Part of this change was the result of dilution, but this effect is small compared with the 60-fold difference observed between pH 8.5 and 13.5 solution conditions. Thus it appears that the observed increase in particle size occurs mainly as a result of association and not of polyelectrolyte expansion.

In experiment LS-5, a KL solution, initially at pH 8.5, was placed in a light-scattering cell and titrated with 0.1 N sodium hydroxide solution. The observed intensity, as shown in Figure 7, steadily decreased as the alkalinity increased and then fell precipitously in the pH range 11.2–11.5.

This result indicates a major change in the size of KL complexes rather than a dilution effect and is taken to be supporting evidence that association accompanies the protonation of the lignin phenolic hydroxyl groups and that a value of about pK_a = 11.5 characterizes the phenolic hydroxyl groups of KL.

Conclusions

The results suggest the existence of large stable complexes of KL in neutral and weakly alkaline solutions and that as alkalinity is increased, these complexes are broken up to yield small molecules. Ultrafiltration experiments indicate the depletion in the concentration of small molecules as the alkalinity of a KL solution is decreased. Light-scattering experiments show that large KL complexes are formed as solution alkalinity is decreased and that the apparent weight average molecular weight may be 60 times greater in solutions at low alkalinities versus high alkalinity. This association may account for the viscosity changes observed by Yaropolov[5] and Lindstrom[6] and the diffusivity changes seen by Benko.[4] Association may also explain the difficulties experienced in accomplishing the fractionation of kraft lignins on a molecular weight basis by use of incremental precipitation by acidification of alkaline solutions.

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Appendix A: Example Calculation of C_p

Let $R = 0.78$ $W_{LS} = 0.16$, pK_a = 11.5, and $C_0 = 160$ g L^{-1}. At pH 13.5, from eq 2

$$\chi_p = \frac{1}{1 + (10^{-14})/[(10^{-11.5})(10^{13.5-14})]} = 0.99 \tag{A1}$$

$$\chi_{TS} = 0.16 + (0.84)(0.99) = 0.99+ \tag{A2}$$

From eq 3 and 4 where $R \cong R'$

$$C_p = (0.99)(160)(1 - 0.78) = 34.9 \text{ g L}^{-1} \tag{A3}$$

At pH 10.2

$$\chi_p = \frac{1}{1 + (10^{-14})/[(10^{-11.5})(10^{10.2-14})]} = 0.99 \tag{A4}$$

$$\chi_{TS} = 0.16 + (0.84)(0.047) = 0.20 \tag{A5}$$

$$C_p = (0.20)(160)(1 - 0.78) = 7.0 \text{ g L}^{-1} \tag{A6}$$

Appendix B: Example Calculation of Fraction of Associated KL

At pH 12.6, $\chi_{TS} = 1.0$: For example, for $i = 3000$ molecular weight and with the XM300 membrane, read from Figure 4, $C_{0,3000} = 700$ mg L^{-1} and $C_{p,3000} = 540$ mg L^{-1}:

$$R'_{3000} = 1 - 540/[(700)(1.0)] = 0.22 \tag{B1}$$

At pH 12.6, $\chi_{TS} = 1.0$: read from Figure 5, $C_{p,3000} = 20$ mg L^{-1}; from rearrangement of eq 4, the concentration of nonassociated KL is

$$C_{0,3000}\chi_{TS} = \frac{C_{p,i}}{1 - R'_i} = \frac{20}{1 - 0.8} = 26 \text{ mg L}^{-1} \tag{B2}$$

Thus the fraction of KL in the associated state is

$$W_i = \frac{\text{total KL}_i - \text{nonassociated KL}_i}{\text{total KL}_i} \tag{B3}$$

$$W_i = \frac{700 - 26}{700} = 0.96 \tag{B4}$$

Nomenclature

B	second virial coefficient
C_i	concentration of the ith lignin species, g L^{-1}
C_0	concentration of lignin in the initial solution, g L^{-1}
C_p	concentration of lignin in the permeate, g L^{-1}
d	distance from the light-scattering cell to detector
$f(i)$	mole fraction of lignin in associated complex
I	ionic strength, mol L^{-1}
I_s	intensity of scattered light
I_0	intensity of incident light
K	constant defined by eq 8
K_w	dissociation constant of water
K_a	dissociation constant of lignin
MW(i)	molecular weight of the ith species
n	refractive index
N_A	Avagadro's number
[OH]	hydroxide ion concentration, mol L^{-1}
$P(\theta)$	form factor
R	rejection ratio
R_g	radius of gyration
R_θ	Rayleigh ratio
W_{LS}	weight fraction of lignin soluble in neutral solution
θ	angle of measurement of scattered light
λ	wavelength of incident light beam

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χ_{TS}	weight fraction of lignin not in associated complexes
χ_p	mole fraction of phenol hydrogen ions

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Preferential Surface Adsorption in Miscible Blends of Polystyrene and Poly(vinyl methyl ether)

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ABSTRACT: The surface structure and properties of miscible blends of polystyrene (PS) with poly(vinyl methyl ether) (PVME) have been studied as a function of the blend composition and constituent molecular weights. The lower surface tension of the PVME compared to that of PS results in preferential adsorption of PVME at the surface. The surface enrichment of PVME is characterized by measurements of the surface tension as a function of the temperature, accomplished with an automated pendant drop apparatus, and by X-ray photoelectron spectroscopy (XPS). Angle-dependent XPS has been used to determine the surface concentration profiles of the blend constituents. The results of these measurements demonstrate that (1) the PVME surface concentration is elevated substantially from that in the bulk, (2) the integrated surface concentration gradient determined from XPS measurements can be modeled as a $\coth^2 [(z/\xi) + \alpha]$ profile where ξ is the screening length, and (3) the degree of surface enrichment depends strongly on the blend composition and molecular weight of the constituents, correlating well with the surface energy difference between PS and PVME.

Introduction

Current technologies frequently employ multiconstituent polymer systems to tailor the material's bulk physical and mechanical properties. Although much emphasis has been placed on understanding the bulk phase relationships and properties of multicomponent polymeric materials, comparatively little is known about their surface structure and properties.

In small-molecule systems, such as metallic alloys[1] and liquid mixtures,[2] it is well-known that the surface composition differs from that of the bulk due to preferential surface adsorption of one constituent. This process is driven, in part, by differences in surface energies and can be expressed classically through the Gibbs adsorption isotherm[3]

$$-\mathrm{d}\gamma = \sum_i \Gamma_i \, \mathrm{d}\mu_i \tag{1}$$

where Γ_i is the surface excess ($\Gamma_i \equiv n_i/A$) of component i, $\mathrm{d}A$ is the fractional surface area, and μ_i is the chemical potential of species i for n_i moles of that component. From (1) it is apparent that a surface concentration gradient exists in multiconstituent systems where the surface is enriched in the component of lower surface energy (i.e., surface tension γ).

Preferential surface adsorption has been documented by surface tension, contact angle, and X-ray photoelectron spectroscopy (XPS) measurements on several multicomponent polymeric systems. In immiscible binary homopolymer blends, for example, the surface behavior is generally dominated by adsorption of the lower surface energy component.[4,5] This phenomenon also occurs for many blend additives.[6] Since equilibrium bulk thermodynamics favors complete demixing of the two homopolymers, the "equilibrium" surface should be occupied exclusively by the constituent of lower surface energy. In actuality, macroscopic equilibrium is usually not attained in immiscible polymer blends, such that the surface structure obtained is dependent on intrinsic factors such as the relative wettabilities of the two constituents and the degree of phase separation, as well as extrinsic factors including

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